Ab initio Emulsion Polymerization by RAFT (Reversible Addition–Fragmentation Chain Transfer) through the Addition of Cyclodextrins

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Dedicated to Professor *Giambattista Consiglio* on the occasion of his 65th birthday

A novel process to produce homo- and copolymers by RAFT polymerization in emulsion is presented. It is known that RAFT-controlled radical polymerization can be conducted in emulsion polymerization without disturbing the radical segregation characteristic of this process, thus leading to polymerization rates identical to those encountered in the corresponding nonliving systems. However, RAFT agents are often characterized by very low water solubility and, therefore, they diffuse very slowly from the monomer droplets, where they are initially solubilized, to the reaction loci, *i.e.*, the polymer particles. Accordingly, when used in emulsion polymerization, they are practically excluded from the reaction. In this work, we show that cyclodextrins, well-known for their ability to form water-soluble complexes with hydrophobic molecules, facilitate the transport across the H_2O phase of the RAFT agent to the polymer particles. Accordingly, chains grow through the entire process in a controlled way. This leads to the production of low-polydispersity polymers with well-defined structure and end functionalities as well as to the possibility of synthesizing block copolymers by a radical mechanism.

1. Introduction. – Despite the recent progresses in living radical polymerization (LRP) by RAFT (reversible addition–fragmentation chain transfer), especially in terms of new RAFT agents and produced polymers [1–3], its application to emulsion polymerization is far from being assessed. On one hand, it has been shown, based on kinetic arguments, that this is the only living mechanism that allows realizing a radical-segregated system where the polymerization rates for the living and the equivalent nonliving processes are identical [4–6]. On the other hand, the application to conventional emulsion polymerization, *i.e.*, the so-called *ab initio* polymerization, did not enjoy much success, and good results have been obtained only in mini-emulsion polymerization [2][3][5].

Mini-emulsion polymerization is generally regarded as more complex than conventional emulsion polymerization, which remains the preferred way to carry out industrial polymerizations. However, the application of RAFT to *ab initio* emulsion polymerization is not straightforward, mainly because of the heterogeneous nature of the process and, specifically, of the partitioning of the RAFT agent among the three phases present in the system: the monomer droplets, the H_2O phase, and the polymer particles. In this respect, to best achieve satisfactory living conditions in *ab initio* emulsion polymerization, the RAFT agent must satisfy three main requirements: *i*) it has to be fully transported to the polymer particles, *ii*) this transport has to be very fast to prevent differences in chain-birth times, and *iii*) it must be delivered homogeneously to all the polymer particles to prevent differences in chains produced in different particles.

These requirements can be met by fulfilling the constraint given by *Eqn. 1*. In *ab initio* emulsion polymerization, three competing processes are taking place simultaneously: nucleation of new polymer particles, transport of the RAFT agent from the monomer droplets (where it is initially solubilized) to the polymer particles, and polymerization inside the particles. In has been shown [5] that the rates of these three processes must satisfy the relation of *Eqn. 1* where R_{nucl}, R_{tr}, and R_{pol} refer to the rates of nucleation, RAFT-agent transport, and polymerization, respectively.

$$R_{\mathrm{nucl}} \gg R_{\mathrm{tr}} \gg R_{\mathrm{pol}} \tag{1}$$

Let us first focus on the first part of *Eqn. 1*: $R_{\mathrm{nucl}} \gg R_{\mathrm{tr}}$. To avoid that the last nucleated particles receive less or no RAFT agent, it is necessary that nucleation is faster than the interphase transport of RAFT agent. This guarantees that requirement *iii*), *i.e.*, the uniform distribution of the RAFT agent, is actually verified. Note that the nucleation rate can be easily adjusted in emulsion polymerization to meet this requirement, *e.g.*, by acting on the initiation rate or on the amount of surfactant in the system.

To fulfill the first two requirements, *i.e.*, a complete and fast transport of the RAFT agent to the polymer particles, the rate of transport must be faster than the rate of polymerization, *i.e.*, $R_{\mathrm{tr}} \gg R_{\mathrm{pol}}$. If $R_{\mathrm{tr}} < R_{\mathrm{pol}}$, only part of the RAFT agent can in fact participate in the polymerization. On the other hand, if R_{tr} and R_{pol} are comparable, the RAFT agent is transported to the particles during the entire duration of the polymerization, and new dormant chains are continuously produced. These chains experience different polymerization times and, therefore, exhibit different chain lengths at the end of the process. Accordingly, the transport of the RAFT agent must be as fast as possible compared to the rate of polymerization, so that 'all' the dormant chains can start growing at the 'same' time.

It is worth noting that another potential drawback of living emulsion processes, the polymerization in the droplets [1], should not represent a problem when using the RAFT mechanism. In nonliving systems, droplet polymerization is negligible for two reasons: first, the total surface of the droplets is much smaller than that of the polymer particles and, therefore, the flux of radicals to the droplets is negligible with respect to that to the particles; second, due to radical segregation, the polymerization rate in the particles is much faster than in the droplets. The same remains true when introducing the RAFT mechanism in the system, since this does not affect neither the droplet/particle-surface ratio nor the kinetics of the polymerization. However, in this case, each radical entering the droplets leads to the growth of many oligomers containing a RAFT end, which become more and more insoluble and, therefore, unlikely to leave the monomer droplets as requested by the emulsion-polymerization mechanism. Nonetheless, if the RAFT agent is fully transported to the polymer particles early on in the polymerization, the loss of RAFT agent due to its polymerization in the droplets is minimized. Note that this argument does not apply to other living processes, such as nitroxide-mediated living polymerization (NMLP) and atom-transfer radical polymerization (ATRP), since no effective radical segregation can be obtained for these two systems and, therefore, the polymerization rate in the droplets and in the particles is comparable [5].

According to the key requirement *i*), in a living *ab initio* emulsion polymerization, we need a rate of transport of the RAFT agent that is intermediate between those of nucleation and polymerization. However, since typical RAFT agents are generally very hydrophobic, their transport rate to the particles is usually too slow, and their application to *ab initio* emulsion polymerization leads to uneffective reaction control [1]. This is a well-known issue in emulsion-polymerization practice, *e.g.*, when monomers having very different water-solubility are polymerized, we may have a number of problems [7], such as poor conversion of the monomer having the lowest water-solubility, presence of coagulum, and/or pooling effects. Similar effects have been also observed in our laboratory, where the living emulsion polymerization in the presence of cumyl dithiobenzoate as RAFT agent always led to formation of coagulum around the stirrer.

Recently, the influence of the RAFT-agent hydrophobicity on the control of an *ab initio* emulsion polymerization of styrene has been investigated [8]. The authors confirmed not only that the rate of diffusion across the H_2O phase strongly depends upon the RAFT agent's water-solubility, but also that this directly affects the quality of the final polymerization. Namely, RAFT agents with larger water-solubilities produced polymers with lower polydispersity values and closer matches between the targeted and the experimental average molecular masses. In the same work, the concentration of the RAFT agents in H_2O was measured by UV/VIS spectroscopy (H_2O), obtaining values of *ca.* $9 \cdot 10^{-4}$ mol/l for cumyl dithiobenzoate, the RAFT agent used in this work. This value is much smaller than the saturation concentration of styrene ($4.3 \cdot 10^{-3}$ mol/l) [9] and methyl methacrylate ($1.5 \cdot 10^{-1}$ mol/l) [9]. Since the rate of transport of a species from the monomer droplets across the H_2O phase to the swollen polymer particles is directly proportional to the saturation concentration in H_2O [10], it is expected that poorly controlled living *ab initio* emulsion polymerization are obtained for these two monomers.

Possible remedies are the addition of an organic solvent or the use of larger concentrations of surfactant, which have been suggested also by *Prescott et al.* [1] as a possible route to favor the transport of the RAFT agent to the polymer particles. However, such additions pose safety and environmental problems, as well as cost and operative drawbacks. Moreover, in the case of organic solvents, this may also induce destabilization of the aqueous dispersion. An alternative could be to select RAFT agents with larger water solubility. However, more-hydrophilic RAFT agents shift the polymerization reaction into the H_2O phase [1], leading to very large induction times. The only notable exception is the use of xanthates [11][12], which, however, suffers from a poor control of the polymer growth, their rate of chain transfer to dormant species being rather small. Finally, a promising technique is also represented by the so-called self-assembling RAFT agents, which involves the formation of amphiphilic living oligomers [13]. However, this approach is still under development, and further assessment is needed before extensive application.

A way out of these difficulties could be the use of cyclodextrins (CDs). Although the detailed mechanism has not been elucidated, it has been shown that the addition of CDs is beneficial in the copolymerization of monomers with largely different water-solubilities [7][14][15]. The unique feature of CDs is their ability to 'entrap' smaller hydrophobic molecules and to form host–guest complexes. These molecules have in fact a conical, tube-like shape, which forms a hydrophobic interior where the guest molecule is entrapped, and a hydrophilic exterior that solubilizes the complex in H_2O. Water-insoluble molecules become water-soluble after treatment with aqueous solutions of CDs without any chemical modification of the guest molecule, since no covalent bonds are formed [16]. As a result, CDs have been used to complex monomers with low water-solubility, *e.g.*, styrene or methyl methacrylate, and to carry out polymerizations in aqueous phase [17]. It has also been reported that CDs can be used to stabilize latexes as an alternative to classical surfactants and to produce very narrow particle-size distributions [18]. This technique also discloses the possibility of copolymerizing water-insoluble and water-soluble monomers [19] and to carry out LRP by ATRP in aqueous solutions [20].

It is worth noting that in the examples above, which refer to aqueous-solution polymerization, an almost equimolar amount of CD and monomer has been used. On the other hand, to promote the polymerization of a water-insoluble monomer in emulsion, CDs are needed only in catalytic amounts. This can be explained by considering that, as a result of the complexation with CDs, monomers with low water solubility have an increased concentration in the H_2O phase and, therefore, become reactive towards polymerization [17]. When polymerization is started in the H_2O phase, the polymer chains keep on growing in the same phase up to a point where the polymer chain, which becomes increasingly water-insoluble, leaves the CD and migrates to an organic phase, *i.e.*, it either precipitates to form new particles or it enters a surfactant micelle. In both cases, emulsion-polymerization conditions are established.

In this work, we propose the use of CDs to run living *ab initio* emulsion polymerization by RAFT. It is shown that this leads to a good control of the polymer growth and to stable and monomodal latexes. Applications to the polymerization of styrene, methyl methacrylate, and to the formation of block copolymers are discussed.

2. Experimental. – 2.1. *Materials.* All chemicals were used as received: the monomers styrene (STY; 99%; *Aldrich*), methyl methacrylate (MMA; 99%; *Fluka*), and *tert*-butyl acrylate (BA; 98%; *Fluka*), the radical initiator potassium peroxodisulfate (KPS; 99%; *Fluka*), the surfactant sodium dodecyl sulfate (SDS; 99%; *Fluka*), and cyclodextrin (CD; randomly methylated β-cyclodextrin with an average degree of substitution of 1.6–1.9; *Cavasol W7 M*, *Wacker Specialties*). H_2O was always doubly distilled before use. All the chemicals for the synthesis of the RAFT agent were used as received from *Aldrich* or *Fluka*.

2.2. *Synthesis of the RAFT Agent.* The RAFT agent cumyl dithiobenzoate (=1-methyl-1-phenylethyl benzenecarbodithioate) was synthesized according to [21]. It is known that the profile of impurities can sensibly alter the final result of the RAFT polymerization [22]. Several experimental runs presented in the following were repeated with different batches of the RAFT agent without observing any important change in the final results.

2.3. *Emulsion-Polymerization Procedure.* To a mixture of CD and RAFT agent, H_2O was added. The system was purged with N_2 and the temp. raised to 70° by a thermostated oil bath and left under vigorous agitation for 30 min. *Via* syringe, a soln. of SDS was added. After 10 min, this was followed by addition of monomer, and immediately after, by addition of a soln. of the initiator KPS in 2 g of H_2O. The temp. was controlled and kept within 1° around the set temp. (70°). Samples were withdrawn at regular time intervals and weighted. These samples were used to monitor monomer conversion and particle size. When needed, further injections of monomer *via* syringe were performed.

In semi-batch reactions, the monomer was added during a fixed period of time by means of a polyvalent syringe pump (*VIT-FIT*; *Lambda*, Switzerland) at constant flow rate. Addition by syringe pump started together with the addition of the initiator.

2.4. *Polymer Characterization*. Conversion was measured gravimetrically in an oven kept at 50° and 100 mbar. Particle diameters were measured by dynamic light scattering (DLS; *Malvern ZetaSizer 5000*). Molecular-mass distribution (*MWD*) was determined by gel-permeation chromatography (GPC) in a *Hewlett-Packard* apparatus (series *1100*) equipped with three columns (*Polymer Standards*; *PLgel 5μm MIXED-C*) and RI detector. The apparatus was calibrated by polystyrene standards (*Polymer Standards*), and THF was used as eluent (1 ml/min, 40°). The *MWD* was estimated by a GPC software provided by *Polymer Standard Service* (Mainz, Germany).

2.5. *Measure of Surfactant CMC*. The critical micellar concentration (*CMC*) of SDS was obtained by measuring the conductivity in H_2O with a *S47-Seven-Multi-Dual* pH/conductivity meter (*Mettler Toledo*) at a const. temp. of 25°. Two distinct linear behaviors were observed by plotting the conductivity against the molar concentration of SDS in H_2O. The intersection of these two linear branches returned the *CMC* value.

3. Results and Discussion. – 3.1. *Influence of Cyclodextrins on Methyl Methacrylate* (MMA) *Emulsion Polymerization*. In the following, several experimental runs involving MMA are discussed to illustrate the main features of an *ab initio* living emulsion polymerization by RAFT in the presence of CDs. Before doing this, it is necessary to characterize the influence of the presence of CDs on the MMA emulsion polymerization under nonliving conditions, *i.e.*, without RAFT agent. In fact, it is reported in the literature that CDs not only change the saturation concentration of monomers in H_2O [23] but also affect the critical micellar concentration (*CMC*) of surfactants [24]. Since CDs are able to form inclusion complexes with many surfactants, and in particular with SDS, the solubility of the surfactant was increased and, therefore, its *CMC* shifted to larger values. This is shown in *Table 1*, where the *CMC* values as a function of CD concentration are reported for the ternary system H_2O/SDS/CD at 50°. A linear dependence of *CMC* upon CD concentration was observed. Repeated experiments after the addition of RAFT agent (CD/RAFT 12) did not show significant deviations from the values of *Table 1*.

Table 1. *Measured Critical Micellar Concentration* (*CMC*) *of SDS as a Function of the Concentration of Cyclodextrin* (CD) *in H_2O for the Ternary System H_2O/SDS/CD.* Temperature 50°.

CD [mmol/l]	0	5	10	15
CMC [mmol/l] of SDS	8.2	16.2	27.0	36.2

The impact of this *CMC* increase on the reaction behavior is shown in *Fig. 1*. In particular, the final particle size increases with increasing concentrations of CDs (*Fig. 1,a*). This is due to the smaller number of surfactant micelles, which causes shorter nucleation times. The consequent reduction in the number of particles has a clear effect upon the rate of polymerization, as shown in *Fig. 1,b*, where the monomer conversion *vs.* polymerization time is plotted for four different CD concentrations. By increasing the CD concentration, the rate of polymerization sensibly decreases. These same effects will be observed in the following experiments, where the RAFT agent is added to establish living conditions.

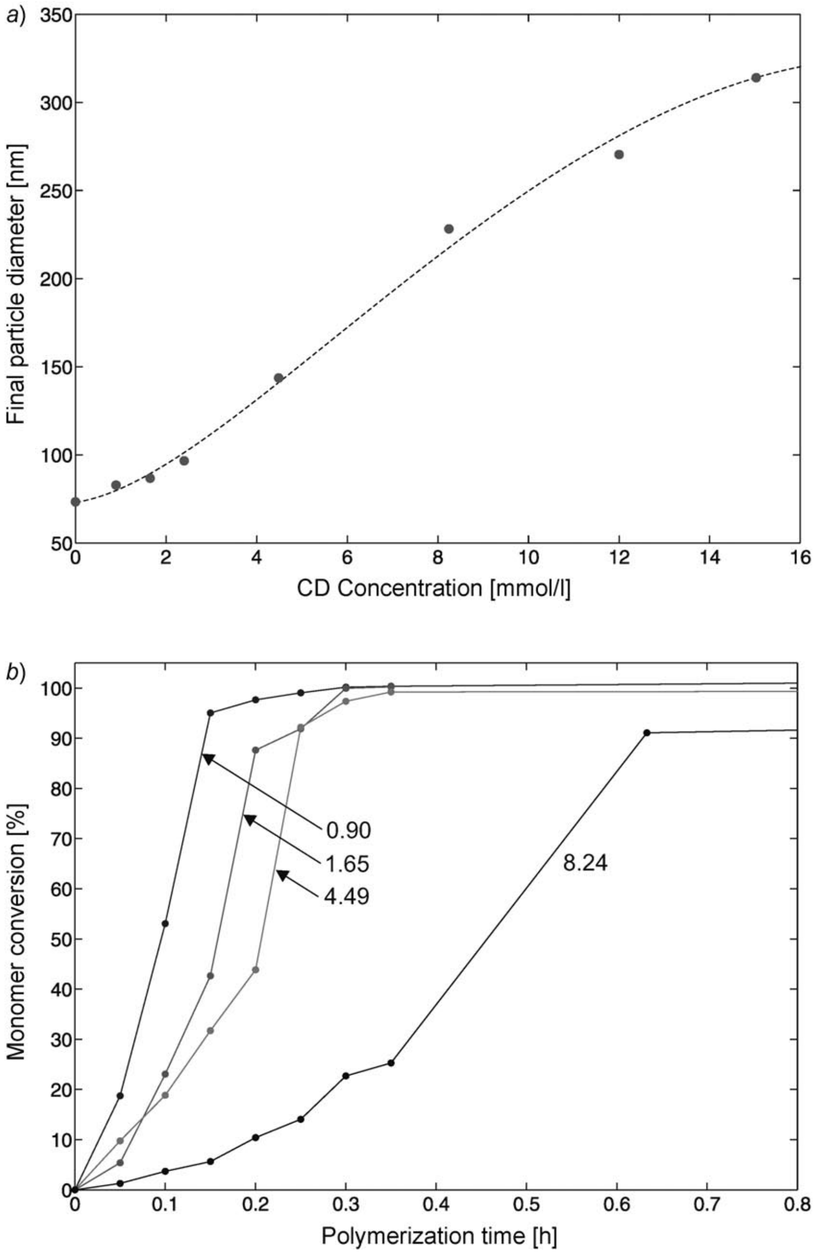

Fig. 1. a) *Final particle diameter* vs. *CD concentration in the H_2O phase and* b) *monomer conversion* vs. *polymerization time for MMA emulsion polymerizations in the presence of CDs* (without RAFT agent). The dashed curve in *Fig. 1,a*, was added to visualize the trend. The numbers in *Fig. 1,b* refer to the corresponding CD concentration [mmol/l]. Other polymerization conditions: temperature 70°, H_2O 40 g, MMA/H_2O 7.5 : 92.5 (*w/w*), SDS 3.5 mmol/l, MMA/KPS 150 : 1 (mol/mol).

3.2. *Living Emulsion Polymerizations in the Presence of CDs.* To identify the main features of the living emulsion polymerization in the presence of CDs, two illustrative experimental runs are initially discussed for the polymerization of MMA and styrene (STY), respectively. The corresponding recipes are summarized in *Table 2*. The results of MMA polymerization are shown in *Fig. 2*, *i.e.*, the conversion *vs.* time and the number average molecular mass M_n and polydispersity P_d *vs.* conversion. As shown in *Fig. 2,a*, the reaction is characterized by a large polymerization rate, complete conversion being observed after 30 min. No evidence of induction time is observed. These findings confirm that, as mentioned above, the synergy between radical compartmentalization and RAFT living mechanism works in reducing the number of terminations while keeping the polymerization rate to values typical of nonliving systems [25]. Given that the decomposition rate of KPS at 70° is *ca.* $2.3 \cdot 10^{-5}$ s^{-1} [26], it can be readily seen that only 4% of the initiator is actually decomposed after 30 min of reaction. Assuming initiation efficiency equal to one, and given that each initiator molecule produces one dead chain, *ca.* 5.3% of dead chains compared to the amount of RAFT agent is expected at the end of this reaction.

Controlled conditions of polymer growth were achieved, as clearly shown by the data in *Fig. 2,b*. The number average molecular mass M_n grows linearly with conversion, and it always remains close to the theoretical value, calculated under the assumption of no chain terminations as $M_n = (M_0/D_0)\chi$, where M_0 represents the initial monomer concentration, D_0 the initial RAFT-agent concentration, and χ the monomer conversion. This confirms that only few dead chains were actually produced, as indirectly confirmed by the polydispersity values P_d of the molecular-mass distribution, *MWD*, always decreasing with conversion and reaching a final value of 1.37. To this regard, it is worth noting that the experimental point at *ca.* 90% conversion having a polydispersity value of 1.8 is clearly an outlier. In fact, it would be impossible to reduce the polydispersity to its final value in the last 10% conversion. Finally, the *MWD* curves in *Fig. 3*, which are normalized with respect to the actual amount of polymer produced, exhibit the continuous shift towards larger molecular masses for increasing conversion values, which is typical of living systems.

To ultimately establish the livingness of the polymer, the polymerization reaction was restarted by adding 7.5 g of MMA *via* syringe in the reaction vessel after 70 min from the reaction start, followed by other 4.0 g of STY after two more hours, with the aim to form a PMMA–PSTY block copolymer. In both cases, the additional reactions were completed within 20 min after each monomer addition. The corresponding *MWD*s are shown in *Fig. 4*: just before MMA addition, just before STY addition, and at the end of the reaction. The average molecular mass of the polymer increases and the polymer peak shifts to larger molecular masses, thus indicating that the reaction is living. Unfortunately, the polydispersity of the *MWD* also increases: whatever the mechanism behind such behavior might be, some dead chains must have been formed. This is evident from the low-molecular-mass tail of the *MWD* of the last two distributions: the overlapping of these two tails indicates that part of the polymer failed to restart after the STY addition.

As a further example of application of CDs in RAFT emulsion polymerization, the polymerization of STY according to the recipe reported in *Table 2* was considered. Even though this recipe is very similar to that used for MMA, the results are somehow

Table 2. *Recipes for the Living* ab initio *Emulsion Polymerization by RAFT of Methyl Methacrylate* (MMA) *and Styrene* (STY)[a])

	Quantity [g]	
	MMA polymerization	STY polymerization
Monomer	9.0	10.0
H_2O	143.8	150.3
CD	2.54	2.25
SDS	0.824	0.592
KPS	0.103	0.192
RAFT agent	0.0785	0.0650
	Ratio	
	MMA polymerization	STY polymerization
Monomer/RAFT (mol/mol)	312.0	402.4
KPS/RAFT (mol/mol)	1.32	2.98
CD/RAFT agent (mol/mol)	6.62	7.09
SDS/CD (mol/mol)	1.50	1.21
Monomer/H_2O (*w*/*w*)	6.26	6.65
SDS/H_2O (*w*/*w*)	0.57	0.39
CD/H_2O (*w*/*w*)	1.77	1.50

[a]) Absolute amounts and significant ratios are reported. Reaction temperature 70°.

less satisfactory. As shown in *Fig. 5,a*, almost complete monomer conversion is achieved in less than 90 min. It can be seen that the induction time, if any, is much shorter than those typically found in the case of seeded STY polymerization with RAFT [2]. However, the conversion curve shows an acceleration of the polymerization rate which was not present in the case of MMA polymerization. Indeed, the control of the *MWD* is satisfactory, although worse than for MMA polymerization, as can be seen in *Fig. 5,b*. The number average molecular mass M_n increases with monomer conversion, and the corresponding polydispersity P_d of the *MWD* decreases. Therefore, the polymerization proceeds according to a living mechanism. However, the large polydispersity values indicate a limited control of the process and, possibly, a generation of new living polymer chains during the whole process [27]. In this context, it is worth noting that the particle-size distribution, *PSD*, as measured by DLS, appears to be monomodal (average diameter 114 nm; variance 0.17). Two explanations are possible for this result. On one hand, the continuous formation of new dormant chains could be due to a slow release of RAFT agent to the particles. On the other hand, it is worth noting that, in similar experiments at lower values of the ratios CD/RAFT and KPS/RAFT (not reported here), bimodal distributions were frequently found, with the presence of very large particles (500 nm or larger), probably formed by droplet nucleation. The presence of these two effects may explain the very large polydispersity values shown in *Fig. 5,b*.

To establish that living conditions were operating, the polymerization was restarted by the addition of 11.0 g of STY after 80 min of reaction. As shown in *Fig. 5,b*, after this

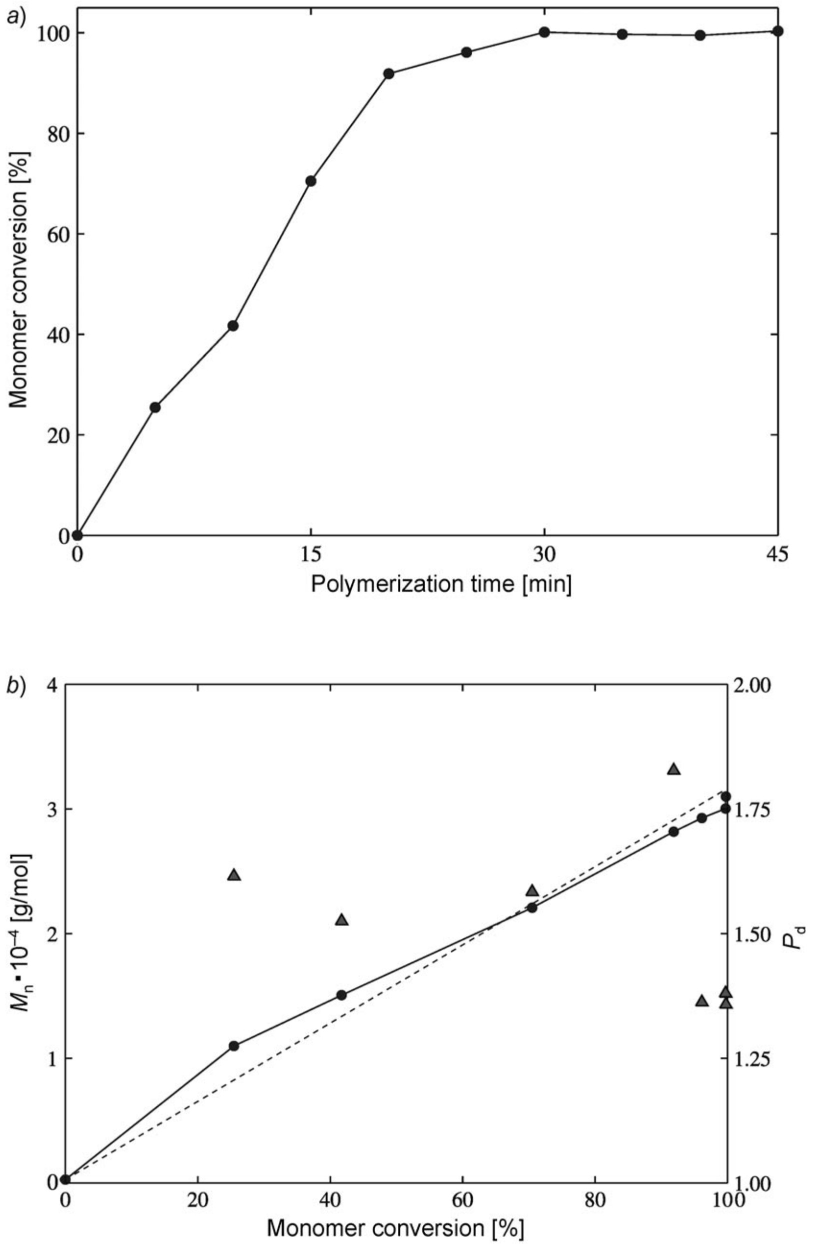

Fig. 2. a) *Monomer conversion* vs. *reaction time and* b) *number average molecular mass* M_n (circles and solid line) *and polydispersity* P_d (triangles) vs. *conversion for the living emulsion polymerization of MMA* (recipe in *Table 2*). The dashed line in *Fig. 2,b*, represents the theoretical number average molecular mass.

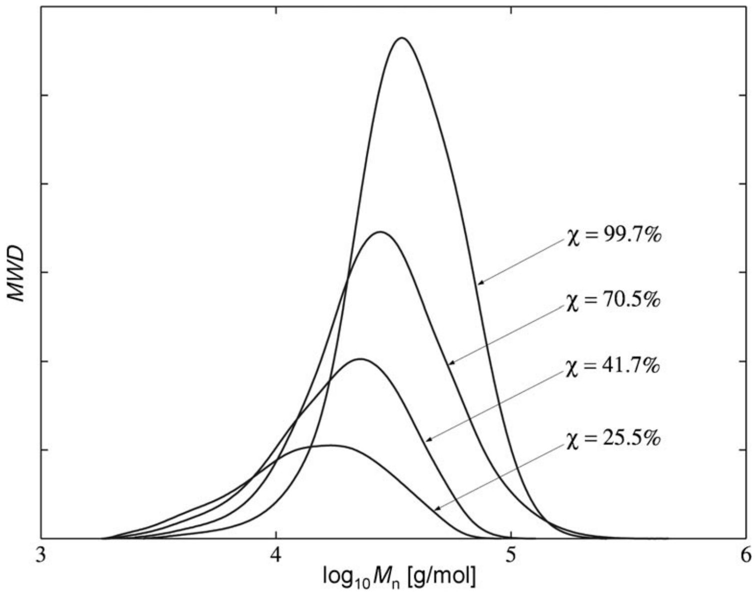

Fig. 3. *Evolution of the molecular-mass distribution* (*MWD*) *with conversion for the living emulsion polymerization of MMA* (recipe in *Table 2*). The area of each peak has been normalized to the corresponding conversion value.

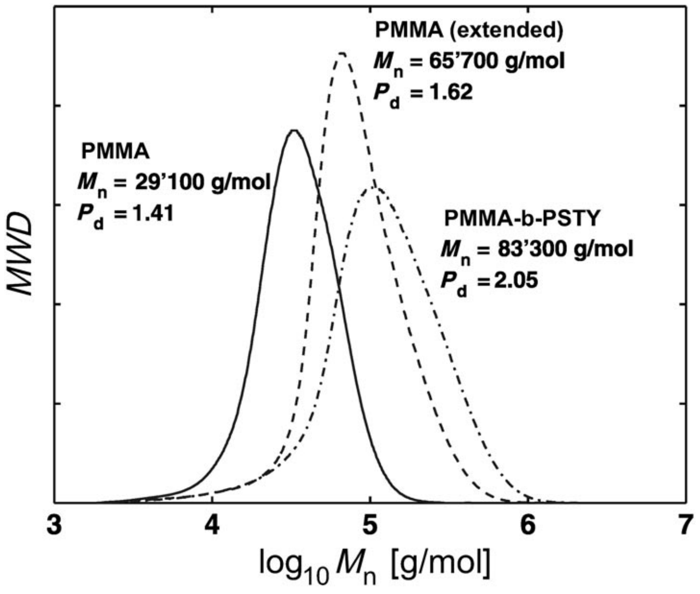

Fig. 4. *Evolution of the molecular-mass distribution* (*MWD*) *with conversion for the restarted living polymerization of PMMA produced as reported in* Table 2. Solid curve: PMMA homopolymer before the addition of MMA; dashed curve: extended MMA homopolymer before the addition of STY; dash-dotted curve: final PMMA–PSTY block copolymer.

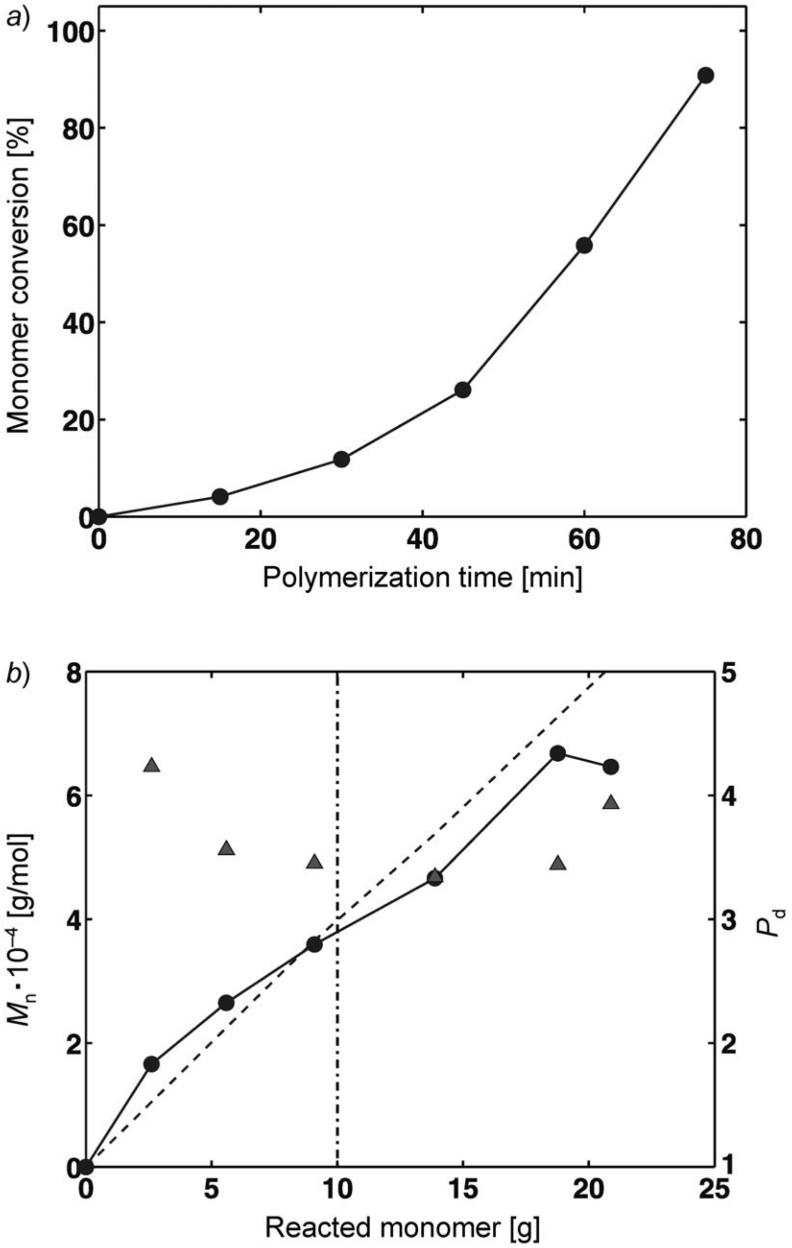

Fig. 5. a) *Monomer conversion* vs. *reaction time and* b) *number average molecular mass* M_n (circles and solid line) *and polydispersity* P_d (triangles) vs. *reacted monomer for the living emulsion polymerization of styrene* (STY) (recipe in *Table 2*). The dashed line in *Fig. 5,b*, represents the theoretical number average molecular mass. The dash-dotted vertical line indicates the conversion at which an additional amount of STY has been injected.

addition (indicated by the dash-dotted vertical straight line), the average molecular mass M_n continued to grow almost linearly. During this additional reaction time, the polydispersity P_d remained close to the values measured at the end of the first step of reaction, and increased only at the very end of the reaction.

3.3. *Role of the Operating Variables on MMA Living Emulsion Polymerization.* In the following, a series of experimental runs is discussed, where the main control parameters for the MMA living emulsion polymerization are systematically changed to analyze their effect on the polymerization behavior. These experimental runs are summarized in *Table 3*, where the corresponding recipes and final results are reported.

In *Runs 1–3*, the effect of the surfactant (SDS) concentration is analyzed first. This parameter plays a primary role in the nucleation process of nonliving systems and, thus, on the number of particles formed in the system. This is confirmed also for the living emulsion polymerization of MMA, where, from the analysis of *Runs 1–3*, it can be observed that the final particle diameter d_p decreases as the SDS concentration is increased. When the logarithm of the number of particles is plotted against the logarithm of the SDS concentration, a linear trend is found. However, the slope of the regression line is 3.7, that is larger than the value 0.6 predicted by the classical *Smith–Ewart* theory [9], indicating a much larger sensitivity to surfactant concentration. This behavior is probably to be ascribed to the active role played by the CDs in determining the *CMC* of the system, although a clear mechanism is not known yet. It is also worth mentioning that, together with the decrease in particle size, an increase in the variance σ_{PSD} of the *PSD* is also observed. This is coherent with longer nucleation

Table 3. *Recipe and Product Characteristics for Different Experimental Runs*: *Mass Ratio Monomer MMA to Water* (M/W%); *SDS Concentration in H_2O* [mmol/l]; *Molar Ratios Monomer to RAFT Agent* (M/RAFT), *CD to RAFT Agent* (CD/RAFT), *CD to SDS* (CD/SDS), *and KPS to RAFT Agent* (KPS/RAFT); *Average Particle Size* d_p [nm] *and Variance* σ_{PSD} *of the Particle-Size Distribution*, *Number Average Molecular Mass* M_n [kg/mol] *and Polydispersity* P_d *of the Molecular-Mass Distribution*; *Monomer Conversion* χ [%] *and Reaction Time* t_R [min]

Run	M/W%	SDS	M/RAFT	CD/RAFT	KPS/RAFT	d_p	σ_{PSD}	M_n	P_d	χ	t_R
1	2.0	2.3	1500	24	10.0	144.0	0.02	60.5	3.76	72.7	106
2	2.0	4.6	1500	24	10.0	60.3	0.07	63.2	3.35	95.3	160
3	2.0	6.9	1500	24	10.0	39.4	0.19	79.9	2.83	94.0	140
4	7.5	17.3	500	2	0.74	297.7	0.23	36.9	3.96	97.5	240
5	7.5	17.3	500	2	3.33	42.3	0.27	44.6	1.41	98.0	19
6	7.5	3.5	500	2	3.33	327.8	0.29	24.1	1.75	70.6	196
7	7.5	17.3	1500	24	10.0	45.7	0.08	103.0	1.93	98.5	20
8	7.5	17.3	1500	12	10.0	38.7	0.10	118.5	1.96	95.0	15
9	7.5	17.3	1500	6	10.0	34.8	0.19	78.7	1.86	94.2	25
10	7.5	17.3	750	12	5.00	57.5	0.13	55.5	1.67	95.3	20
11	7.5	17.3	750	6	5.00	41.8	0.20	74.6	1.69	99.0	19
12	7.5	17.3	750	3	5.00	37.7	0.22	58.7	1.52	91.3	19
13	7.5	17.3	750	3	1.00	283.5	0.20	37.5	2.86	92.9	240
14	7.5	17.3	500	12	3.33	84.0	0.03	40.6	1.66	98.8	98
15	7.5	17.3	500	8	3.33	65.8	0.17	41.3	1.43	98.0	140
16	7.5	17.3	500	6	3.33	48.1	0.14	45.0	1.48	97.2	23
17	7.5	17.3	500	4	3.33	46.8	0.25	41.9	1.45	97.8	24

times for larger surfactant concentrations. Finally, it should be noted that *Runs 1–3* produced large P_d values of the *MWD*. This must mainly be ascribed to the large KPS/RAFT agent ratio adopted and, therefore, to the large amount of dead chains produced in this case.

A similar trend is observed in *Runs 5* and *6* of *Table 3*, where the SDS concentration was changed for a system having a larger monomer fraction in H_2O and a larger RAFT-agent concentration with respect to the previous runs. Also in this case, a marked influence of the SDS concentration was observed. Moreover, by increasing the SDS concentration, the polydispersity value P_d of the *MWD* was decreasing, as it was the case for *Runs 1–3*. Therefore, one could conclude that larger SDS concentrations produce narrower *MWD*s. It is also interesting to compare *Runs 4* and *5*, where a fivefold change in the initiator concentration was introduced. It can be noticed that, as predicted by the *Smith–Ewart* theory of nucleation, lower initiator concentrations produce larger particles. However, also in this case, a quite strong influence was observed. The corresponding slope of the plot log(N_p) *vs.* log(KPS) (where N_p is the number of particles) is *ca.* 3.5, again much larger than that predicted by the *Smith–Ewart* theory, equal to 0.4. The same large sensitivity can be observed for *Runs 12* and *13* of *Table 3*, which correspond to a larger RAFT concentration.

In Runs *7–9*, *10–12*, and *14–17* of *Table 3*, a series of reactions were carried out keeping the molar ratio monomer/RAFT agent constant and equal to 1500, 750, and 500, respectively, and decreasing the concentrations of CDs in H_2O (all the other concentration values were constant). The change in CD concentration significantly affects the final particle-size distribution. In particular, as the CD concentration decreases, the final polymer-particle size decreases. This is due to the effect of CD on the surfactant *CMC* mentioned above: larger CD concentrations lead to larger *CMC* values, smaller number of micelles, and, therefore, larger polymer particles at the end of the reaction. The corresponding increase of the *PSD* broadness (σ_{PSD}) is coherent with this explanation, which implies increasing nucleation times at decreasing CD concentrations. It was verified that by running the experiment without CDs, a large fraction of very small particles was formed (about 20 nm in diameter for the case M/RAFT 500), coherently with the observed trend on the average particle size. However, formation of coagulum was always observed at the same time. This is in agreement with what was observed for the living polymerization of STY without CDs, and, probably, it is connected to the increasing trend in the *PSD* variance observed for decreasing CD concentrations. Accordingly, it can be concluded that CDs in the H_2O phase not only favor the formation of living polymer, but also avoid the destabilization of the system.

Different conclusions can be drawn for the effect of the amount of CD upon the *MWD*. The results in *Table 3* for the same runs indicate that the number average molecular mass M_n is irregularly affected by changes in the CD concentration: for the smallest monomer/RAFT agent ratio (M/RAFT; *Runs 14–17*), the average molecular mass seems to remain constant, as one could expect due to the fact that the amount of RAFT participating in the reaction is always similar. This is not true at the larger M/RAFT ratios (*Runs 7–9* and *10–12*) where larger M_n values (closer to the theoretical values) are obtained at the intermediate value of the CD/RAFT ratio. Despite these differences, the polydispersity value P_d decreases with decreasing concentration of CDs in the system for all three values of the monomer/RAFT agent ratio.

Finally, the influence of the RAFT agent concentration was analyzed (*Table 3*) by keeping the ratio CD/RAFT constant (*Runs 8*, *10*, and *14*). By increasing the M/RAFT ratio, the average particle size d_p decreases, while no clear trend is observed for the variance of the *PSD*, which remains anyway relatively small. Note that, since the ratio CD/RAFT is kept constant, by increasing the M/RAFT ratio, the absolute CD concentration also increases, thus leading to a decrease in the particle size, as explained above. With respect to the *MWD*, as the M/RAFT ratio increases, the corresponding M_n increases since a smaller number of dormant chains is growing in the system. However, it should be mentioned that the measured values remain always somewhat smaller than the theoretical ones. Finally, since the same initiator (KPS) concentration was used in all the experimental runs, roughly the same number of terminated chains is expected at the end of each reaction. Accordingly, the livingness of the process decreases for increasing M/RAFT ratios, since the fraction of dead chains increases, and this explains the corresponding increase in the polydispersity values P_d of the *MWD*.

More interesting is the comparison between runs at different RAFT-agent concentration and constant concentration of CDs, as it is the case for *Runs 7*, *10*, and *15* (M/CD 62.5), *8*, *11*, and *17* (M/CD 125), and *9*, *12*, and *5* (M/CD 250). The dependence of the *MWD* on the amount of RAFT agent in the system has been just commented. However, it can also be noticed that the RAFT-agent concentration is also slightly affecting the average particle size, which is increasing for larger RAFT-agent concentrations. A clear explanation for such an effect is not available yet.

3.4. *Semi-Batch Living Emulsion Polymerizations in the Presence of CDs.* When discussing the experimental runs reported in *Table 3*, it was noticed that better control upon the livingness of the polymer at constant values of the M/RAFT ratio can be achieved by operating at small CD/RAFT ratios. At the same time, an increase of the *PSD* broadness was observed (especially for the lowest M/RAFT ratios), which will soon counterbalance the positive effect upon the *MWD* of the reduced amount of CDs. Particles with very different sizes are in fact growing at very different rates, thus producing polymer chains of different length.

We found that this *PSD* broadening is avoided when running the reaction in the semi-batch mode, *i.e.*, by adding monomer at constant rate for a fixed amount of time. The corresponding results are reported in *Table 4*, where different experiments with different addition times of the monomer are compared. It can be observed that the variance σ_{PSD} of the *PSD* remains small in all cases. In particular, these values are much smaller than those of the corresponding batch reaction (*Run 5* of *Table 3*), where the same recipe is used but all the monomer is added at the beginning of the polymerization. Moreover, the average molecular masses are closer to the theoretical value, in agreement with the selected operating mode. In fact, since no monomer is added before adding the initiator, monomer droplets are hardly formed in the system, due to the slow addition of the monomer and the fast polymerization rate. Accordingly, droplet polymerization is minimized, if not cancelled. The decrease of M_n and the increase of polydispersity P_d at increasing addition times observed in *Table 4* could probably be ascribed to the increased reaction times and, therefore, to the increased role of termination. It is also worth noticing that *Run 22* was operated very close to starved conditions, since more than 90% conversion was found after 32 min of reaction, *i.e.*, 4 min after completion of monomer addition. Under these conditions, the reaction

Table 4. *Recipes for the Semi-Batch Living Emulsion Polymerization of MMA* [a])

Run	Addition time [min]	d_p [nm]	σ_{PSD}	M_n [kg/mol]	P_d
20	6	46.3	0.05	48.4	1.50
21	15	45.3	0.04	46.4	1.46
22	28	38.3	0.04	43.2	1.72

[a]) Polymerization conditions: temperature 70°; water 40 g; initial amount of MMA 0 g; final MMA/H_2O 7.0% (*w*/*w*); final MMA/RAFT 500 (mol/mol); CD/RAFT 2 (mol/mol); final MMA/KPS 150 (mol/mol); SDS 17.3 mmol/l.

rate of the RAFT exchange largely decreases due to gel effects, as reported for bulk systems [28], thus contributing to the increase of the polydispersity value.

As mentioned in the introduction (*Sect. 1*), living-radical polymerization is a particularly efficient technique to produce block copolymers [29–31]. To this regard, the same procedure of monomer addition shown above turned out to be very useful to produce living random copolymers of MMA and *tert*-butyl acrylate (BA). Earlier attempts to copolymerize BA with MMA in a batch reactor, by using similar recipes as those reported in *Table 3*, always gave rise to bimodal particle-size distributions. On the other hand, by adding the mixture of the two monomers under semi-batch conditions, it was found that the variance of the *PSD* could be drastically reduced. This is shown by the results in *Table 5*, where three different MMA/BA living copolymerizations in emulsion are reported. All the polymerizations were restarted once the initial reaction step, with MMA/BA 70 : 30, had reached complete conversion, by adding with a syringe pump an amount of monomer close to that used in the first part of the polymerization, but with composition MMA/BA 30 : 70.

The addition time was equal to the addition time used for the first step. The reduction of the *PSD* variance after the first polymerization step becomes particularly evident when long addition times of the monomer mixture were used, *i.e.*, when the system operates under 'starved' conditions. Notably, a reduction of particle size d_p is obtained at the same time. In terms of *MWD*, all the runs are characterized by final M_n values larger than the targeted molecular mass, probably indicating that not all the RAFT agent took part in the reaction. The evolution of M_n with monomer conversion is shown in *Fig. 6,a* (*Run 25* of *Table 5*), where the dotted vertical line indicates the beginning of the second addition. It can be noticed that M_n is always larger than the theoretical value, represented by the dashed line. Even more important are the values of the *MWD* polydispersity (triangles in *Fig. 6,a*), which, in spite of the fact that all the runs were operated close to starved conditions (*i.e.*, with large polymer fractions inside the particle), are quite small. It is worth pointing out that operating under starved conditions is essential to keep the copolymer composition constant and equal to the feed composition. The corresponding *MWD*s of the polymer are shown in *Fig. 6,b* (*Run 25* of *Table 5*). The shift of the polymer peak towards larger molecular masses at increasing values of the monomer conversion is evident, which represents a strong confirmation of the livingness of the polymerization.

Finally, the so-obtained MMA/BA random copolymer, with composition MMA/BA 70 : 30, was restarted, as mentioned before, with a different composition of the mono-

Table 5. *Recipes for the Semi-Batch Living Emulsion Copolymerization of MMA and BA* (70:30 in weight)[a])

Run	Addition time [min]	MMA/BA 70:30					MMA/BA 30:70		
		d_p	σ_{PSD}	M_n	M_n^{theo}	P_d	M_n	M_n^{theo}	P_d
23	15	80.7	0.50	51.9	34.8	3.52	73.4	64.9	5.75
24	28	54.3	0.39	58.8	34.1	2.27	86.7	67.7	4.17
25	77	34.8	0.20	46.7	32.8	2.35	75.1	68.8	5.39

[a]) Polymerization conditions: temperature 70°; water 40 g; initial amount of monomer 0 g; final M(total)/water 7.0% (*w*/*w*); final M(total)/KPS 150 [mol/mol]; CD/RAFT agent 1.3 [mol/mol]; SDS 17.3 mmol/l. The results corresponding to the polymer extension experiments are reported in the last three columns of the table. The average molecular mass M_n and the theoretical average molecular mass M_n^{theo} of the *MWD* are expressed in kg/mol, the particle diameter d_p in nm.

mer mixture, *i.e.*, MMA/BA 30:70. This procedure is aimed at producing a block copolymer, where the first polymer block is rigid (large MMA fractions) and the second one is soft (large BA fractions). The measured average molecular masses are reported in the eighth column of *Table 5*. It can be noticed that the M_n values are always larger than the theoretical ones, although the discrepancy is quite small. The same discrepancy is shown in *Fig. 6,a* (*Run 25* of *Table 5*). In all these experiments, the polydispersity values P_d are sensibly larger than those of the first block. For *Run 25* of *Table 5*, the final *MWD* is shown in *Fig. 6,b* (dash-dotted curve). With this respect, it is worth pointing out that the system was again operated under starved conditions and that, due to the large fraction of BA used for the second block, branching reactions are likely to take place [32]. Therefore, a value of polydispersity larger than 4 can be easily justified. The same observation (branched chains) could explain the irregular shape of the *MWD* in *Fig. 6,b*.

4. Conclusions. – In this work, we propose a possible solution to the problem of the interphase transport of the RAFT agent to the polymer particles in *ab initio* emulsion polymerization, which is based on the addition of CDs to increase the aqueous solubility of the RAFT agent. It is shown that, in the presence of CDs, the emulsion polymerization proceeds since the beginning according to a living mechanism, with a linear increase of the number average molecular mass *vs.* conversion, generally low polydispersity values, and a clear shift of the *MWD*s towards larger molecular masses at increasing monomer conversions. Note that the polymerization proceeds without noticeable production of coagulum, and generally stable and monodispersed latexes are obtained. The results are particularly satisfactory in the case of the living polymerization of MMA, where low-polydispersity homopolymers and block copolymers were produced. In addition, as observed earlier in the case of mini-emulsion [5], the controlled process proceeds at the same rate as the corresponding one under nonliving conditions also for *ab initio* emulsion polymerization. This is due to the specific living mechanism selected, RAFT being the only living mechanism that preserves the radical segregation typical of emulsion polymerization. Accordingly, the use of CDs allows us to

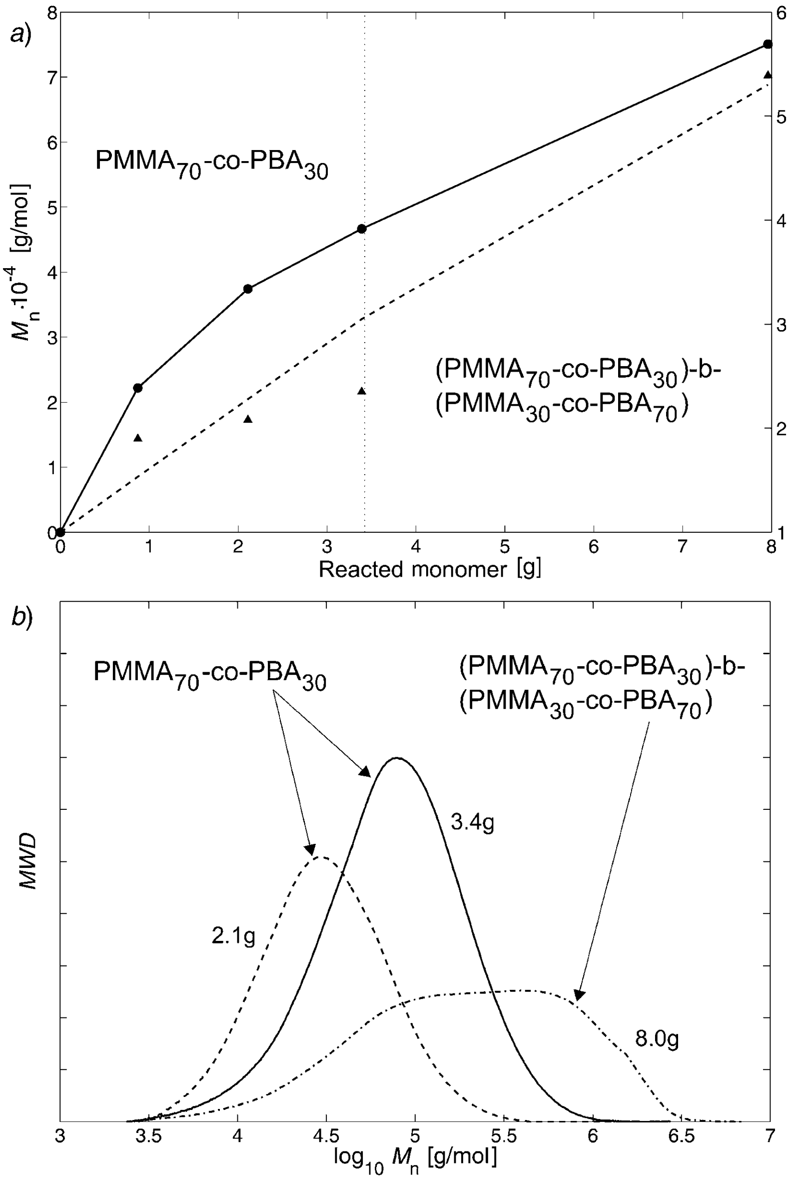

Fig. 6. a) *Number average molecular mass* M_n (circles and solid line) *and polydispersity* P_d (triangles) vs. *reacted monomer and* b) *evolution of the molecular-mass distribution* MWD *with conversion for the living emulsion copolymerization of MMA and BA* (*Table 5*, *Run 25*). The dashed line in *Fig. 6,a* represents the theoretical number average molecular mass, while the vertical dotted line indicates the conversion at which the polymerization was restarted. The numbers in *Fig. 6,b*, indicate the amounts of reacted monomer corresponding to the *MWD* curves.

focus the design of the RAFT agent not on its ability to be transported across the H_2O phase, but rather on its ability in controlling the polymer architecture.

A complete experimental screening of the main control parameters was carried out in this work in the case of the polymerization of MMA, to analyze their effect on the polymerization behavior. In particular, it was found that the nucleation process is very sensitive to the concentrations of initiator and surfactant, to an extent much larger than that predicted by the classical *Smith–Ewart* theory. This is probably due to the active involvement in the nucleation process of CDs, which were shown to strongly influence the surfactant *CMC*. Moreover, it was shown that the control on the polymer growth is improved by operating at small CD/RAFT agent ratios. The reason for such an effect is not clear. In particular, it is not clear whether this is due to a faster delivery of the RAFT agent to the particles or to the decrease of the particle size. At the same time, it was observed that CDs are effective to avoid latex destabilization. Finally, it was shown that the semi-batch addition of monomer increases the quality of the process, in particular narrowing the final particle-size distributions. This procedure became very useful when copolymerizing BA with MMA at constant composition, *i.e.*, under starved conditions.

Somehow less-convincing results were obtained in the case of styrene polymerization: large polydispersity values were always observed, even though the ability of forming block copolymers indicates that the process remains living. In any case, this result is not achievable in the absence of CDs, where a large formation of coagulum was always observed. These difficulties can be attributed to the fact that the interphase transport of the RAFT agent remains too slow so that the constraints posed by *Eqn. 1* are not fully met even in the presence of CDs. An alternative explanation could be the presence of droplet nucleation, which could take place at the beginning of the reaction, when slow polymerization rates are always observed.

REFERENCES

[1] S. W. Prescott, M. J. Ballard, E. Rizzardo, R. G. Gilbert, *Aust. J. Chem.* **2002**, *55*, 415.
[2] S. W. Prescott, M. J. Ballard, E. Rizzardo, R. G. Gilbert, *Macromolecules* **2002**, *35*, 5417.
[3] M. P. Tonge, J. B. McLeary, J. J. Vosloo, R. D. Sanderson, *Macromol. Symp.* **2003**, *193*, 289.
[4] A. Butté, G. Storti, M. Morbidelli, *Macromolecules* **2000**, *33*, 3485.
[5] A. Butté, G. Storti, M. Morbidelli, *Macromolecules* **2001**, *34*, 5885.
[6] M. F. Cunningham, *Prog. Polym. Sci.* **2002**, *27*, 1039.
[7] W. Lau, U.S. Pat. 5,521,266, 1996.
[8] S. Nozari, K. Tauer, A. M. I. Ali, *Macromolecules* **2005**, *38*, 10449.
[9] R. G. Gilbert, 'Emulsion Polymerization, a Mechanistic Approach', Academic Press, London, 1995.
[10] J. Delgado, M. S. Elaasser, C. A. Silebi, J. W. Vanderhoff, J. Guillot, *J. Polym. Sci., Part B: Polym. Phys.* **1988**, *26*, 1495.
[11] M. J. Monteiro, J. de Barbeyrac, *Macromolecules* **2001**, *34*, 4416.
[12] M. J. Monteiro, M. M. Adamy, B. J. Leeuwen, A. M. van Herk, M. Destarac, *Macromolecules* **2005**, *38*, 1538.
[13] C. J. Ferguson, R. J. Hughes, D. Nguyen, B. T. T. Pham, R. G. Gilbert, A. K. Serelis, C. H. Such, B. S. Hawkett, *Macromolecules* **2005**, *38*, 2191.
[14] G. Schornick, A. Kistenmacher, H. Ritter, J. Jeromin, O. Noll, M. Born, PCT Pat. WO97/09354, 1997.
[15] S. Rimmer, P. Tattersall, *Polymer* **1999**, *40*, 5729.
[16] C. C. Rusa, C. Luca, A. E. Tonelli, *Macromolecules* **2001**, *34*, 1318.

[17] J. Storsberg, H. Ritter, *Macromol. Rapid Commun.* **2002**, *21*, 236.

[18] J. Storsberg, H. van Aert, C. van Roost, H. Ritter, *Macromolecules* **2003**, *36*, 50.

[19] P. Casper, P. Glockner, S. Ritter, *Macromolecules* **2000**, *33*, 4361.

[20] J. Storsberg, M. Hartenstein, A. H. E. Muller, H. Ritter, *Macromol. Rapid Commun.* **2000**, *21*, 1342.

[21] E. Rizzardo, J. Chiefari, B. Y. K. Chong, F. Ercole, J. Krstina, J. Jeffery, T. P. T. Le, R. T. A. Mayadunne, G. F. Meijs, C. L. Moad, G. Moad, S. H. Thang, *Macromol. Symp.* **1999**, *143*, 291.

[22] R. Plummer, Y. K. Goh, A. K. Whittaker, M. J. Monteiro, *Macromolecules* **2005**, *38*, 5352.

[23] H. Ritter, M. Tabatabai, *Prog. Polym. Sci.* **2002**, *27*, 1713.

[24] P. C. Shanks, E. I. Franses, *J. Phys. Chem.* **1992**, *96*, 1794.

[25] I. M. Kolthoff, I. K. Miller, *J. Am. Chem. Soc.* **1951**, *73*, 3055.

[26] E. J. Behrman, J. O. Edwards, *Rev. Inorg. Chem.* **1980**, *2*, 179.

[27] M. F. Cunningham, K. Tortosa, J. W. Ma, K. B. McAuley, B. Keoshkerian, M. K. Georges, *Macromol. Symp.* **2002**, *182*, 273.

[28] A. D. Peklak, A. Butté, G. Storti, M. Morbidelli, *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 1071.

[29] M. J. Monteiro, M. Sjoberg, J. van der Vlist, C. M. Gottgens, *J. Polym. Sci., Part A: Polym. Chem.* **2000**, 38, 4206.

[30] W. W. Smulders, C. W. Jones, F. J. Schork, *Macromolecules* **2004**, *37*, 9345.

[31] J. Zhu, X. L. Zhu, D. Zhou, *J. Macromol. Sci.: Pure Appl. Chem., A* **2004**, *41*, 827.

[32] A. Ghielmi, G. Storti, M. Morbidelli, *Chem. Eng. Sci.* **2001**, *56*, 937.

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