

NEW POLYMERIZATION PROCESSES

EDUARDO VIVALDO-LIMA, CARLOS GUERRERO-SÁNCHEZ, CHRISTIAN H. HORNING,
IRAÍS A. QUINTERO-ORTEGA, AND GABRIEL LUNA-BÁRCENAS

15.1 INTRODUCTION

As the environmental policies for reduction of emissions of different chemical substances become more restrictive, the idea of developing new and alternative (more sustainable) methods for producing polymeric materials has gained considerable interest in recent years. In this context, the reduction in the consumption of volatile organic compounds (VOCs) as well as the use of alternative energy sources and reaction configurations during polymer manufacturing has become a priority in research development. The design of new polymerization processes must be carried out on the basis of promoting both energy savings and reduction of VOCs, and implementing the principles of green chemistry whenever possible [1].

The best way to avoid using organic solvents is to develop solvent-free processes, but problems associated with the high viscosities attained in polymerization processes make this route impractical in most instances. The second best choice is then to replace organic solvents with environmentally benign ones, such as water, ionic liquids (ILs), fluorinated phases, and compressed (e.g., supercritical) fluids. Each one of these approaches has advantages and disadvantages [2, 3]. Solvent-free processes may be considered as the “ideal” and the cleanest way of chemical manufacture. However, in polymer industry, bulk processes require an enormous amount of energy and high temperatures to overcome the problems related to the transportation of highly viscous polymer melts, which in some cases may provoke side-reactions and/or degradation of the products (Chapter 1).

The use of water, as a readily available, inexpensive, and harmless solvent, is a well-established approach in polymer

synthesis. In this regard, one can mainly find radical polymerizations performed via emulsion, suspension, and dispersion processes (Chapter 14). Even though water would be the most suitable selection for developing green polymerization processes, this approach cannot be used in moisture-sensitive systems, such as ionic polymerizations (Chapters 7 and 8).

This chapter provides an overview of the state of the art on emerging technologies with potential use in the production of polymeric materials. The addressed technologies in this chapter include the use of alternative solvents for polymer synthesis (e.g., supercritical CO₂ (scCO₂) and ILs), the preparation of polymer composites based on ILs, as well as the use of alternative reactor and energy technologies. Given the fact that some of the new polymerization processes emphasized in this chapter involve the use of compressed fluids, a subsection of this chapter is devoted to expand some of the key concepts of phase behavior of polymer systems presented in Chapter 25, but emphasizing high pressure systems (mainly associated with scCO₂).

15.2 POLYMERIZATIONS IN BENIGN OR GREEN SOLVENTS

15.2.1 Polymerizations in Compressed and Supercritical Fluids (SCF)

15.2.1.1 Phase Behavior of Polymer Systems in High Pressure Fluids The basic description and definitions of the different phenomena associated with phase equilibria in polymer solutions are described in Section 25.2.5. Topics such as construction and interpretation of binary

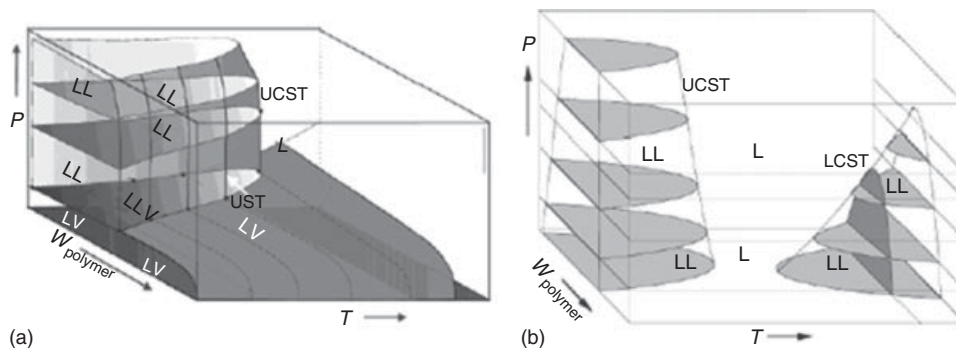


Figure 15.1 Schematic three-dimensional temperature–pressure–composition phase diagrams of polymer–solvent system: (a) UCST-LLE, VLE, and VLE; (b) UCST- and LCST-LLE. *Source:* Adapted with permission from Seiler M, Rolker J, Arlt W. *Macromolecules* 2085;2003:36 [4]. Copyright 2003 American Chemical Society.

phase diagrams, the definition of upper critical solution temperature (UCST) and lower critical solution temperature (LCST), miscibility regions, and the basic theoretical treatment for phase separation are covered there.

To obtain a more general insight, both P – w and T – w diagrams are transferred into the three-dimensional phase diagram, which is illustrated in Figure 15.1.

In Figure 15.1a, only UCST behavior is illustrated. Vapor–liquid equilibrium as well as vapor–liquid–liquid equilibrium, where two liquid phases are in equilibrium with one vapor phase, can be distinguished. In Figure 15.1b, one can recognize the two LLE regions in the T – w plain. With increasing pressure, the two-phase regions become smaller. Usually, the slope of the UCST line is steeper than that for LCST.

Another projection of the three-dimensional T – P – w diagram is the illustration of pressure versus temperature at critical concentration, shown in Figure 15.2, and reveals some further insights into the behavior of polymer–solvent systems.

One can see again that the miscibility of the system becomes better with increasing pressure since the temperature difference between the UCST and LCST curve becomes larger. The points where the UCST and LCST curve settle on the VLE line are called *upper critical equilibrium point (UCEP)* and *lower critical equilibrium point (LCEP)*, respectively (sometimes, one can find “end point” instead of “equilibrium point” in the literature). At these points, two liquid phases and one vapor phase are in equilibrium.

It is worthy to emphasize that Figure 15.2 illustrates the solution behavior at the critical concentration. However, in the literature, one often finds the terms UCST and LCST in pressure–temperature diagrams that describe the phase separation behavior of a solution at any constant concentration. If this concentration is different from the critical concentration, which is even not always necessarily known, strictly speaking, the correct designation should be UST (upper solution temperature) and LST (lower solution

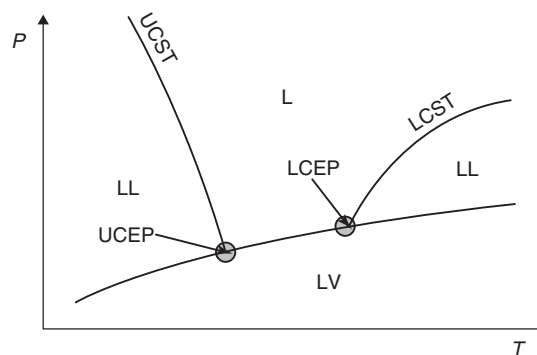


Figure 15.2 Schematic pressure–temperature phase diagram at the critical concentration of a polymer–solvent system with UCST and LCST phase separation. *Source:* Adapted with permission from Kiamos AA, Donohue MD. *Macromolecules* 1994;27(2):357 [5]. Copyright 1994 American Chemical Society.

temperature), respectively. Consequently, the end points of the curves should be named UEP (upper end point) and LEP (lower end point) instead of UCEP and LCEP, respectively. The terms UCST and LCST are used here, however, just keeping in mind that the actual critical concentration is not usually known.

The addition of a compressed or supercritical gas to a polymer–solvent system, which acts as an antisolvent because of the introduction of free volume, has various effects [6]: (i) all phase transition curves shift to higher pressure, which is needed to keep the gas in solution, and (ii) the LCST curve shifts to lower temperatures since the free-volume effect is enhanced.

Eventually both UCST and LCST curves can merge to a single curve. Figure 15.3 shows the qualitative influence of gas on the phase behavior of polymer–solvent systems in a P – T diagram at constant concentration and a T – w diagram at constant pressure.

If the UCST and LCST curves are merged, the so-called hour glass shape is formed as can be seen in the

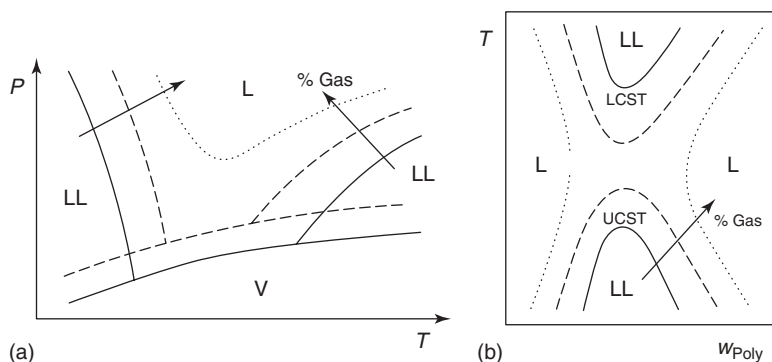


Figure 15.3 Effect of gas content on phase behavior of a polymer-solvent system: (a) pressure-temperature diagram at constant concentration and (b) temperature-composition diagram at constant pressure. *Source:* Adapted with permission from ter Horst MH, Behme S, Sadowski G, de Loos TW. *J Supercrit Fluids* 2002;14:181 [7]. Copyright 2002 Elsevier.

$T-w$ diagram. In that case, there exists no temperature at which the system is completely miscible over the whole concentration range.

The phase behavior of polymers in supercritical fluid (SCF) solvents has been reviewed by Kirby and McHugh [8]. The effect of supercritical carbon dioxide on polymer-solvent mixtures is addressed elsewhere [5].

The effect of the variation of the molecular mass of the polymer on the equilibrium lines is comparable to the effect of gas concentration. This is due to the fact that small solvent molecules dissolve small molecules better than bigger ones. Thus, by increasing the molecular weight of the polymer, the immiscibility region is expanded. UCST and LCST move toward each other until they eventually merge to the hour glass shape. The effect of several variables on the location of the UCST and LCST is qualitatively illustrated in Figure 15.4.

A monodisperse polymer population is an idealization. Rather, one has to consider the polymer as a multicomponent mixture of many species with identical molecular

structure but different molecular masses. This complicates the illustration of phase diagrams.

To explain the behavior of a polymeric multicomponent system, the polymer is considered as a mixture of two polymer species, P1 and P2. By doing this, the polymer-solvent system can be illustrated using a ternary Gibbs triangular diagram. It is assumed that one species of the polymer, P1, has a lower molecular mass than P2 and is completely miscible with the solvent, whereas P2 exhibits an immiscibility region (Figure 15.5).

Adding solvent to a polymer mixture F at T_1 , the immiscibility region is entered at point C1, where the solution turns cloudy. This is why this point is also called *cloud point*. At this moment, a second phase appears whose concentration is given by S1. Since the amount of the second phase is so small, its concentration is experimentally not accessible and this point is named *shadow point*. Adding more solvent, the two-phase region is finally left at the other side at the cloud point C2 with the corresponding shadow point S2.

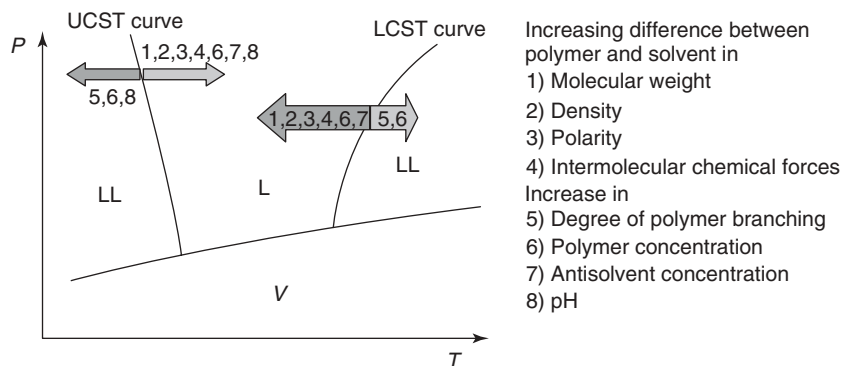


Figure 15.4 Effect of various variables on LCST and UCST shown schematically in a pressure-temperature diagram. *Source:* Adapted with permission from Seiler M. *Chem Eng Tech* 2002;2:237 [9]. Copyright 2002 Wiley-VCH Verlag GmbH & Co. KGaA.

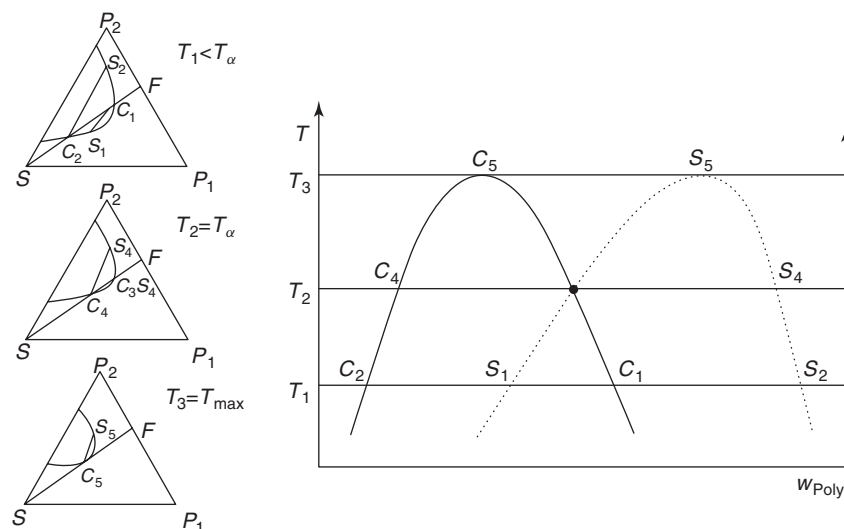


Figure 15.5 Effect of molecular weight dispersity (\mathcal{D}) (formerly known as polydispersity) using schematic Gibbs triangle diagrams for polymer–solvent system, generation of cloud point curve and shadow curve in temperature–composition diagram.

At other temperatures, the shape of the immiscibility region differs. For example, at a higher temperature T_2 , it could be that the two-phase region is entered at its critical point, and so both phases have the same concentration. However, they can still be distinguished by their different densities. Or, at an even higher temperature T_3 , the two-phase region is tangented at only one point. This would be the UCST.

One can illustrate these circumstances in the usual (pseudobinary) T – w diagram, w_{poly} being the summarized weight fraction of both polymer species. By doing this, information about the distribution of the polymer species in the different phases is not available. However, it is known that along the cloud point curve, the concentration is always equal to the initial polymer distribution F , whereas it differs strongly along the shadow curve. Usually, there is an enrichment of longer polymer chains in the shadow phase.

Typically, in literature, one can only find data of cloud point curves since the shadow phase is experimentally not accessible. This data can be obtained using different methods. Usually, a temperature- and pressure-controlled autoclave is used. The polymer solution of known concentration is charged into the autoclave and is then tempered and pressurized. By varying either temperature or pressure, holding the other property constant, the cloud point pressure or cloud point temperature can be determined. Often the cloud point is defined as a rather subjective change of color of the solution, which becomes turbid when the second phase appears. By repeating this formalism for a broad range of initial solution concentrations, cloud point curves can be created over a large range of temperature, pressure, and concentration.

15.2.1.2 Earlier High Pressure Polymerization Processes

The use of high pressures in polymerization processes, where the monomer is compressed but not necessarily in its supercritical region, is not new. Strange and Bliss polymerized butadiene and its substituted derivatives by applying a pressure of 300–400 MPa (much higher than the critical pressure of butadiene of 4.322 MPa) [10, 11]. In 1936, ICI patented a process for ethylene polymerization using free radical initiators in the presence of benzaldehyde at 170 °C and 190 MPa, clearly in the supercritical region of ethylene ($T_{\text{cr}} = 9.25$ °C, $P_{\text{cr}} = 5.04$ MPa), and small-scale production started in 1939 [12]. However, the motivation for high pressure applications in the early processes was not from environmentally benign grounds. High pressures were used to polymerize monomers that would not polymerize at atmospheric pressure, to increase polymerization rate, to increase molecular weight, and to obtain some additional information about the processes [11].

15.2.1.3 Polymerization in Supercritical Carbon Dioxide (scCO₂)

Background and Overview CO₂ is an attractive alternative to organic solvents for various applications because it is nontoxic, nonflammable, inexpensive, and environmentally relatively benign [6, 13]. An extensive review about the potential of CO₂-based technology was presented by the group of DeSimone [14]. Its critical conditions can be easily be obtained ($T_{\text{cr}} = 31.1$ °C, $P_{\text{cr}} = 7.38$ MPa). Because of its low value of polarizability per volume, compressed or supercritical CO₂ is able to dissolve most small nonpolar molecules, but just a few polymers that have low cohesive

densities, for example, fluoroacrylates, fluorocarbons, fluoroethers, and siloxanes [6, 14–17]. However, besides these few “CO₂-philic” polymers, CO₂ rather behaves like an antisolvent in polymer solutions, which is the basis for many industrial processes.

As all SCFs, scCO₂ offers interesting properties that lie between those of a gas and a liquid. As liquids, they exhibit high density and can swell polymers [6, 14, 18–20]. As gases, they have low viscosity and relatively high diffusivity. scCO₂ is highly compressible; its density and, therefore, solvent properties, such as viscosity and dielectric constant, can be tuned by varying the temperature and pressure of the system [6, 15]. Its solvent power can thus be controlled precisely.

Compressed gases exhibit various effects that can be exploited in industrial processes [6, 21]: (i) tunability of the solvent power of a solvent by addition of a fluid antisolvent and pressure variation; (ii) controllability of phase transition kinetics by variation of the gas content and system pressure; (iii) swelling of polymers and decreasing of the glass transition temperature (transition of a polymer from a viscous melt to a hard noncrystalline glassy state) by dissolution of compressed gases; and (iv) decrease of viscosity and higher diffusion and transition coefficients by dissolution of compressed gases.

Polymerizations in scCO₂ Many polymers have been synthesized in scCO₂, including fluoropolymers, polysiloxanes, poly(methyl methacrylate), polystyrene, and polycarbonates, as reviewed elsewhere [22–24]. The literature on polymer chemistry in scCO₂ is extensive and keeps growing, as evidenced from the review by Kendall et al. [23]. Specifically, the homopolymerizations of styrene [25–30] and methyl methacrylate (MMA) [15, 31–41] in scCO₂ have been studied in some depth in the literature, from an experimental perspective. In this section, we emphasize the modeling of polymerization processes in scCO₂. To do so, three case studies are considered: (i) the modeling of homogeneous (single-phase) systems [42]; (ii) the modeling of heterogeneous free radical homopolymerizations [43]; and (iii) the modeling of heterogeneous free radical copolymerization with crosslinking [44]. All these cases were addressed using the principles and modeling tools described in Chapter 12.

CASE STUDY 1: HOMOGENEOUS HOMO- AND COPOLYMERIZATIONS IN scCO₂ The first case analyzed [42] was the homogeneous homopolymerization of dihydroperfluorooctyl acrylate (FOA) in supercritical carbon dioxide at the same conditions reported by DeSimone et al. [45]. Once the model was implemented, parameter sensitivity analyses were carried out. The first objective was to test the model implementation, namely, to verify that the expected trends were predicted by the model. The second objective of these

sensitivity analyses was to determine bounds on the values of the propagation and termination kinetic rate constants, k_p and k_t , respectively, in case it was necessary to use them as fitting parameters to the experimental data from the literature that were available. The second system modeled for this case study was the surfactant-free precipitation copolymerization of TFE/VAc (approximated as homogeneous) in supercritical carbon dioxide. This is a reasonable assumption, since the copolymerization proceeds mostly in a single phase because the monomer acts as a cosolvent, enhancing the solubility of the produced polymer during the reaction [46]. In that study, the initial composition of fluoromonomer was increased from 13.1% to 83.3%, on a molar basis, in five cases (13.1%, 34.5%, 50%, 67.7%, and 83.3%). The five cases were simulated with the model, which for this case consisted of a conventional homopolymerization (even the copolymerization was described with the same model equations, but considering the kinetic rate constants as pseudokinetic rate constants, as explained in Chapter 12). Although not enough experimental information was available, nor reported kinetic rate constants for these monomers at such conditions, fairly good agreement was obtained by using reasonable kinetic rate constants, as it can be observed in Figure 15.6 for the case of copolymer composition in the copolymerization of TFE/VAc.

CASE STUDY 2: COMPARISON OF MATHEMATICAL MODELS FOR FREE RADICAL HOMOPOLYMERIZATION OF VINYL MONOMERS IN scCO₂ In this case study, a comparison of performance of the different kinetic models proposed in the literature for dispersion polymerization of styrene and MMA in scCO₂ is presented. The models used by Quintero-Ortega et al. [43] (models 1 and 2) and those presented by the groups of Kiparissides [47] (model 3) and Morbidelli [48] (model 4) for MMA homopolymerization are used for the comparison. The differences among these models are related to the calculation of the partition of components between the two phases and are summarized in Table 15.1.

Figure 15.7 shows that models 1–3 perform equally well for the prediction of polymerization rate (Fig. 15.7a) and molecular weight development (Fig. 15.7b). However, the predictions of monomer and solvent concentrations in both phases differ significantly (Fig. 15.8). Moreover, when interpolating the parameters of these three models to consider a system with lower pressure, and now comparing models 1, 2, and 4, it is observed that models 1 and 2 perform poorly, and model 4 reproduces reasonably well the behavior of this system (Fig. 15.9).

Although the overall performance of the models compared in this case study, measured in terms of predictions of polymerization rate and molecular weight development, can be considered acceptable if adequate and reliable parameters are used, it is clear that important differences exist, and that the study of component partitioning between the

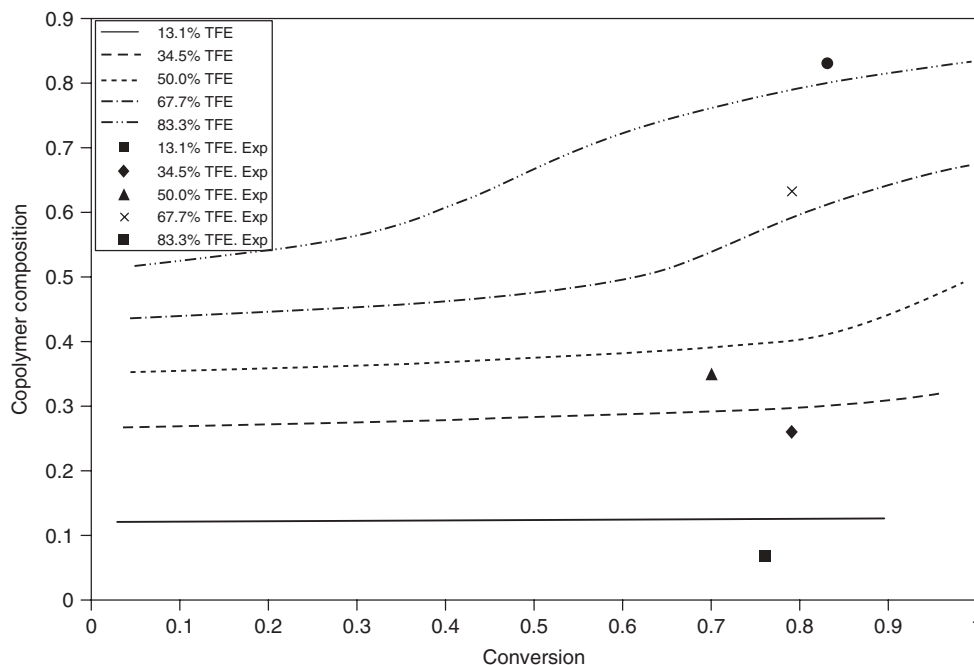


Figure 15.6 Effect of fluoromonomer composition on copolymer composition in copolymerization of TFE and VAc at the experimental conditions of Baradie and Shoichet [46]. *Source:* Reprinted with permission from Quintero-Ortega IA, Vivaldo-Lima E, Gupta RB, Luna-Bárceñas G, Penlidis A. *J Macromol Sci Pure Appl Chem* 2007;44:205 [42]. Copyright 2007 Taylor & Francis Group, LLC.

phases in dispersion polymerization of vinyl monomers is still far from complete. The disagreement observed in some of the dispersion polymerization cases seems to be related to inadequate estimates or inadequate modeling of the partition of components between the two phases.

CASE STUDY 3: MODELING OF COPOLYMERIZATION OF VINYL/DIVINYLMONOMERS IN scCO_2 A mathematical model for the free radical copolymerization kinetics with crosslinking of vinyl/divinyl monomers in carbon dioxide at supercritical conditions was developed by Quintero-Ortega et al. [44]. The copolymerization of styrene and divinylbenzene was analyzed as case study. The effects of the kinetic and physical parameters on monomer conversion, molecular weight development, copolymer composition, appearance of the gelation point, gel fraction, and average crosslink density were studied. Model predictions showed the expected trends, although the system was quite sensitive to pressure, which makes an interesting and promising way to tailor some of the polymer properties. The model corresponds to the case with crosslinking explained in Chapter 12 of this handbook, but considering a two-phase situation, using the modeling approach called *model 1* of the preceding case study for calculation of the partition of the recipe components between the two phases. Figure 15.10 shows the remarkable effect of pressure on the polymerization kinetics, molecular weight development,

and evolution of network formation. Calculations were carried out using parameters for a styrene/divinylbenzene copolymerization at 65°C .

15.2.1.4 Polymerization in Other Compressed Green Solvents Supercritical water ($T_{\text{cr}} = 374.15^\circ\text{C}$, $P_{\text{cr}} = 22.1$ MPa) is a very effective reaction medium for oxidation reactions [3, 50, 51]. However, corrosion and elevated investment costs are adverse issues that make the intense use of this technology difficult [3].

Besides supercritical water and scCO_2 , another compressed fluid successfully used in the development of green polymerization processes is 1,1,1,2-tetrafluoroethane (R134a, $T_{\text{cr}} = 101.1^\circ\text{C}$, $P_{\text{cr}} = 4.06$ MPa). Some advantages/characteristics of R134a are [52] as follows: (i) it is nontoxic and nonflammable and is widely regarded as having zero ozone depletion potential; (ii) it has found widespread use as a CFC replacement in refrigeration and auto air conditioning systems; in addition, its low toxicity has led to approval for use in metered dose inhalers; (iii) its global warming potential is estimated to be 1300 times that of CO_2 , but a widely held view is that HFCs will have a very small impact on overall climate change, which will arise mostly from the accumulation of CO_2 in the atmosphere from the burning of fossil fuels; (iv) although it is more expensive than CO_2 , and any HFC-based process would likely require effective recycling of the solvent,

TABLE 15.1 Differences between the Four Models*

	Model 1 [44]	Model 2 [43]	Model 3 [47]	Model 4 [48]
Assumptions	Homogeneous at the beginning; appearance of second phase at solubility limit	Two phases from the beginning of the reaction	Two phases from the beginning of the reaction	Two phases from the beginning of the reaction
Reaction loci	Homogeneous up to x_s , then heterogeneous. At x_c polymerization proceeds only in the dispersed phase	Both, continuous and dispersed phases	Both, continuous and dispersed phases	Both, continuous and dispersed phases
Reactions considered	Initiation, propagation, chain transfer to monomer and termination, in both phases	Initiation, propagation, chain transfer to monomer and termination, in both phases	Initiation, propagation, chain transfer to monomer and termination, in both phases	Initiation, propagation, chain transfer to monomer and termination, in both phases
Diffusion-controlled (DC) effects	DC propagation and termination only in the dispersed phase	DC initiation, propagation, chain transfer to monomer and termination, in both phases	DC propagation and termination, in both phases	DC initiation, propagation and termination, in both phases
Partition of low molecular weight species between the phases	Semiempirical expressions that relate solubility and conversion are used	Phase transfer and concentrations in each phase are controlled by partition coefficients and equilibrium considerations	Monomer, initiator, and solvent are at equilibrium concentrations, which are calculated using the Sanchez–Lacombe EOS	Monomer, initiator, and solvent are at equilibrium concentrations, which are calculated using the Sanchez–Lacombe EOS
Polymeric species concentrations	Living oligoradicals in the continuous phase; living and dead polymer in the dispersed phase	The propagating radicals transfer to the dispersed phase as soon as they reach the critical chain length	The polymer is at interphase equilibrium. Concentrations are evaluated using the Sanchez–Lacombe EOS	A chain-length-dependent equilibrium partition coefficient for polymer chains between continuous and dispersed phases is considered. Radical partition (RP) model [48]
Calculation of the MWD	The averages M_n and M_w are calculated from the moments of the MWD	The full MWD is calculated using Galerkin's method [49]	The averages M_n and M_w are calculated from the moments of the MWD	Full MWD calculated using the discretization method of Kumar and Ramkrishna [48]

*Source: Adapted with permission from Quintero-Ortega IA, Jaramillo-Soto G, García-Morán PR, Castellanos-Cárdenas ML, Luna-Bárceñas G, Vivaldo-Lima. E. *Macromol React Eng* 2008;2:304 [43]. Copyright 2008 Wiley-VCH Verlag GmbH & Co. KGaA.

energy-efficient recycling of R134a may be practical since it was developed originally as a refrigerant; and (v) regarding its degree of polarity, CO₂ is symmetrical and has no permanent dipole moment (although it does possess a substantial quadrupole moment), while R134a is moderately polar and has a significant dipole moment (2.1 D).

Wood and Cooper [53] successfully synthesized crosslinked polymer microspheres by dispersion polymerization of MMA and trimethylolpropane trimethacrylate (TRIM) in R134a using perfluoropolyether stabilizers and moderate pressures (10–20 bar). However, the authors reported that the production of linear homopolymers from MMA, styrene, acrylonitrile, and acrylic acid using the same stabilizers was not successful, since low yields

and modest molecular weights, as well as nonuniform latex particles were observed with these monomers. In a subsequent study by the same group [52], successful production (yields up to 95%, molecular weights as high as 42,000.00 g/mol and microspheres of 4–5 μm in diameter) of polystyrene in R134a using poly(vinyl acetate) macromonomer stabilizers was reported.

More recently, López-Luna et al. [54] reported the successful enzyme-mediated syntheses of polyester structures in scCO₂ and R-134a. Lipase-mediated synthesis of relatively high molecular weight poly(δ-valerolactone) (PVL) was reported in scCO₂ and liquid R-134a solvent media. However, they found that polymers and copolymers

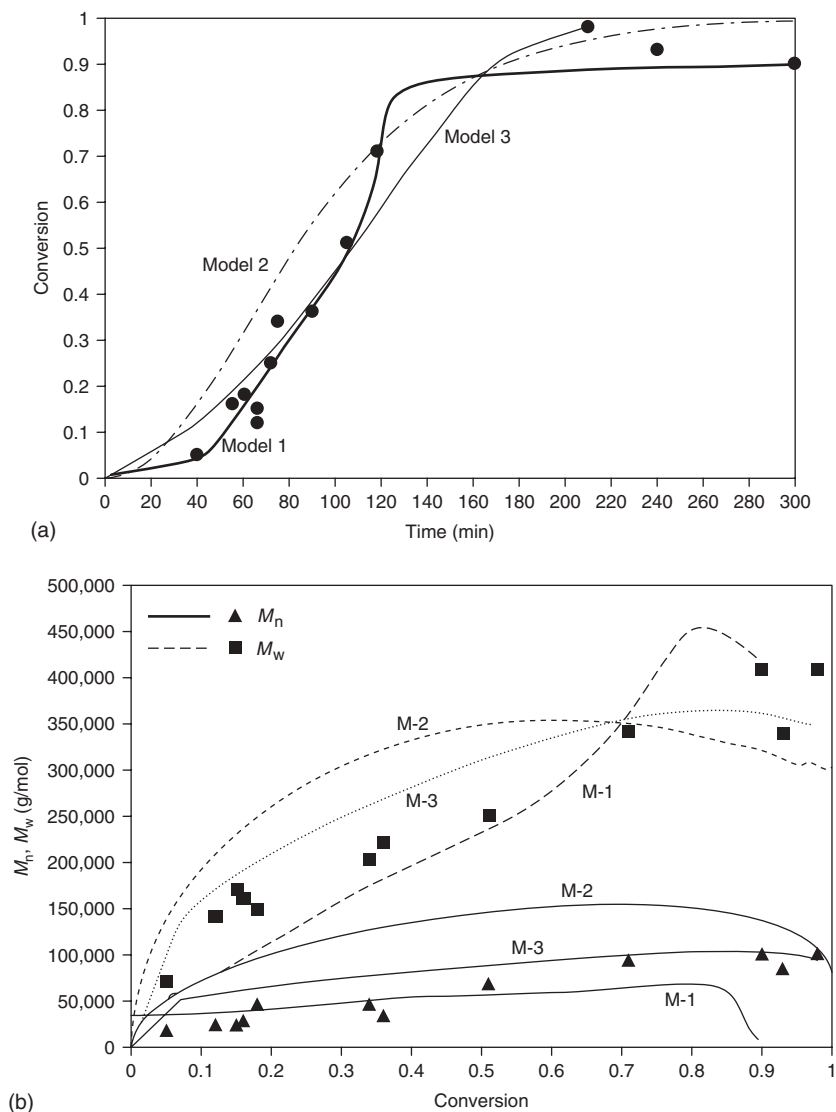


Figure 15.7 Polymerization of MMA in scCO_2 at 65°C and 206.8 bar: comparison of experimental data [39] of (a) monomer conversion versus time and (b) number- and weigh-average molecular weights, M_n and M_w , versus conversion, against predicted profiles obtained with models 1–3. *Source:* Reprinted with permission from Quintero-Ortega IA, Jaramillo-Soto G, García-Morán PR, Castellanos-Cárdenas ML, Luna-Bárceñas G, Vivaldo-Lima, E. *Macromol React Eng* 2008;2:304 [43]. Copyright 2008 Wiley-VCH Verlag GmbH & Co. KGaA.

from 2,2-bis(hydroxymethyl)butyric acid (BHB) and ϵ -caprolactone (CL), aimed at achieving hyperbranched polyesters, presented low solubility in compressed CO_2 and good solubility in liquid R134a. Lipase-mediated hyperbranched poly(VL-*co*-BHB), as well as poly(CL-*co*-BHB), were successfully synthesized in liquid R134a.

15.2.2 Polymerizations in Ionic Liquids

ILs, a new class of substances composed entirely of ions that are in liquid state at temperatures below 100°C , have

been proposed for different applications [55, 56]. In polymer chemistry, ILs have been investigated as reaction media, initiators, monomers, catalysts and exothermic moderators [2, 57, 58], as well as additives to polymers (flame retardants, plasticizers, electrolytes, as well as gelling and porogenic agents) [59–61] and self-assembly processes [60, 62]. This is mainly due to the fact that, unlike conventional substances, the properties of ILs (e.g., viscosity, solubility, miscibility, ionic conductivity, and melting point) can be readily tuned in a wide range by varying the composition of their respective ions [55]. Moreover, ILs are considered

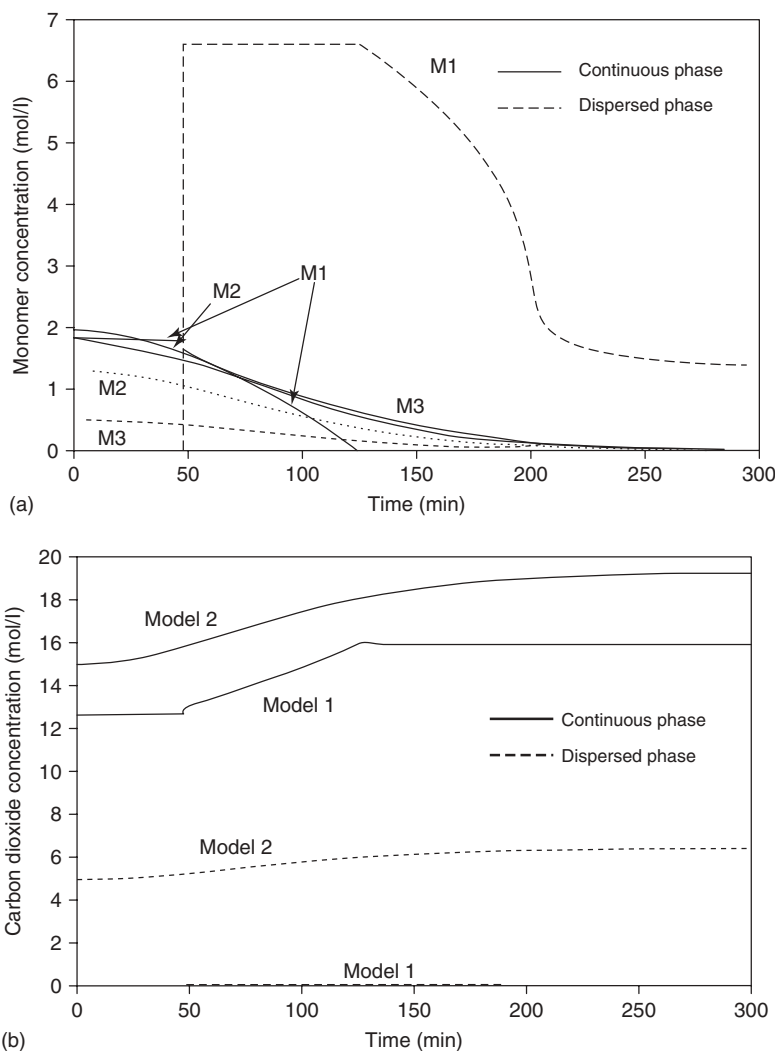


Figure 15.8 Polymerization of MMA in $sc\text{CO}_2$ at 65°C and 206.8 bar: (a) monomer and (b) solvent (CO_2) calculated concentration using models 1–3. *Source:* Reprinted with permission from Quintero-Ortega IA, Jaramillo-Soto G, García-Morán PR, Castellanos-Cárdenas ML, Luna-Bárceñas G, Vivaldo-Lima. E. *Macromol React Eng* 2008;2:304 [43]. Copyright 2008 Wiley-VCH Verlag GmbH & Co. KGaA.

as stable and “environmentally friendly” compounds due to their negligible vapor pressure and flammability, and liquid state in a broad temperature range [55]. Recently the use of ILs as new solvent systems has also triggered unprecedented possibilities for the design of advanced materials [63–65] and polymer-based physical–chemical systems [66, 67].

As addressed in the literature [2, 57], the use of ILs as solvents in polymerization processes can be advantageous in certain cases. For instance, the rate of the propagation reaction in radical polymerizations can be enhanced in the presence of ILs, while the rate of termination decreases as compared to polymerizations performed in conventional solvents, resulting in polymers with higher molar masses.

Because of the fact that ILs are able to dissolve many organometallic and inorganic catalysts used in some polymerizations [e.g., in atom transfer radical polymerization (ATRP)], these reactions can be homogeneously performed in ILs without the inconvenience of a multiphase reaction; an additional advantage is the feasibility of recycling solutions of expensive catalysts. The high charge density of ILs can also have a significant influence on the stereochemistry of polymers synthesized in chiral ILs and on the reaction mechanisms of ionic polymerizations, which are not commonly observed in polymerizations reactions in conventional organic solvents. The remarkable thermal stability and nonvolatility of ILs can be very suitable to perform polycondensation reactions, where the removal of

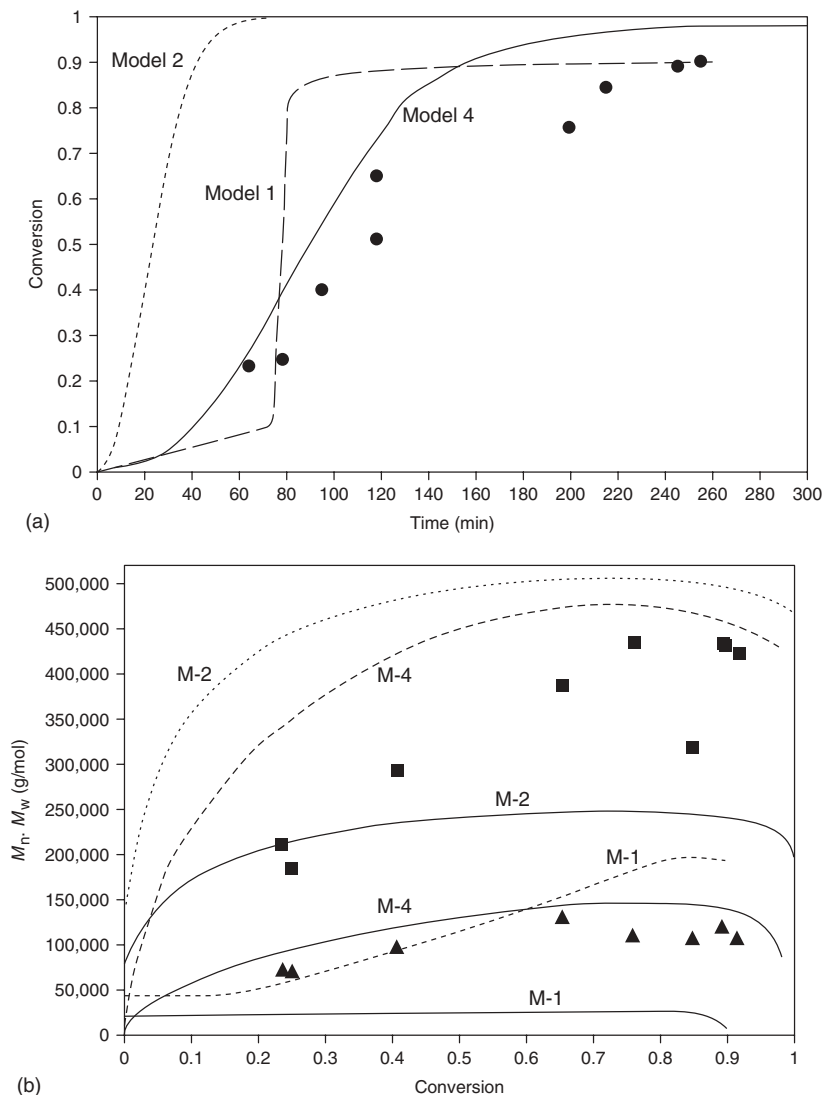


Figure 15.9 Polymerization of MMA in scCO₂ at 65 °C and 140 bar (initial pressure): comparison of experimental data [48] of (a) monomer conversion versus time and (b) number- and weight-average molecular weights, M_n and M_w , versus conversion, against predicted profiles obtained with models 1, 2, and 4. *Source:* Reprinted with permission from Quintero-Ortega IA, Jaramillo-Soto G, García-Morán PR, Castellanos-Cárdenas ML, Luna-Bárceñas G, Vivaldo-Lima E. *Macromol React Eng* 2008;2:304 [43]. Copyright 2008 Wiley-VCH Verlag GmbH & Co. KGaA.

byproducts at high temperatures is required for obtaining polymer with high molar masses. ILs have also been proposed as moderators in exothermic polymerization reactions and related processes to avoid thermal runaways [2]. Other reactions such as coordination, electrochemical, enzymatic polymerizations, depolymerizations at high temperatures, and dissolution and modification of cellulose can be favorably carried out in ILs [2, 57]. For instance, the use of milder reaction conditions, reuse of catalysts without loss of activity (or even polymerizations in the absence of catalyst), higher yields, high conductive polymer films, and longer enzymatic activities have been reported. It is also

worth noting that ILs are not always inert when used as reaction media, which can lead to undesired side reactions in some cases [2, 57]. This implies a meticulous selection of ILs for specific reactions.

Nevertheless, the replacement of VOCs by ILs does not necessarily imply that polymeric materials and their related processes will become automatically more efficient and “cleaner.” For instance, in far too many investigations in the literature where ILs are used as reaction media in polymer synthesis [2, 57], suitable approaches for the isolation and purification of the obtained polymers, and the recycling of the used ILs are not addressed since

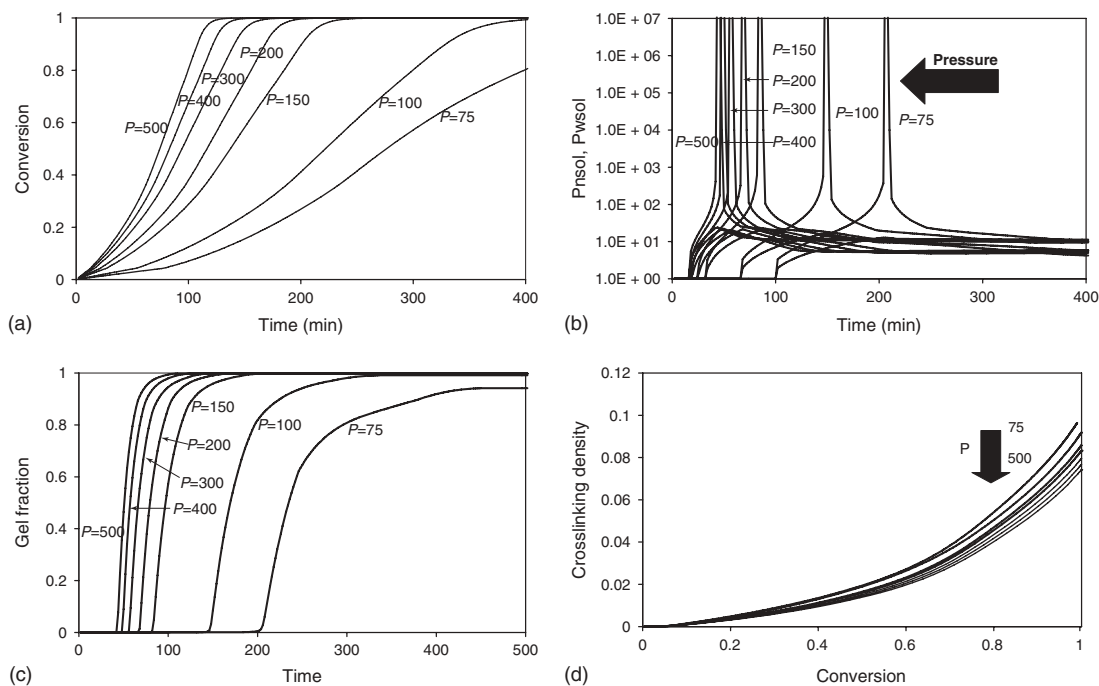


Figure 15.10 Effect of the operating pressure, P , on (a) polymerization rate, (b) number- and weight-average chain lengths, (c) gel fraction, and (d) crosslinking density. *Source:* Reprinted with permission from Quintero-Ortega IA, Vivaldo-Lima E, Luna-Bárceñas G, Alvarado JFJ, Louvier-Hernández JF, Sanchez IC. *Ind Eng Chem Res* 2005;44:2823 [44]. Copyright 2005 American Chemical Society.

the use of conventional organic solvents to recover the product is commonly necessary. These approaches obviate the advantages of ILs as replacements of VOCs. From this point of view, the “green” properties of ILs are in many cases exaggerated, and it is not always clear what the advantages of replacing conventional chemical compounds with ILs are. Moreover, the improvement of synthetic methods and commercial availability of most ILs are still required since they are more expensive than conventional solvents. Hence, the use of ILs as reaction media for polymerization processes can be only justified in specific cases where the properties of ILs show significant positive effects, which would be difficult to obtain in conventional solvents. All these aspects together open up possibilities to envision a real application of ILs as solvents in large-scale industrial processes.

Moreover, the entire life cycle of ILs in any application must be integrally considered including energy use, demand of nonrenewable resources, transportation, health, safety, biodegradability, and (eco-)toxicity [2, 57]. In this regard, conventional solvents or chemical compounds such as CO_2 , water, and alcohols (e.g., methanol and ethanol) may be more suitable than ILs. For instance, the production of ILs requires a considerable amount of energy, and additional manufacturing and purification steps, which might hinder their aforementioned advantages. In addition, the (eco-)

toxicity of ILs is not fully known, and suitable strategies for their disposal still have to be determined, which further limits their application.

To overcome the current drawbacks of ILs in polymeric materials, it is mandatory to develop suitable and efficient recycling strategies. In addition, the use of ILs coupled with alternative and efficient energy sources may provide “cleaner” and more energetically integrated polymerization processes. For instance, this vision could, indeed, be achieved by combining ILs as reaction media with microwave energy as a heating source, both applied to different stages of polymer manufacturing. This approach is addressed in the following section.

15.3 ALTERNATIVE ENERGY SOURCES FOR POLYMERIZATION PROCESSES

15.3.1 Microwave-Activated Polymerization

Microwave energy is a form of electromagnetic radiation with wavelengths between 1 mm and 1 m (located between infrared radiation and radio frequencies). Microwave irradiation was first proposed as a heating method several decades ago, but it was during the last decade that it rapidly became a well-established technique for different chemical reactions

and processes, especially in organic synthesis [68–70]. Microwave irradiation is an alternative, efficient, selective, and fast volumetric heating method, which increases the energy of molecules by directly interacting with their dipole moments. In general, the principle of microwave heating is based on the ability of polar substances to absorb and transform microwave irradiation into heat. In this regard, the permanent dipoles of a molecule rapidly try to align to the direction of a constantly changing electric field, which provokes the rotation of the molecule and friction with other molecules, and subsequently, the energy of the entire system is lost in the form of heat [68–70]. Microwave irradiation can offer some advantages as compared to convective and conductive heating methods (e.g., higher heating rates, selective heating, homogeneous heating without temperature gradients, higher yields for a certain reaction time, and energy savings) [68–70].

Microwave energy has also been extensively used as an efficient heating method for different types of polymerization reactions (e.g., free- and controlled radical polymerizations, polycondensations, and ring-opening polymerizations) and polymer processing (e.g., curing processes, recycling of plastics, and polymer modification methods) [71–76]. Regarding the theoretical understanding of microwave irradiation on free radical polymerizations, the group of Vivaldo-Lima has proposed a “microwave promoted initiation step” (similar to thermal self-initiation) in the reaction scheme and successfully modeled microwave irradiated emulsion polymerizations [77], as well as controlled radical polymerizations (nitroxide-mediated radical polymerization (NMRP) [78] and reversible addition-fragmentation chain transfer (RAFT) [79]).

The use of ILs as reaction media for microwave assisted chemical modifications can result advantageous [80–82]. In general, most of conventional organic solvents are flammable and volatile, which can become a serious limitation for chemical reactions performed at high temperature due to the fact that the pressure in the reactors can increase considerably. In this regard, ILs possess extremely low vapor pressure, high thermal stability, high dielectric constant, and rather low heat capacity [56]. These properties enable ILs to interact very efficiently with microwave irradiation through an ionic conduction mechanism, which results in an extremely fast heating without any significant pressure increase in the reactions vessels (at least not due to the presence of ILs). In fact, it has been demonstrated that the use of small amounts of ILs can have a significant effect on the heating profiles of solvents and monomers under microwave irradiation [83]. Moreover, microwave irradiation has also been proposed for the synthesis of ILs themselves as an alternative to increase their purity and to reduce the organic waste related to these processes [84, 85]. Due to these advantages, ILs have been proposed as reaction media for different microwave-assisted polymerizations. For instance,

the microwave-assisted ring opening polymerizations of ϵ -caprolactone and trimethylene carbonate was significantly enhanced in the presence of suitable ILs [86, 87].

The microwave-assisted cationic ring opening polymerization of 2-ethyl-2-oxazoline performed in ILs can show higher polymerization rates (i.e., lower activation energies) and lower molecular weight dispersities (\bar{M}_w/\bar{M}_n) as compared to the polymerization performed in acetonitrile [88]. It was suggested that the presence of additional ionic moieties (ILs) can have a significant influence on the association constant between the living polymer chain ends and their respective counterions, which can have a positive or negative effect on the polymerization kinetics depending on the type of IL used [88]. Additional homogeneous microwave-assisted polymerizations of other oxazoline monomers and the free radical polymerization of MMA using water-soluble ILs as reaction media have also been investigated [83]. Other microwave-assisted free radical homo- and copolymerizations using ILs as reaction media have been investigated and directly compared with conventional heating and conventional organic solvents [89–91]. For these later cases, it was found that certain combinations of ILs with microwave irradiation can also have positive and negative effects on the polymerization rates as compared to the reaction systems performed under conventional heating or conventional organic solvents.

Microwave-assisted polycondensation reactions in ILs have also allowed the enhanced synthesis of polyamides and polyurethanes; the comparison between microwave synthesis conditions in ILs with conventional heating methods and conventional organic solvents has also been addressed [92, 93]. Pretreatment methods combining microwave irradiation and ILs for cellulose dissolution and modification have been also proposed [94, 95]. Microwave irradiation can enhance the solubility of cellulose in ILs and decrease the degree of polymerization of regenerated cellulose after IL dissolution, which can be beneficial for improving cellulose hydrolysis [95].

In spite of the numerous advantages that ILs and microwave irradiation can offer to perform polymerization reactions as described above, only few reports in the literature adequately address the problems of polymer isolation and IL recycling, avoiding entirely the use of VOCs, and the efficient use of microwave irradiation as an alternative energy source when combined with ILs [83]. For instance, a polymerization reaction where the monomer is soluble in a water soluble IL, but not its polymer, was described for the cationic ring opening polymerization of 3-ethyl-3-hydroxymethyloxetane, whereby the polymerization starts as a homogeneous system but the polymer then precipitates during the course of the reaction [96]. Afterward, the polymer can be isolated from the reaction mixture by filtration or decantation and the water-soluble IL recovered. Other

examples describe the heterogeneous free radical polymerizations in aqueous solutions of ILs or pure ILs (under conventional heating), where ILs can perform as reaction media and/or as surfactants to stabilize the heterogeneous reaction systems (monomers and polymers insoluble in IL) [97–99]. In these latter cases, it was shown that the polymer can be obtained as a precipitate, which is washed with water to remove the remains of IL and isolated by a simple filtration; thereafter, the IL is recovered from the resulting aqueous solution by distillation, or the IL aqueous solution itself can be used directly to carry out further polymerization reactions [97–99]. Following a similar approach, in the homogeneous (monomers and polymers soluble in IL) microwave-assisted cationic ring opening polymerization in ILs of hydrophilic polymers (2-ethyl-2-oxazoline) it was demonstrated that the use of hydrophobic ILs is convenient since it facilitates the isolation of the hydrophilic polymer by a simple extraction with water and the IL can also be easily recovered and used in further reaction cycles [88]. In this last example, in the homogeneous (monomers and polymers soluble in IL) microwave-assisted synthesis of hydrophobic polymers in water soluble ILs as a reaction media, it was shown that IL recycling was possible by adding water to the reaction mixture, subsequent filtration for the recovery of the polymer, and followed by a microwave-assisted distillation of the remaining solution to remove the water from the IL before usage in additional reaction cycles [83]. Microwave-assisted distillations in this type of integrated processes may give room to additional energy savings [83, 100]. Thus, it is believed that these and other similar synthetic hybrid techniques, combining ILs as reaction media with microwave irradiation to perform polymer synthesis could open up possibilities for the development of “greener” and more efficient polymerization processes allowing for depletion VOCs emissions as well as for energy savings.

15.3.2 Polymerization under Irradiation of Other Wavelengths

The last two decades brought along the renaissance of sonochemical research so that ultrasound has become a more common laboratory tool to enhance chemical synthesis. The use of ultrasound in chemical systems increases rates, improves yields and selectivities, prevents catalyst deactivation, and improves heat and mass transfer [101].

Radiation-induced polymerization (photopolymerization) is an efficient method for fast generation of highly crosslinked polymer networks from liquid resin systems.

Various types of radiation such as ultraviolet (UV) radiation, and electron beams can be used for initiation of polymerization reactions. Curing of polymer matrices by UV irradiation can be applied to a variety of processes in the production of composite components, as long

as the component can be directly irradiated. Wet lay-up techniques, vacuum infusion-type processes with UV-transparent membranes, filament winding, and prepreg processes have been adapted to UV curing. Unlike thermal curing, the curing time is in the order of minutes rather than hours, which means a significant reduction in cycle time. The radiation can be generated by a variety of sources suitable for various specific applications and different curing strategies. The most frequently used radiation sources are mercury arc lamps. Because of the absorption of radiation passing through matter, the thickness of laminates for efficient application of UV curing is limited. The curing mechanism is either radical polymerization for acrylate-based resins or cationic polymerization for epoxies and vinyl ethers. The properties of the UV-cured polymer matrix are determined by the crosslinking density. This depends on the type and concentration of the photoinitiator and of the (optional) diluents, the intensity and the duration of the irradiation, and the temperature at which the curing process takes place [102].

Radiation crosslinked engineering plastics are low-cost materials, which can be tailored to suit specific applications and can be readily adapted and processed for use in mass production. Until recently, radiation crosslinking was limited to only a few applications: the manufacture of rubber for tyres, cables, pipes (for underfloor heating systems), and heat-shrinkable tubes. Crosslinking was then performed with electron accelerators of low energies (0.1–3 MeV), allowing only surface treatments (limited to a few millimetres of depth). High energy electron accelerators (10 MeV) and γ -plants (strong capacity of penetration of the radiation) were developed since, allowing treatments of thicker parcels and pallets (1 m deep), enabling the radiation crosslinking of molded plastic parts, directly in their packaging [103].

15.4 POLYMERIZATION IN MICROREACTORS

Microreactor technology for chemical processing is currently an area of rapid growth with many application fields. The last two decades have seen the development of a large variety of different microstructured devices for chemical reactions. An overview of the research in microreactor technology can be found in numerous journal reviews and books [104–112]. Microreactors are devices containing fluidic pathways in the submillimeter range. Most designs have a single or multiple parallel channels with diameters between 10 and 1000 μm , where the chemical reaction takes place. The most common microreactor types are tubular, chip-based, or platelet-type designs, but there is a large number of different devices, many of which are tailored for specific applications. They can be fabricated from a variety of different materials, including glass, metal, polymers,

ceramics, and others and, depending on design, temperature and solvent stability of the material, they are used for gas phase, liquid phase, or heterogeneous processes. Microreactors have a very large surface area to volume ratio, which leads to high heat and mass transfer rates for any transfer process involving the channel walls. Liquid flow in microchannels is generally laminar, and mixing is often based on molecular diffusion processes, which for most applications is very efficient because of the small channel geometries. These characteristics lead to a series of process benefits in many reaction systems, such as increased conversion and selectivity or enhanced process control and safety. A key benefit of microreactor technology over classical batch processing is the ability to increase the reactor throughput by a simple “numbering-up” of the basic flow components, as opposed to a classical scale-up approach, which often requires several design steps, ranging from normal laboratory scale through a pilot-plant stage to the final production scale. A major problem of microfluidic channels are blockages caused by fouling or scaling. For this reason, most particle-containing or precipitate-forming reaction systems are not suitable for use in these devices. Most applications of microreactors lie within the wider field of organic chemistry [113–118], ranging from the laboratory synthesis of drug-like molecules or natural products in milligram quantities to the production scale processing of speciality chemicals or renewable fuels.

Microreactor technology has also been adopted for the use in polymer synthesis, for various reasons, such as the excellent heat transfer properties of the reactors and the resulting improvement of temperature control of the process. Compared to many other areas of organic chemistry, where reaction takes place in simple mono- or biphasic systems, the highly viscous nature of many solution phase polymerizations makes it more challenging to perform them in a microreactor system, as pressure drop is large in miniaturized flow channels. General reviews on polymerization in microstructured reactors were published by Hessel et al. [119] and Wilms et al. [120]; the article by Schork and Guo [121] gives an overview on miniemulsion polymerizations in continuous microreactor systems. One of the first investigations on solution phase polymerization in a specialized microreactor system was conducted by Iwasaki and Yoshida [122]. This work describes the free radical polymerization (FRP) of five different monomers in a steel reactor system containing capillaries with 500 μm inner diameter. The results were compared to macroscale batch processing and advantages of the microreactor system were identified in particular for exothermic reactions using acrylate monomers. Later work by the same group demonstrated the numbering-up of a continuous flow microreactor system to the pilot plant scale for the use in free radical polymerization of MMA [123]. Here, a stainless steel shell and tube microreactor was developed consisting

of 94 microtubes (500 μm i.d.) with a total volumetric hold-up of 9.6 ml. The shell was divided into two sections, accounting for the different temperatures in the two stages of the process. Hot oil was introduced in the first section of the shell to carry out the polymerization at 100 °C, and coolant in the second for fast termination. The authors concluded that precise temperature control by effective heat transfer, which is an inherent advantage of microreactor systems, was responsible for the effective control of the molecular weight distribution of the polymer. Serra et al. [124, 125] have conducted numerical simulations of FRP in multilamination microreactors, using a multiphysics model that simultaneously takes into account hydrodynamics, heat, and mass transfer (convection, diffusion, and chemical reaction).

Within the field of radical polymerization, special attention was recently drawn to the use of microreactors for controlled radical polymerization techniques, namely, ATRP, NMRP and RAFT. Shen and Zhu [126] have devised a column reactor packed with silica-gel-supported copper bromide–hexamethyltriethylenetetramine (HMTETA) for the continuous ATRP of homo- and block copolymers of MMA. Wu et al. [127] report the use of microfluidic chips made from thiolene polymer for continuous ATRP of 2-hydroxypropylmethacrylate. Control over the molecular properties of the product was achieved by varying either the flow rate or the relative concentrations of reactants. Enright et al. [128] conducted continuous nitroxide-mediated miniemulsion polymerizations in a steel tubular reactor to prepare a latex of polystyrene homopolymer dispersed in water. The authors report that by chain extension of the polystyrene latex it was possible to synthesize polystyrene-*block*-poly(butyl acrylate) diblock and polystyrene-*block*-poly(butyl acrylate)-*block*-polystyrene triblock copolymers. Rosenfeld et al. [129, 130] described the continuous NMRP of styrene and *n*-butyl acrylate at high temperature in a steel microtube reactor. The authors state that the main advantage of their microreactor system is its ability to handle highly exothermic chemical reactions because of its high surface to volume ratio and the possibility to carry out the polymerization process in homogeneous conditions, ultimately resulting in lower \bar{D} values when compared to a conventional lab-scale batch reactor. This work was then extended to investigate the influence of mixing characteristics of an additional interdigital multilamination micromixer on monomer conversions, molecular weights, and \bar{D} for the synthesis of block copolymers inside the reported microreactor platform. Russum et al. [131, 132] conducted RAFT polymerizations in a continuous miniemulsion using a tubular steel reactor. Comparative batch polymerizations were carried out, and it was found that in general the two reaction systems behaved similarly, from a kinetic point of view. Hornung et al. [133–135] investigated solution phase RAFT polymerizations in tubular stainless steel reactors.

The continuous flow process was automated further by including inline degassing of the monomer stock solution prior to reaction, and post-polymerization stages, such as RAFT end group removal.

Microreactors have also been used for ionic polymerization or polycondensation processes. Nagaki et al. [136] have synthesized polystyrene-poly(alkyl methacrylate) block copolymers by butyllithium initiated anionic polymerization in an integrated flow microreactor system. A high level of control of molecular weight was achieved at temperatures between -28 and $+24$ °C due to fast mixing, fast heat transfer, and residence time control. Santos and Metzger [137] have studied a cationic ethane polymerization in a microfluidic device using a Ziegler–Natta catalyst system. The polymerization intermediates were studied directly from the solution using an inline mass spectrometer and their catalytic activity was proved. Honda et al. [138] have developed a microfluidic system for the synthesis of poly(amino acid) using an anionic ring-opening polycondensation. The authors found that the microreactor produced polymers with narrower molecular weight distribution in comparison to polymers obtained from a batch process. Kessel et al. [139] performed the polycondensation of trialkoxysilanes to poly(silsesquioxane)s in a microreactor setup. Wilms et al. [140] have used a slit-interdigital micromixer system for the synthesis of hyperbranched polymers, employing the ring-opening multibranching polymerization of glycidol. The characteristics of the microstructured reactor were used to engineer a continuous flow process for the preparation of well-defined hyperbranched polyglycerols with molecular weights up to 1000 g/mol.

Besides the synthesis of bulk polymers, microreactor technology is also used for more specialized polymerization applications such as the formation of polymer membranes or particles [119, 141–146]. Bouqey et al. [142] synthesized monodisperse and size-controlled polymer particles from emulsions polymerization under UV irradiation in a microfluidic system. By incorporating a functional comonomer, polymer microparticles bearing reactive groups on their surface were obtained, which could be linked together to form polymer beads necklaces. The ability to confine and position the boundary between immiscible liquids inside microchannels was utilized by Beebe and coworkers [145] and Kitamori and coworkers [146] for the fabrication of semipermeable polyamide membranes in a microfluidic chip via interfacial polycondensation.

The use of microreactor technology for polymer chemistry presents an interesting alternative to conventional processing methods, in both batch and macroscale continuous flow. Microreactors offer a better process control of many exothermic polymerization processes, leading to increased product quality such as narrower polydispersity, and they allow for the synthesis of novel polymeric materials for a range of new applications.

ACKNOWLEDGMENTS

E.V.-L. acknowledges financial support from Consejo Nacional de Ciencia y Tecnología (CONACYT, México) (Project CONACYT 101682), DGAPA-UNAM (Project PAPIIT 119510), and Instituto de Ciencia y Tecnología del Distrito Federal (ICyTDF, México) (Project PICSA11-56). G. L.-B. acknowledges the help from Sebastian Stolz in the preparation of some of the figures and analyses of Section 15.2.1.1.

REFERENCES

1. US Environmental Protection Agency. Green Chemistry. Available at <http://www.epa.gov/greenchemistry/>. Accessed 2012 April 4.
2. Erdmenger T, Guerrero-Sanchez C, Vitz J, Hoogenboom R, Schubert US. *Chem Soc Rev* 2010;39:3317.
3. Kemmere MF. Chapter 1: Supercritical carbon dioxide for sustainable polymer processes. In: Kemmere MF, Meyer T, editors. *Supercritical Carbon Dioxide in Polymer Reaction Engineering*. Weinheim: Wiley-VCH; 2005. p 1 ff.
4. Seiler M, Rolker J, Arlt W. *Macromolecules* 2003;36:2085.
5. Kiamos AA, Donohue MD. *Macromolecules* 1994;27(2):357.
6. McHugh MA, Krukoni VJ. *Supercritical Fluids Extraction: Principles and Practice*. 2nd ed. Stoneham (MA): Butterworth-Heinemann; 1994.
7. ter Horst MH, Behme S, Sadowski G, de Loos TW. *J Supercrit Fluids* 2002;14:181.
8. Kirby CF, McHugh MA. *Chem Rev* 1999;99:565.
9. Seiler M. *Chem Eng Tech* 2002;2:237.
10. Strange EH, Bliss HGW, inventors. British patent 3,045,1913.
11. Sivergin YM. Chapter 6: Polymerization under pressure. In: Kovarskii AL, editor. *High-Pressure Chemistry and Physics of Polymers*. Boca Raton: CRC Press, Inc; 1994. p 195 ff.
12. Whiteley KS, Heggs TG, Koch H, Mawer RL, Immel W. Polyolefins. In: Elvers B, Hawkins S, Schulz G, editors. *Plastics, Properties and Testing of Polyvinyl Compounds*. 5th ed. Vol. A21. New York: VCH Publishers; 1992. p 487 ff.
13. McHugh MA, Guckes TL. *Macromolecules* 1985;18:674.
14. Taylor DK, Carbonell R, DeSimone JM. *Annu Rev Environ Resour* 2000;25:115.
15. Hsiao YL, Maury EE, DeSimone JM, Mawson M, Johnston KP. *Macromolecules* 1995;28:8159.
16. Mawson SM, Johnston KP, Combes JR, DeSimone JM. *Macromolecules* 1995;28:3182.
17. Luna-Barcenas G, Mawson S, Takishima S, DeSimone JM, Sanchez IC, Johnston KP. *Fluid Phase Equilib* 1998;146:325.
18. Kamiya Y, Mizoguchi K, Terada K, Fujiwara Y, Wang JS. *Macromolecules* 1998;31:472.
19. Li D, Han B. *Macromolecules* 2000;39:4506.

20. Lee CT, Ryoo W, Smith PG, Arellano J, Mitchell DR, Lagow RJ, Webber SE, Johnston KP. *J Am Chem Soc* 2003;125:3181.
21. Bungert B, Sadowski G, Arlt W. *Ind Eng Chem Res* 1998;37:3208.
22. Canelas DA, DeSimone JM. *Adv Polym Sci* 1997;133:103.
23. Kendall JL, Canelas DA, Young JL, DeSimone JM. *Chem Rev* 1999;99:543.
24. Charpentier PA, Kennedy KA, DeSimone JM, Roberts GW. *Macromolecules* 1999;32:5973.
25. Wang R, Cheung HM. *J Appl Polym Sci* 2004;93:545.
26. Beuermann S, Buback M, Isemer C, Lasik I, Wahl A. *Macromolecules* 2002;35:3866.
27. Shiho H, DeSimone JM. *J Polym Sci A Polym Chem* 2000;38:1146.
28. Shiho H, DeSimone JM. *J Polym Sci A Polym Chem* 1999;37:2429.
29. Canelas DA, DeSimone JM. *Macromolecules* 1997;30:5673.
30. Canelas DA, Betts DE, DeSimone JM. *Macromolecules* 1996;29:2818.
31. Hwang HS, Gal Y-S, Johnston KP, Lim KT. *Macromol Rapid Commun* 2006;27:121.
32. Woods HM, Nouvel C, Licence P, Irvine DJ, Howdle SM. *Macromolecules* 2005;38:3271.
33. Deniz S, Baran N, Akgün M, Uzun IN, Dincer S. *Polym Int* 2005;54:1660.
34. Rosell A, Storti G, Morbidelli M. *Macromolecules* 2004;37:2996.
35. Wang W, Griffiths RMT, Giles MR, Williams P, Howdle SM. *Eur Polym J* 2003;39:423.
36. Fehrenbacher U, Ballauff M. *Macromolecules* 2002;35:3653.
37. Christian P, Howdle SM. *Macromolecules* 2000;33:237.
38. Beuermann S, Buback M, Schmaltz C, Kuchka F-D. *Macromol Chem Phys* 1998;199:1209.
39. O'Neill ML, Yates MZ, Johnston KP, Smith CD, Wilkinson SP. *Macromolecules* 1998;31:2838.
40. van Herk AM, Canelas DA, Quadir MA, DeSimone JM, Manders BG. *Macromolecules* 1997;30:4780.
41. Shaffer KA, Jones TA, Canelas DA, DeSimone JM. *Macromolecules* 1996;29:2704.
42. Quintero-Ortega IA, Vivaldo-Lima E, Gupta RB, Luna-Bárcenas G, Penlidis A. *J Macromol Sci Pure Appl Chem* 2007;44:205.
43. Quintero-Ortega IA, Jaramillo-Soto G, García-Morán PR, Castellanos-Cárdenas ML, Luna-Bárcenas G, Vivaldo-Lima E. *Macromol React Eng* 2008;2:304.
44. Quintero-Ortega IA, Vivaldo-Lima E, Luna-Bárcenas G, Alvarado JFJ, Louvier-Hernández JF, Sanchez IC. *Ind Eng Chem Res* 2005;44:2823.
45. DeSimone JM, Guan Z, Elsbernd CS. *Science* 1992;257:945.
46. Baradie B, Shoichet MS. *Macromolecules* 2002;35:3569.
47. Chatzidoukas C, Pladis P, Kiparissides C. *Ind Eng Chem Res* 2003;42:743.
48. Mueller PA, Storti G, Morbidelli M. *Chem Eng Sci* 2005;60:377.
49. Wulkow M. *Macromol Theor Simul* 1996;5:393.
50. Modell M, inventors. US patent 4338199. 1982.
51. Thomason TB, Modell M. *Hazard Waste* 1984;1:453.
52. Wood CD, Cooper AI. *Macromolecules* 2003;36:7534.
53. Wood CD, Senoo K, Martin C, Cuellar J, Cooper AI. *Macromolecules* 2002;35:6743.
54. López-Luna A, Gallegos JL, Gimeno M, Vivaldo-Lima E, Bárcenas E. *J Mol Catal B Enzym* 2010;67:143.
55. Deetlefs M, Seddon KR. *Chim Oggi* 2006;24:16.
56. Plechkova NV, Seddon KR. *Chem Soc Rev* 2008;37:123.
57. Kubisa P. *Prog Polym Sci* 2009;34:1333.
58. Winterton N. *J Mater Chem* 2006;44:4281.
59. Brazel CS, Rogers RD, editors. *Ionic Liquids in Polymer Systems-Solvents, Additives and Novel Applications*. ACS Symposium Series. Vol. 913. Washington: American Chemical Society; 2005.
60. Ueki T, Watanabe M. *Macromolecules* 2008;41:3739.
61. Lui J, Yan F, Texter J. *Prog Polym Sci* 2009;34:431.
62. Greaves TL, Drummond CJ. *Chem Soc Rev* 2008;37:1709.
63. Guerrero-Sanchez C, Lara-Ceniceros T, Jimenez-Regalado E, Rasa M, Schubert US. *Adv Mater* 2007;19:1740.
64. Casamada Ribot J, Guerrero-Sanchez C, Hoogenboom R, Schubert US. *J Mater Chem* 2010;20:8279.
65. Casamada Ribot J, Guerrero-Sanchez C, Hoogenboom R, Schubert US. *Chem Commun* 2010;46:6971.
66. Guerrero-Sanchez C, Gohy JF, D'Haese C, Thijs HML, Hoogenboom R, Schubert US. *Chem Commun* 2008;44:2753.
67. Guerrero-Sanchez C. *Ionic Systems in Materials Science: New Materials and Processes Based on Ionic Liquids and/or Ionic Polymerizations*. Saarbrücken: VDM Verlag Publisher; 2008.
68. Tierney JP, Lidstrom P, editors. *Microwave Assisted Organic Synthesis*. Oxford: Blackwell Publishing; 2005.
69. Kappe CO. *Angew Chem Int Ed* 2004;43:6250.
70. Kappe CO, Dallinger D, Murphree S. *Practical Microwave Synthesis for Organic Chemists*. Weinheim: Wiley-VCH; 2008.
71. Bogdal D, Penczek P, Pielichowski J, Prociak A. *Adv Polym Sci* 2003;163:193.
72. Wiesbrock F, Hoogenboom R, Schubert US. *Macromol Rapid Commun* 2004;25:1739.
73. Hoogenboom R, Schubert US. *Macromol Rapid Commun* 2007;28:368.
74. Zhang C, Liao L, Gong S. *Green Chem* 2007;9:303.
75. Bogdal D, Prociak A. *Microwave Enhanced Polymer Chemistry and Technology*. Oxford: Blackwell Publishing; 2007.
76. Mallakpour S, Rafiee Z. *Iran Polym J* 2008;17:907.
77. Aldana-García MA, Palacios J, Vivaldo-Lima E. *J Macromol Sci Pure Appl Chem* 2005;42:1207.

78. Hernández-Meza JJ, Jaramillo-Soto G, García-Morán PR, Palacios-Alquisira J, Vivaldo-Lima E. *Macromol React Eng* 2009;3:101.
79. Hernández-Ortiz JC, Jaramillo-Soto G, Palacios-Alquisira J, Vivaldo-Lima E. *Macromol React Eng* 2010;4:210.
80. Hoffmann J, Nuechter M, Ondruschka B, Wasserscheid P. *Green Chem* 2003;5:296.
81. Martinez-Palou R. *J Mex Chem Soc* 2007;51:252.
82. Martinez-Palou R. *Mol Divers* 2009;14:3.
83. Guerrero-Sanchez C, Lobert M, Hoogenboom R, Schubert US. *Macromol Rapid Commun* 2007;28:456.
84. Varma RS, Namboodiri VV. *Chem Commun* 2001:643–644.
85. Deetlefs M, Seddon KR. *Green Chem* 2003;5:181.
86. Liao L, Liu L, Zhang C, Gong S. *Macromol Rapid Commun* 2006;27:2060.
87. Liao LQ, Zhang C, Gong S. *J Polym Sci A Polym Chem* 2007;45:5857.
88. Guerrero-Sanchez C, Hoogenboom R, Schubert US. *Chem Commun* 2006;25:3797.
89. Schmidt-Naake G, Woecht I, Schmalfluss A, Gluck T. *Macromol Symp* 2009;275–276:204–218.
90. Woecht I, Schmidt-Naake G. *Macromol Symp* 2009; 275–276:219–229.
91. Gluck T, Woecht I, Schmalfluss A, Schmidt-Naake G. *Macromol Symp* 2009;275–276:230–241.
92. Mallakpour S, Kowsari E. *Iran Polym J* 2006;15:239.
93. Mallakpour S, Rafiee Z. *Polymer* 2007;48:5530.
94. Zhang Z, Zhao ZK. *Bioresour Technol* 2010;101:1111.
95. Ha SH, Mai NL, An G, Koo YM. *Bioresour Technol* 2011;102:1214.
96. Biedron T, Bednarek M, Kubisa P. *Macromol Rapid Commun* 2004;25:878.
97. Guerrero-Sanchez C, Erdmenger T, Sereda P, Wouters D, Schubert US. *Chem Eur J* 2006;12:9036.
98. Yan F, Texter J. *Chem Commun* 2006;25:2696.
99. Guerrero-Sanchez C, Wiesbrock F, Schubert US. *ACS Symp Ser* 2005;913:37.
100. Gamallo-Lorenzo D, Barciela-Alonso MC, Moreda-Pineiro A, Bermejo-Barrera A, Bermejo-Barrera P. *Anal Chim Acta* 2005;542:287.
101. Toukoniitty B, Mikkola J-P, Murzin DY, Salmi T. *Appl Catal Gen* 2005;279:1.
102. Endruweit A, Johnson MS, Long AC. *Polym Compos* 2006;27:119.
103. Rouif S. *Nucl Instrum Methods Phys Res B* 2005;236:68.
104. Hessel V, Renken A, Schouten JC, Yoshida J, editors. *Micro Process Engineering: A Comprehensive Handbook*, 3 Volume Set. Weinheim: Wiley-VCH; 2009.
105. Wirth T, editor. *Microreactors in Organic Synthesis and Catalysis*. Weinheim: Wiley-VCH; 2008.
106. Kockmann N, editor. *Micro Process Engineering: Fundamentals, Devices, Fabrication, and Applications*. Weinheim: Wiley-VCH; 2006.
107. Hessel V, Hardt S, Löwe H, Müller A, Kolb G, editors. *Chemical Micro Process Engineering*, 2 Volume Set. Weinheim: Wiley-VCH; 2005.
108. Ehrfeld W, Hessel V, Löwe H. *Microreactors: New Technology for Modern Chemistry*. Weinheim: Wiley-VCH; 2000.
109. Kiwi-Minsker L, Renken A. *Catal Today* 2005;79:2.
110. Kolb G, Hessel V. *Chem Eng J* 2004;98:1.
111. Jähnisch K, Hessel V, Löwe H, Baerns M. *Angew Chem Int Ed* 2004;43:406.
112. Löwe H, Ehrfeld W. *Electrochim Acta* 1999;44:3679.
113. Seeberger PH, Blume T, editors. *New Avenues to Efficient Chemical Synthesis, Emerging Technologies*. Berlin: Springer; 2007.
114. Ley SV, Baxendale IR. *Chimia* 2008;62:162.
115. Kirschning A, Solodenko W, Mennecke K. *Chem Eur J* 2006;12:5972.
116. Zhang XL, Wiles C, Painter SL, Watts P, Haswell SJ. *Chim Oggi* 2006;24:43.
117. Ley SV, Baxendale IR. *Nat Rev Drug Discov* 2002;1:573.
118. Fletcher PDI, Haswell SJ, Pombo-Villar E, Warrington BH, Watts P, Wong SYF, Zhang XL. *Tetrahedron* 2002;58:4735.
119. Hessel V, Hardt S, Löwe H, Serra C, Hadziioannou G. *Chem Ingen Technik* 2005;77:1693.
120. Wilms D, Klos J, Frey H. *Macromol Chem Phys* 2008; 209:343.
121. Schork FJ, Guo J. *Macromol React Eng* 2008;2:287.
122. Iwasaki T, Yoshida J. *Macromolecules* 2005;38:1159.
123. Iwasaki T, Kawano N, Yoshida J. *Org Process Res Dev* 2006;10:1126.
124. Serra C, Sary N, Schlatter G, Hadziioannou G, Hessel V. *Lab Chip* 2005;5:966.
125. Serra C, Schlatter G, Sary N, Schönfeld F, Hadziioannou G. *Microfluid Nanofluidics* 2007;3:451.
126. Shen Y, Zhu S. *AIChE J* 2002;48:2609.
127. Wu T, Mei Y, Cabral JT, Xu C, Beers KL. *J Am Chem Soc* 2004;126:9880.
128. Enright TE, Cunningham MF, Keoshkerian B. *Macromol React Eng* 2010;4:186.
129. Rosenfeld C, Serra C, Brochon C, Hadziioannou G. *Chem Eng Sci* 2007;62:5245.
130. Rosenfeld C, Serra C, Brochon C, Hadziioannou G. *Lab Chip* 2008;8:1682.
131. Russum JP, Jones CW, Schork FJ. *Macromol Rapid Commun* 2004;5:1064.
132. Russum JP, Jones CW, Schork FJ. *Ind Eng Chem Res* 2005;44:2484.
133. Hornung CH, Guerrero-Sanchez C, Brasholz M, Saubern S, Chiefari J, Moad G, Rizzardo E, Thang SH. *Org Process Res Dev* 2011;15:593.
134. Hornung CH, Nguyen X, Dumsday G, Saubern S. *Macromol React Eng* 2012; published online. DOI: 10.1002/mren.201200029.
135. Hornung CH, Postma A, Saubern S, Chiefari J. *Macromol React Eng* 2012;6:246.

136. Nagaki A, Miyazaki A, Yoshida J. *Macromolecules* 2010;43:8424.
137. Santos LS, Metzger JO. *Angew Chem Int Ed* 2006;45:977.
138. Honda T, Miyazaki M, Nakamura H, Maeda H. *Lab Chip* 2005;5:812.
139. Kessler D, Löwe H, Theato P. *Macromol Chem Phys* 2009;210:807.
140. Wilms D, Klos J, Frey H. *Chem Eng Technol* 2007;30:1519.
141. Serra CA, Chang Z. *Chem Eng Technol* 2008;31:1099.
142. Bouquey M, Serra C, Berton N, Prat L, Hadziioannou G. *Chem Eng J* 2008;135(Suppl. 1):S93.
143. Karnik R, Gu F, Basto P, Cannizzaro C, Dean L, Kyei-Manu W, Langer R, Farokhzad OC. *Nano Lett* 2008;8:2906.
144. Huang S, Khoo H, Chang Chien S, Tseng F. *Microfluid Nanofluidics* 2008;5:459.
145. Zhao B, Viernes NOL, Moore JS, Beebe DJ. *J Am Chem Soc* 2002;124:5284.
146. Hisamoto H, Shimizu Y, Uchiyama K, Tokeshi M, Kikutani Y, Hibara A, Kitamori T. *Anal Chem* 2003;75:350.