**Part III
Polymerization**

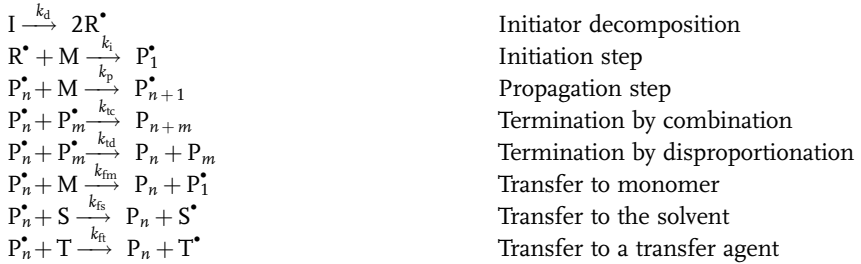# 12
Free Radical Polymerization

Christophe Serra

12.1
Introduction

12.1.1
Mechanism

Polymerization can be considered as the process that converts small molecules (monomers) into long polymer molecules (macromolecules) by virtue of a chemical reaction, which creates covalent bonds between monomer units. Free radical polymerization (FRP) is the polymerization method most widely used to obtain macromolecules on the industrial scale. The FRP mechanism relies on the high reactivity of radicals and their strong ability to add to double bonds. This addition polymerization technique usually starts with the thermal or UV-initiated decomposition of an initiator (I), which generates two primary radicals ($R^{\bullet}$). Then, in the presence of unsaturated monomers (M), the unpaired electron of the primary radicals adds to the double bond of the monomer and consequently generates another radical containing one monomer unit ($P_1^{\bullet}$). This new radical can react with another monomer unit and so on. This leads to the growth of the growing polymer chain ($P_n^{\bullet}$) until this radical is deactivated by termination or transfer to another molecule. The termination is a bimolecular reaction between the two growing polymer chains ($P_n^{\bullet}$ and $P_m^{\bullet}$), which occurs either by disproportionation, two dead polymer chains (P_n and P_m) are formed with a chain length equal to those of the two growing radicals, or by combination, one dead polymer chain (P_{n+m}) is formed with a chain length equal to the sum of those of the two growing radicals. The transfer can occur through multiple reactions and concern mainly the reaction between a growing polymer chain ($P_n^{\bullet}$), the monomer, the solvent and/or a transfer agent. The transfer generates one dead polymer chain (P_n), the chain length of which is equal to that of the growing polymer chain, and a new radical that can initiate a new polymer chain.

This common FRP mechanism is summarized by the following scheme of reactions [1]:

$$I \xrightarrow{k_d} 2R^\bullet \qquad \text{Initiator decomposition}$$
$$R^\bullet + M \xrightarrow{k_i} P_1^\bullet \qquad \text{Initiation step}$$
$$P_n^\bullet + M \xrightarrow{k_p} P_{n+1}^\bullet \qquad \text{Propagation step}$$
$$P_n^\bullet + P_m^\bullet \xrightarrow{k_{tc}} P_{n+m} \qquad \text{Termination by combination}$$
$$P_n^\bullet + P_m^\bullet \xrightarrow{k_{td}} P_n + P_m \qquad \text{Termination by disproportionation}$$
$$P_n^\bullet + M \xrightarrow{k_{fm}} P_n + P_1^\bullet \qquad \text{Transfer to monomer}$$
$$P_n^\bullet + S \xrightarrow{k_{fs}} P_n + S^\bullet \qquad \text{Transfer to the solvent}$$
$$P_n^\bullet + T \xrightarrow{k_{ft}} P_n + T^\bullet \qquad \text{Transfer to a transfer agent}$$

In the long-chain approximation, it is assumed that the monomer is mainly consumed in the propagation step. Hence the rate of polymerization (r_p) is considered as the rate of the propagation reaction:

$$r_p = k_p P^\bullet M \tag{12.1}$$

where k_p is the propagation rate constant, $P^\bullet$ the concentration of all growing polymer chains whatever their chain length and M the monomer concentration. Another common assumption made for FRP is the quasi steady-state approximation (QSSA), which states that all radicals do not accumulate in the reactor. Hence the rate of production of radicals equals that of their consumption. This leads to the following equation:

$$2k_d f I = 2k_t P^\bullet \tag{12.2}$$

where f is the initiator efficiency, I the concentration of initiator, k_d the initiator decomposition rate constant and $k_t(k_{tc} + k_{td})$ the termination rate constant. The initiator efficiency is defined as the percentage of radicals formed by the initiator decomposition which initiates a growing polymer chain. By combining Equations 13.1 and 13.2, the propagation rate can be expressed as

$$r_p = k_p \sqrt{\frac{k_d f I}{k_t}} M \tag{12.3}$$

Due to the statistical nature of polymerization reactions, the dead polymer chains have different chain lengths. Thus a polymer is always a mixture of macromolecules exhibiting a distribution of chain lengths. This distribution is usually characterized by the number-average chain length (NACL) or the weight-average chain length (WACL) and the polydispersity index (PDI) defined as WACL/NACL. If all macromolecules have the same chain length, PDI would be equal to 1 and the polymer is monodisperse. For ideal conditions, FRP leads to PDI equal to 1.5 for a termination by combination and 2 for a termination by disproportionation [2]. These figures represent the lower values of the PDI since a broader chain length distribution (higher PDI) is obtained when the operating conditions (temperature, mixing, initiator and monomer concentrations) vary with time.

12.1.2
Main Features of FRP

Most of the commodity polymers are synthesized through FRP from vinylic, stryrenic and acrylic monomers. FRP displays some specific features in comparison with other polymerization techniques such as step growth, ionic or coordination polymerizations. Polymers with high molecular weights (high chain lengths) are synthesized at the early stage of the polymerization. The depletion of monomer is observed during the whole time scale of the polymerization. FRP is a versatile polymerization technique which can be used in conjunction with homogeneous processes, bulk or solution, or heterogeneous processes, emulsion and suspension. Moreover, FRP can be performed in many reactor configurations, either continuous, batch or semi-batch.

Most of the monomers commonly polymerized through FRP give rise to an exothermic propagation reaction with reaction enthalpies up to $-100 \, \text{kJ mol}^{-1}$. If the heat released by the polymerization is not suitably removed from the reactive medium, an increase in the reactor temperature is observed. If nothing is done, this increase in temperature accelerates the polymerization reaction and consequently the amount of heat released by the polymerization increases, also leading to a thermal runaway. This uncontrolled increase in the temperature can lead to consequences as dramatic as an explosion [3]. Indeed, the pressure inside the reactor can rapidly increase due to the boiling of the low molecular weight compounds (monomer, solvent). Even if such an ultimate event can be avoid by appropriate means, the simple fact that the polymerization leaves its normal course to an uncontrollable course has great consequences on the polymer properties. First, one can observe a significant broadening of the chain length distribution; PDI is increasing. Second, NACL may vary by several orders of magnitude.

Another problem that can face FRP processes is the large increase in the reactive medium viscosity, which can reach up to seven decades for bulk and highly concentrated solution processes. This increase is followed by a decrease in the reactants' molecular diffusion coefficients and a reduction in thermal and mass transport [3]. As a consequence, the reaction course is highly affected by the viscosity. However, all the reactions of the FRP scheme are not affected in the same way. The initiator decomposition involves only one small molecule, hence its rate constant k_d is virtually not affected by the viscosity increase. Propagation and transfer reactions involve a small molecule and a growing polymer chain. While the molecular diffusion coefficient of the former is slightly reduced, the latter undergoes a large reduction of its coefficient due to its important length. Therefore, the rate constants k_p and k_f decrease as the viscosity increases. Finally, the most affected reactions are the termination reactions for which two large molecules have to react together. Thus the rate constants k_{tc} and k_{td} are strongly reduced as the viscosity increases. As an overall consequence, the polymerization rate (Equation 12.3) increases. This is the gel or Trommsdorff effect. This uncontrolled acceleration of the polymerization reaction rate leads also, like the thermal runaway, to broadening of the chain length distribution.

12.1.3
Goodness of Mixing

Mixing is an extremely important issue in FRP processes [4]. First, it allows removal of the heat released by the polymerization reaction by establishing a convective thermal flow from the heart of the reactor to the reactor's cold surfaces. Second, it can prevent segregation. This phenomenon is characterized by chunks of reactive fluid acting like individual small batch reactors flowing inside the main reactor. It also prevents the formation of hot spots. Bad mixing, for instance between on one hand the monomer phase and on the other hand the solvent and initiator phase, will then generate important local concentration gradients. Since the propagation reaction is a very fast and exothermic chemical reaction [5], zones of high monomer concentrations will produce high molecular weight polymers and will release a lot of energy. Therefore, a hot spot is formed which can lead to degradation of the polymer and/or the monomer. Finally, it controls the polymerization rate in heterogeneous processes where polymerization reactions are strongly dependent on the amount of interfacial area between the immiscible phases. It is worth noting that even for a homogeneous polymerization, and due to the differences in physical properties of the polymer and monomer, the polymer becomes to some extent immiscible with its monomer, generating intrinsically a heterogeneous reactive medium.

12.2
Use of Microsystems in FRP

12.2.1
Advantages

Microsystems have several characteristics which make them suitable to address issues that cannot be solved easily in large-scale reactors. These characteristics are [6]:

1. A high surface area-to-volume ratio, which makes them particularly suitable for the study, the process and the control of highly exothermic reactions. Indeed, the heat released by the reaction can be easily removed from the reactive medium.
2. A small characteristic length (of the order of tens to hundreds of microns) which favors diffusional transport over the kinetics. Then, these microsystems are suitable for fast chemical reactions.
3. A high interfacial area-to-volume ratio up to $30\,000\,\mathrm{m^2\,m^{-3}}$, whereas these ratios generally do not exceed $2000\,\mathrm{m^2\,m^{-3}}$ for laboratory apparatus and $100\,\mathrm{m^2\,m^{-3}}$ for industrial reactors. This makes microsystems suitable for interfacial chemical reactions.
4. A small internal volume, which allows one to manipulate very expensive products (e.g. catalyst) or very dangerous reagents (e.g. cyanides, peroxides).

In the particular area of FRP, the characteristics specified above can contribute significantly to improving the control over macromolecular synthesis [7]. Indeed, it is expected that fast and highly exothermic polymerization reactions will be greatly

affected by the heat and mass transfer ability of these microsystems and that lower polydispersity indices can be reached. Consequently, the use of these microsystems should avoid or alleviate any thermal runaway, Trommsdorff effect and mass and thermal transfer limitations, which are well known to be critical issues in any large-scale FRP reactors. All these phenomena affect considerably the chain length distribution by increasing the polydispersity index and thus lead to a loss of control of the macromolecular synthesis.

12.2.2
Experimental Investigations of the Use of Microsystems in FRP

12.2.2.1 Micromixer-assisted Polymerization of Acrylate Resins
Acrylic monomers are among the most reactive monomers which can be polymerized by FRP. As stressed in Section 12.1.3, the mixing of the monomer and initiator solutions is of primary importance. Uneven mixing can lead to local zones highly concentrated in monomer, where the extremely fast propagation reaction generates high molecular weight compounds. Above a certain chain length, the polymer might not be miscible in the monomer and precipitation occurs. This was experienced by Bayer *et al.*, who reported the severe fouling of a 5 mm static mixer (Figure 12.1) in the continuous flow polymerization of different acrylates with a tubular reactor [8]. The polymer which clogged the static mixer was analyzed by size-exclusion chromatography (SEC). Its molecular weight ranged from 10^5 to 10^6 g mol^{-1}.

To avoid such fouling, a micromixer (IMM, Mainz, Germany) was used prior to the static mixer. This micromixer laminates both inlet solutions into 36 lamellae of 25 μm thickness. The generation of such thin lamellae and the subsequent rapid and efficient mixing did not lead to the precipitation of the polymer; the static mixer never became clogged (Figure 12.2). The polymer synthesized had a number-average molecular weight of 10^4 g mol^{-1}.

A successful micromixer-assisted pilot plant was designed by researchers at Axiva (formerly Aventis) [8] for the production of acrylates. In the scale-up of the above-described laboratory-scale experiments, the numbering-up approach was used as the performance of the micromixer is directly related to its small dimensions. Therefore, 28 micromixers were used to mix the inlet flows of four tubular reactors (Figure 12.3). A capacity of 2000 tons per year was achieved without any fouling problem. Axiva filed a patent [9] on the use of such a micromixer for the continuous production of polymers.

Figure 12.1 Photograph of the static mixer fouled by the precipitate of high molecular weight acrylic polymer. From Ref. [8].

Figure 12.2 Photograph of the static mixer after premixing of the reactant fluids by a micromixer. From Ref. [8].

12.2.2.2 FRP in Microreactors

As stressed in Section 12.1.2, thermal transport is an important issue in FRP. The AIBN-initiated FRP of five different monomers was investigated by Iwasaki and Yoshida [10] in a microreactor system (Figure 12.4) composed of a T-shaped micromixer (M1: 800 μm i.d.), a primary microtube for achieving complete mixing (R1: 250 μm i.d., 2 m length), a microtube reactor immersed in a 100 °C oil bath (R2: 500 μm i.d., 9 m length) and a microtube immersed in a 0 °C water bath for polymerization quenching (R3: 500 μm i.d., 1 m length). The results were compared with those obtained in a conventional macroscale batch reactor.

For butyl acrylate (BA), the molecular weight distribution was found to be narrower than that for the batch reactor, as can be seen in Figure 12.5. The PDI for this polymer is then lower in the microreactor system (Table 12.1). The difference was smaller but still noticeable for benzyl methacrylate (BMA) and methyl methacrylate (MMA) and almost zero for vinyl benzoate (VBz) and styrene (St) (Table 12.2). The authors claimed that the observed results are directly related to the superior heat transfer ability of the microtube reactor. The more exothermic the polymerization reaction,
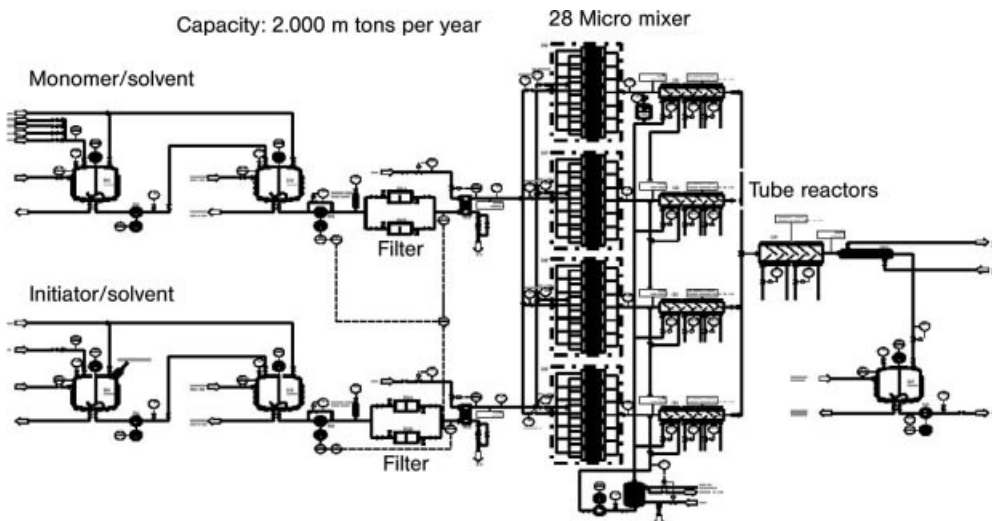
Figure 12.3 Micromixer-assisted acrylate polymerization plant. From Ref. [8].
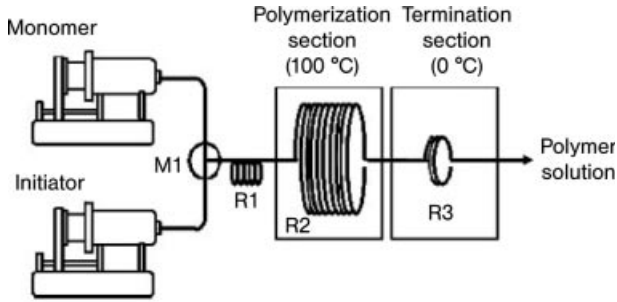
Figure 12.4 Microreactor system for the FRP of five different monomers. From Ref. [10].

the more effective the microsystem is in controlling the molecular weight distribution.

These results are in accord with the power released by the polymerization when the monomer is incorporated into the growing polymer chain. This power ($\mathcal{P}$) is given by

$$\mathcal{P} = r_p \Delta H V_R = k_p P^\bullet M \Delta H V_R \tag{12.4}$$

where ΔH is the propagation reaction enthalpy and V_R the reactor volume. Radicals are fairly reactive, hence the concentration $P^\bullet$ is usually kept low whatever the monomer. For a given volume, and monomer concentration, the power is simply related to the product of k_p and ΔH. Then, the amount of heat released by the polymerization reaction is not only a function of the reaction enthalpy but also the rate constant of that reaction, i.e. how fast the reaction is (Table 12.3). From Table 12.3, the power released by the polymerization decreases in the order BA > BMA > MMA > St, which corresponds exactly to the gain in the PDI reduction between the macro-scale reactor and microtube reactor. Hence the higher the power, the better is the control of the macromolecular synthesis in the microreactor system.
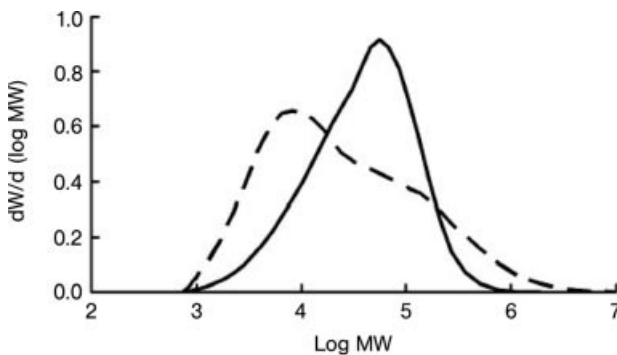
Figure 12.5 Molecular weight distribution of poly(butyl acrylate) produced in the microreactor system (solid line) and in the macroscale batch reactor (dashed line). The residence time was 4 min. From Ref. [10].

Table 12.1 Results for the FRP of butyl acrylate. From Ref. [10].

Reactor	Residence time or reaction time (min)	Yield (%)	M_n ($\times 10^3$)	PDI (M_w/M_n)
Microreactor	1.5	72.4	33.0	3.63
	2.0	86.5	26.1	3.59
	3.0	86.5	22.8	3.14
	4.0	89.6	20.8	3.16
Macro-scale batch reactor	5.0	89.3	19.2	3.35
	2.0	50.0	27.1	212
	3.0	82.1	10.0	9.61
	3.5	86.0	9.3	10.0
	4.0	88.0	9.3	10.3

Since the control of the molecular weight distribution in microtube reactors was demonstrated, Iwasaki *et al.* [11] investigated the large-scale production of polymers by numbering-up microreactors. AIBN-initiated FRPs of BA and MMA were conducted in a Type 1 numbering-up reactor with various residence times. The results were then compared with those obtained with the previously single-tube microreactor system (Figure 12.3). The Type 1 numbering-up reactor (Figure 12.6) is composed of 94 microtube reactors (510 μm i.d., 600 mm length) in a shell (60 mm i.d., 600 mm length). The shell has two different sections. The first section (500 mm length) is traversed by hot oil whereas the second is in contact with a cooling fluid. For MMA, polydispersity indices, number-average molecular weights and monomer conversions were in good agreement for the two systems. However, for BA, a lower monomer conversion was systematically obtained with the Type 1 numbering-up reactor. In contrast to MMA, for which the monomer conversion was less than 26%, the BA conversion was higher than 65%. Hence the viscosity of the reactive medium significantly increased along the microtube reactors. According to the authors, this

Table 12.2 Results for the FRP of styrene. From Ref. [10].

| Reactor	Residence time or reaction time (min)	Yield (%)	M_n ($\times 10^3$)	PDI (M_w/M_n)
Microreactor	5.0	14.4	4.7	1.74
	7.5	24.8	4.8	1.70
	9.9	27.3	5	1.76
	11.9	31.1	5.1	1.69
	15.0	34.2	5.3	1.74
Macro-scale batch reactor	5.0	5.7	5.6	2.05
	7.5	10.9	5.5	1.79
	10.0	18	5.3	1.76
	15.0	29.4	5.5	1.72
	20.0	38.6	5.6	1.70

Table 12.3 Enthalpies and propagation rate constants for various monomers.[a]

Parameter	Monomer				
	BA	BMA	MMA	VBz	St
k_p (at 30 °C) (L mol^{-1} s^{-1})	3496	1410	248	185	106
ΔH (kJ mol^{-1})	−78	−60	−55	–	−70
$k_p \times \Delta H$ (kW L mol^{-2})	−272688	−84600	−13,640	–	−7420

[a]From *Polymer Handbook*, 4th edn, (eds. J. Brandrup, E.H. Immergut, E.A. Grulke, associate eds. A. Abe and D.R. Bloch), John Wiley & Sons, Inc., New York, **1999**.

high viscosity might have clogged some microtube reactors. Therefore, the overall volume was reduced, which implied a decrease in the residence time.

From the use of the Type 1 numbering-up reactor, it was learnt that the flow uniformity is probably the most important parameter to consider when numbering-up reactors. Iwasaki *et al.* then developed a Type 2 numbering-up reactor with special attention to the flow uniformity. This Type 2 numbering-up reactor (Figure 12.7) consists of five shells (178 mm length each) coupled with tube connectors. In the first shell, a single microtube is branched to eight other microtubes in a low-temperature environment. The next three sections are heated with hot oil to promote the polymerization reaction. These sections contain eight coiled microtube reactors of 1950 mm length with successive increases in i.d.: 250, 500 and 1000 µm. Finally, the fifth section allows merging of all eight microtube reactors into one microtube at low
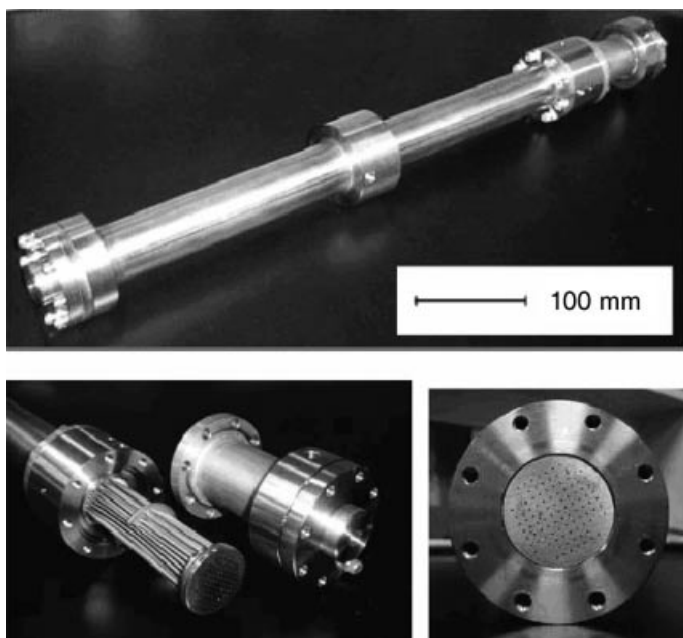
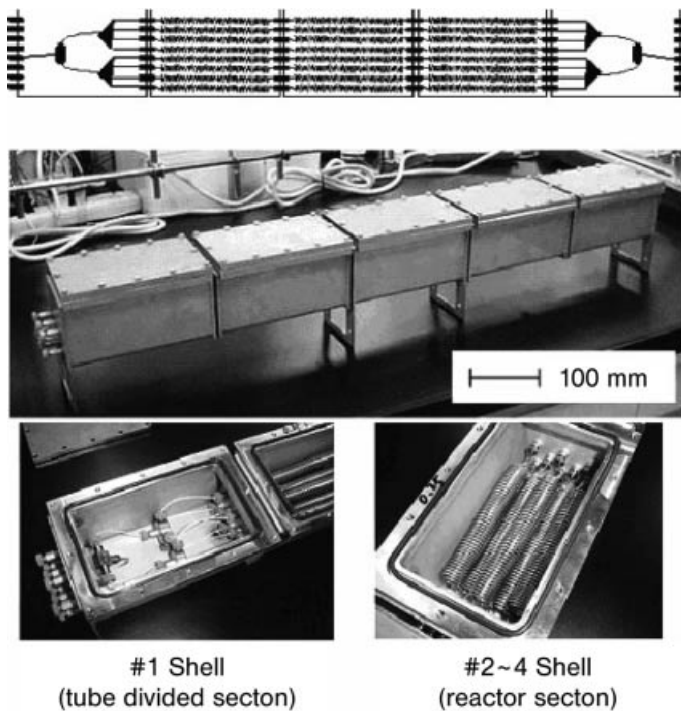**Figure 12.6** Type 1 numbering-up reactor. From Ref. [11].

Figure 12.7 Type 2 numbering-up reactor. From Ref. [11].

temperature to quench the polymerization. AIBN-initiated FRP of BA performed in a single tube of varying i.d. $(250 + 500 + 1000\,\mu\text{m})$ gave similar results to those obtained with this Type 2 numbering-up reactor, demonstrating that good flow uniformity was achieved in the latter system.

Finally, a pilot plant was constructed based on the Type 2 numbering-up reactor (Figure 12.8). This pilot plant has been operated continuous for 6 days, producing up
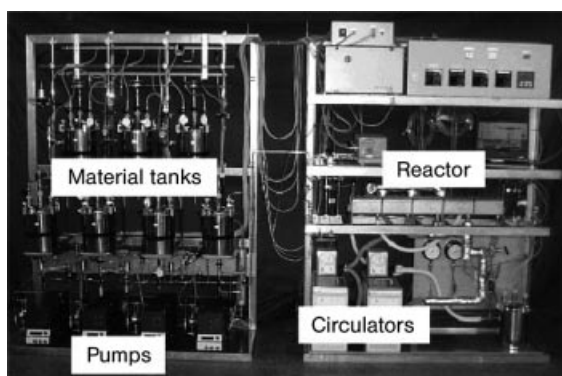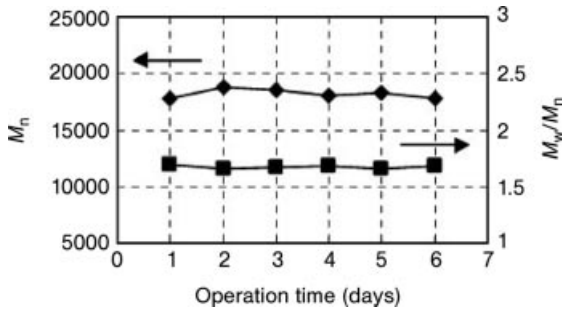

Figure 12.8 Photograph of the microchemical pilot plant, From Ref. [1].

Figure 12.9 Variation of the number-average molecular weight and polydispersity index of poly-MMA with number of days of operation. From Ref. [11].

to 4 kg of poly-MMA without any increase in the pressure or reactor temperature. The quality of the polymer was constant over 1 week of operation, as can be seen in Figure 12.9. This pilot plant demonstrates that microsystems can be applied to the relatively large-scale production of polymers.

12.2.2.3 Numerical Simulations of Styrene FRP in Microsystems

For bulk and semi-dilute processes, the increase in the viscosity of the reactive medium makes at one point the polymerization diffusion controlled, as stressed in Section 12.1.2. This was studied by Serra *et al.* in a numerical study of the semi-dilute (30% solvent) styrene FRP in multi- and bilamination microreactors having the same volume [12, 13]. The multilamination microreactor used (Figure 12.10a) was actually a micromixer (SFIMM from IMM, Mainz, Germany). This micromixer uses the principle of interdigital multilamination and geometric focusing. The two inlet flows (pure styrene and solvent + initiator) are delaminated into 69 streams of 250 μm thickness and distributed in staggered rows along an arc. Then, the fluids are
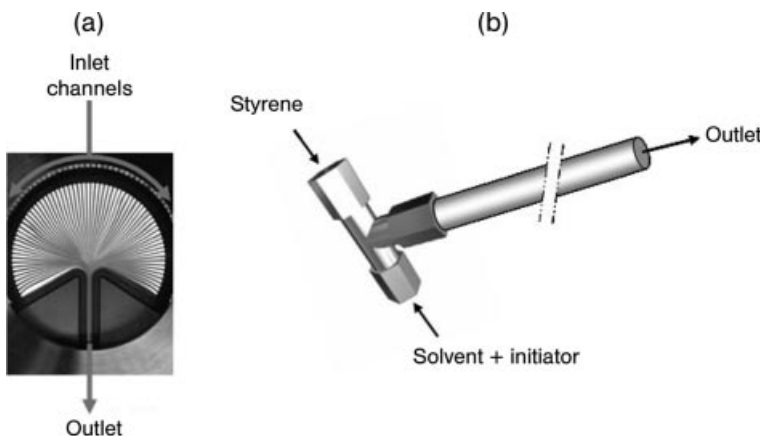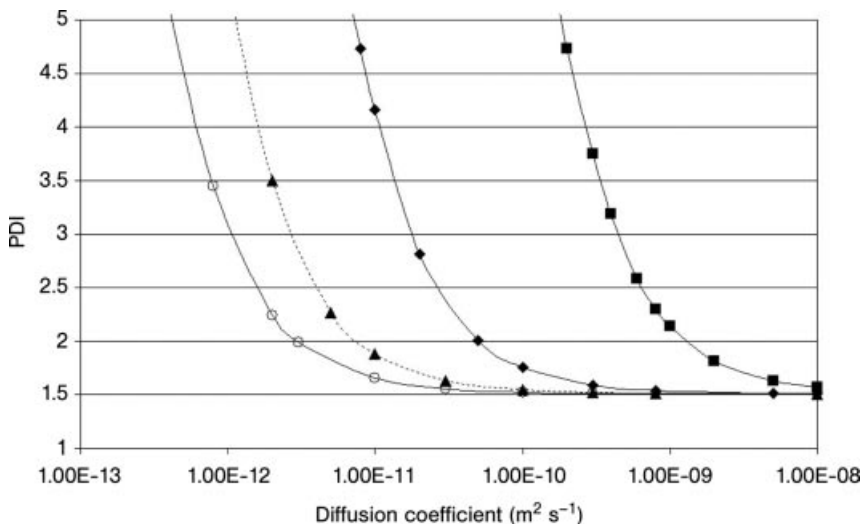

Figure 12.10 (a) Multilamination and (b) bilamination microreactors. From Ref. [13].

focused in a delta-shaped section and exit the microsystem through a 500 μm wide straight channel where the fluid lamellae have an average thickness of 4 μm. The bilamination microreactor considered was simply a tubular reactor of different radii with a T-shaped inlet manifold (Figure 12.10b).

The numerical simulations were performed with the help of a multiphysics CFD software package. The finite elements method allowed the set of partial differential equations resulting from the hydrodynamics, thermal and mass transfer (convection, diffusion and chemical reaction) to be solved. The results of the polymerization, expressed as the monomer conversion (X_M), number-average chain length (DP_n) and polydispersity index (PDI), were computed from a model describing the evolution of the moments of the chain length distribution. These three parameters were analyzed as a function of the chemical species diffusion coefficient assuming that a decrease in this coefficient will mimic an increase in the viscosity of the medium. It was found that the range of diffusion coefficients over which the polydispersity index can be maintained close to the theoretical value of 1.5 for ideal conditions increases as the tube reactor radius decreases (Figure 12.11).

This result can be explained considering the radial Peclet number, which is defined as the ratio of the characteristic time of diffusion in the direction perpendicular to the main flow to the characteristic time of convection in the flow direction (i.e. the mean residence time, τ). Thus it can be expressed as follows:

$$Pe_R = \frac{L^2}{D\tau} \tag{12.5}$$

Figure 12.11 Variation of polydispersity index with respect to the diffusion coefficient. Multilamination microreactor (▲); bilamination microreactor with tube radius of 0.24 mm (○), 1 mm (◆) and 5 mm (■). From Ref. [13].
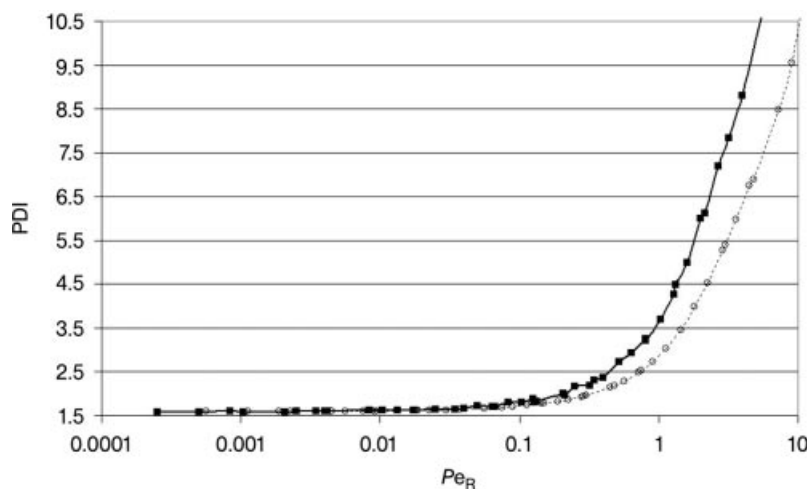
Figure 12.12 Comparison of the polydispersity index obtained in a multilamination microreactor (filled symbols) and in a tubular reactor (open symbols) as a function of the radial Peclet number. From Ref. [12].

where L is the characteristic length of the reactor (tube radius of channel width) and D the diffusion coefficient. As the characteristic length of the reactor increases, i.e. for high radial Peclet number, the reactive medium cannot be fully homogenized by the diffusional transport before leaving the system, resulting in a high polydispersity index and a loss of control of the polymerization (Figure 12.12). As seen in Figure 12.4, the multilamination microreactor exhibits behavior similar to that of a tubular reactor, the length and radius of which would be 8.23 m and 0.39 mm, respectively. However, owing to its shorter length (15 mm), the multilamination microreactor induces less pressure drop and thus requires less input energy. Furthermore, it can be easily cleaned up in case of fouling.

12.3
Conclusion

Due to their unique features, microsystems truly represent new process tools for the synthesis of polymer through free radical polymerization. Phenomena such as thermal runaway, Trommsdorff effect and segregation, which are commonly encountered in conventional polymer reactors, can be reduced or alleviated when microreactors and micromixers are employed. Moreover, successful implementation of microsystems, in an already-existing production line as well as the numbering approach have proved that despite their small internal volume microsystems can be considered for large scale polymer production.

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