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Polymerization strategies to overcome limiting monomer conversion in silicone-acrylic miniemulsion polymerization

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Abstract

The limiting conversion phenomenon observed in high solid content silicone-modified acrylic miniemulsion polymerizations was investigated. It was found that the limiting conversion was mainly due to the formation of inactive radicals upon propagation of butyl acrylate radicals with the vinyl end groups of the polydimethylsiloxane. Polymerization strategies that allowed overcoming this problem and achieving high monomer conversion were implemented.
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1. Introduction

Waterborne polymer−polymer hybrid latexes are an opportunity to develop new materials combining the positive properties of both polymers in a synergetic way. Alkyd resins [1−4], polyurethanes [5−8] and epoxy [9−12] combined with acrylic polymers are the most common combinations. Because it is expected that properties would improve with intimate contact between the components of the hybrid system, the acrylic monomers are polymerized in the presence of a preformed polymer that contains reactive groups. As the use of conventional emulsion polymerization is precluded because the resins are not soluble in water, Wang et al. [2] proposed the use of miniemulsion polymerization [13,14] to produce these materials. Unfortunately, miniemulsion polymerization in the presence of a preformed resin often leads to unacceptable concentrations of residual monomer due to a limiting monomer conversion [1−3,5]. This is a serious problem that hinders the commercialization of these products.

Several hypotheses have been proposed to explain the limiting monomer conversion including impurities within the resin [2,5], degradative chain transfer [2,15] and segregation of the resin within the polymer particle [15]. It is believed that segregation results in alkyd-rich regions in which the radicals cannot enter because they are incompatible with the resin [15], and hence the monomer solubilized in those alkyd-rich domains cannot react. Hudda et al. [16] analyzed by simulation the different hypothesis for the methyl methacrylate−alkyd system, concluding that retardative chain transfer was not capable of producing the limiting conversion, and that phase segregation was the most likely cause of the limiting conversion. However, due to the partitioning of the monomer into the different phases, a fraction of monomer must be present in the region where the radicals stayed, and therefore, limiting conversion with zero rate of polymerization was rather unlikely.

Furthermore, it has been reported that complete conversion was achieved during the polymerization of acrylic monomer−alkyd dispersions in the presence of a preformed acrylic latex [17]. This seems to challenge the segregation model because it shows that monomer may diffuse not only out of the segregated resin but also through the aqueous phase to the alkyd-free particles.

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Waterborne silicone-modified acrylic systems are interesting materials as they may combine the mechanical strength of the acrylic polymers with the good water repellency and thermal resistance of the silicones. The synthesis of silicone–acrylic latexes by miniemulsion polymerization have been reported [18,19], but very low solid contents were used and the phenomenon of limiting conversion was not investigated.

In this work the limiting monomer conversion phenomenon occurring in the high solid silicone-modified acrylic miniemulsion polymerization was investigated with the aim of implementing strategies to overcome this problem. Both batch and semicontinuous processes were considered. Batch processes are not commonly employed in the commercial manufacture of waterborne polymers because these processes are prone to suffer thermal runaways and they do not control product quality. Nevertheless, they find application in the polymerization of the initial charge of the reactor during the semicontinuous process. More importantly for the purpose of this work, batch polymerizations are very useful to unveil the mechanisms of complex processes.

2. Experimental

2.1. Materials

Technical grade monomers, methyl methacrylate (MMA, Quimidroga), butyl acrylate (BA, Quimidroga) and acrylic acid (AA, Aldrich) were used without purification. Polydimethylsiloxane divinyl terminated (PDMS, Mw = 25 000, Aldrich), and non-reactive PDMS (AK50) supplied by Wacker Chemie were used as-received. Stearyl acrylate (SA, Aldrich) was used as reactive costabilizer, and Dowfax 2A1 (alkyldiphenyloxide disulfonate, Dow Chemical) as surfactant. Potassium persulfate (KPS, Fluka), ammonium persulfate (APS, Panreac), sodium metabisulfite (SBS, Aldrich), *tert*-butyl hydroperoxide (TBHP, Panreac), ascorbic acid (AsAc, Panreac) and azobisisobutyronitrile (AIBN, Fluka) were used as initiators. Distilled water was used throughout all the work.

2.2. Miniemulsification

The organic phase was prepared by dissolving the PDMS (different PDMS contents) and the reactive costabilizer (SA, when used) in the monomer mixture (MMA/BA/AA (49/50/1 wt%)). The aqueous phase was prepared by dissolving the surfactant (Dowfax 2A1) in water. Both phases were mixed for 10 min using a magnetic stirrer at 1000 rpm. The coarse emulsion was sonified in a Branson Sonifier 450 (480 W/L) and then homogenized in a two-valve Manton-Gaulin high pressure homogenizer (LAB 60.10). The main operation variables in the Manton-Gaulin are the pressure used in the valves and the number of cycles that the coarse emulsion is passed through the apparatus. In this work two sets of pressures were used: 41 MPa and 4 MPa for the first and second valve,

respectively, and 55 MPa and 5 MPa. In addition, different number of cycles (4 and 14 cycles) were used.

2.3. Polymerization processes

Batch polymerizations were carried out in a 1 L glass reactor equipped with reflux condenser, stirrer, sampling device and nitrogen inlet. Reaction temperature was set constant by controlling the temperature of the fluid in the jacket by means of a thermostatic bath and a heat exchanger. The miniemulsion (50 wt% organic phase) was added to the reactor and kept under a nitrogen atmosphere using a flow rate of 12–15 mL/min. When the reaction temperature was reached, the initiator was injected.

Semicontinuous polymerizations were carried out in the same reactor set-up than the batch polymerizations. Two different strategies were used. In the first one, a 33 wt% of the miniemulsion (50 wt% organic phase) was used as initial charge and it was allowed to polymerize during 1 h. Then, the rest of the miniemulsion and the initiator system (APS/SBS) were fed over a period of 4 h. In the second one, the polymerizations were performed by charging in the reactor a 10 wt% miniemulsion containing 30 wt% PDMS and polymerizing it for 2 h in batch. Then, the remaining mixture of monomers (MMA/BA/AA (49/50/1 wt%)), the initiator system (APS/SBS) and the surfactant (Dowfax 2A1) were fed for 3 h. The final product reached 50 wt% solid content, and final PDMS concentration was 3 wt% with respect to the total monomer.

All the reactions were carried out at 70 °C. Samples were withdrawn at regular intervals, and the polymerization was short-stopped with hydroquinone. The conversions were determined gravimetrically. The conversion in both batch and semicontinuous processes was calculated with respect to the monomer, namely the PDMS content was not taken into account.

Table 1 presents a summary of the reactions performed in batch (run names starting by B), semicontinuous with miniemulsion feeding (run names starting by SM) and semicontinuous with neat monomer feeding (run names starting by SN).

2.4. Quantification of silicone incorporation

The degree of incorporation of PDMS was determined by ¹H NMR spectroscopy (Bruker Avance 500 MHz) after selective extraction of the unreacted PDMS with hexane.

2.5. Transmission electron microscopy (TEM)

TEM micrographs were obtained with a TEM Hitachi 7000FA. The latexes were stained with phosphotungstic acid, placed on copper grids covered with Formvar R and dried in a UV lamp. Six different regions of each sample were analyzed to assure a representative image.

Table 1
Formulations used in the polymerizations

	Monomers[a]	PDMS[a]	SA[a]	Dowfax 2A1[a]	Solid content (%)	Initiator[a]
BM0	100[b]	–	4	1.8	50	0.75 KPS
BM3	100[b]	3	–	1.8	50	0.75 KPS
BM12	100[b]	12	–	1.8	50	0.75 KPS
BM25	100[b]	25	–	1.8	50	0.75 KPS
BM3K1.4	100[b]	3	–	1.8	50	1.4 KPS
BM3TA	100[b]	3	–	1.8	50	0.5 (TBHP/AsAc)
BM3SK	100[b]	3	–	1.8	50	0.75 KPS
						2 KPS
BM3SAS	100[b]	3	–	1.8	50	0.75 KPS
						2 (APS/SBS)
BM3STA	100[b]	3	–	1.8	50	0.75 KPS
						2 (TBHP/AsAc)
NBM25	100[b]	25[c]	–	1.8	50	0.75 KPS
SM0	100[b]	–	4	1.8	50	0.5 (APS/SBS)
SM3	100[b]	3	4	1.8	50	0.5 (APS/SBS)
SM12	100[b]	12	–	1.8	50	0.5 (APS/SBS)
SM25	100[b]	25	–	1.8	50	0.5 (APS/SBS)
SNM1	100[b]	3	–	0.25	50	0.5 (APS/SBS)
SNM2	100[b]	3	–	0.5	50	0.5 (APS/SBS)
SNM3	100[b]	3	–	0.25	50	1 (APS/SBS)

BM: batch reactions; SM: semicontinuous reactions with miniemulsion feeding; SNM: semicontinuous reactions with neat monomer feeding.
[a] Relative weight amounts.
[b] MMA/BA/AA (50/49/1 wt%).
[c] Non-reactive PDMS.

3. Results

3.1. Batch miniemulsion polymerizations

Fig. 1 presents the evolution of the gravimetric monomer conversion for varying amounts of divinyl terminated PDMS (DV-PDMS). It can be seen that no evidence of limiting conversion was found when no DV-PDMS was used (run BM0), whereas a limiting conversion was observed when DV-PDMS was used. Fig. 2 presents the TEM images of latex BM25. It can be seen that, together with polyacrylate particles and particles containing grafted acrylics and PDMS, there is a fraction of particles with segregated PDMS forming the core of the particle. Since th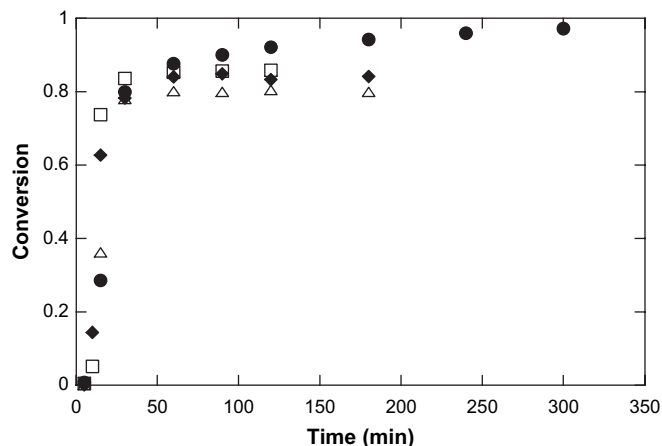e non-reacted monomer is partitioned between the different types of particles, it could be questioned why particles that contain no DV-PDMS not continue to polymerize. The main reason was that the volume fraction of such particles was low, and in consequence also the reaction rate. Therefore, if the reaction occurred it was negligible during the period of time of the experiment.

In order to elucidate if the retention of the monomer in the segregated PDMS is one of the factors responsible for the

Fig. 1. Evolution of conversion in batch miniemulsion polymerization with varying concentrations of DV-PDMS; (●) BM0; (□) BM3; (◆) BM12; (△) BM25.
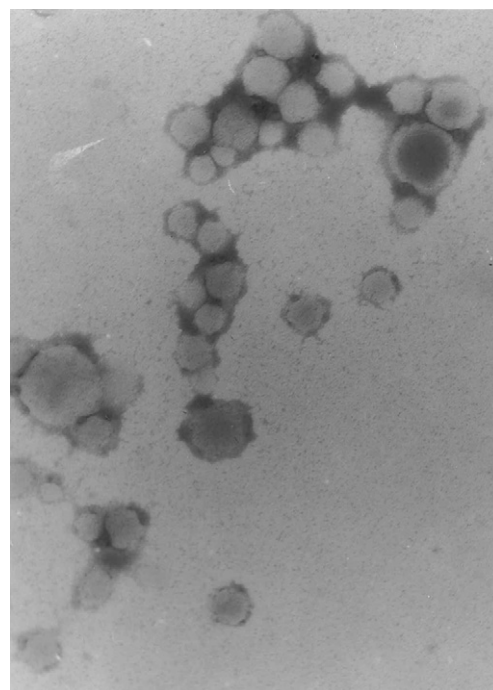

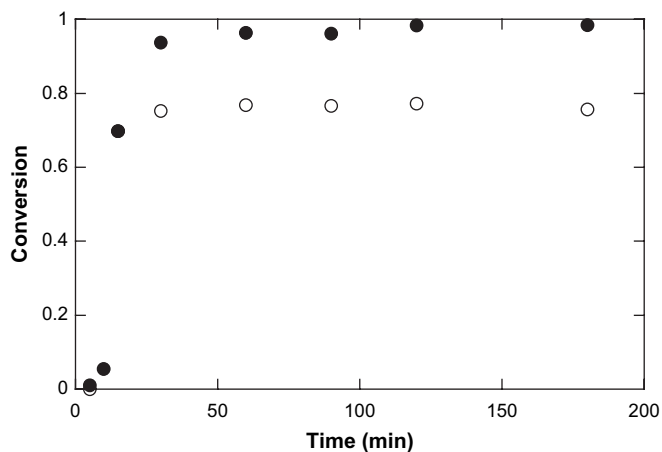Fig. 2. Morphology of latex BM25.

Fig. 3. Evolution of monomer conversion in the batch miniemulsion polymerization; (●) NBM25 and (○) BM25.

limiting conversion, a batch miniemulsion polymerization using a non-reactive PDMS (NBM25) was carried out. Fig. 3 shows that complete conversion was reached in run NBM25 (non-reactive PDMS), whereas a similar reaction with reactive PDMS (run BM25) led to limiting conversion. Fig. 4 shows that most the NBM25 particles presented PDMS-rich core morphologies. Therefore, limiting conversion could not be attributed to monomer retention by the segregated PDMS core.

From a kinetic point of view, the limiting conversion could be due to the fact that not enough radicals were produced or/and because they became inactive along the polymerization process. To check those hypotheses, reaction BM3 was performed at 80 °C. This should increase the rate of radical production from the thermal initiator, as well as the propagation
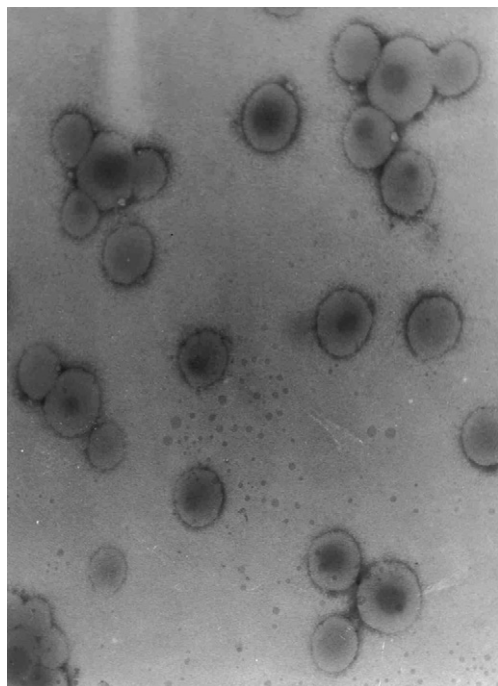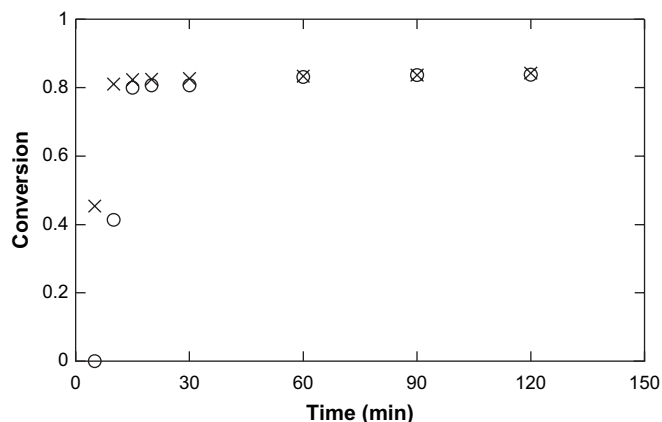

Fig. 4. Morphology of latex NBM25.

rate constant. A faster initial polymerization rate was observed but the same limiting conversion was reached (Fig. 5).

Fig. 6 shows that using twice the initiator concentration (run BM3K1.4) led to a higher polymerization rate but still a relatively low limiting conversion was obtained. This behaviour could not be attributed to the diminution of radical generation along the polymerization, because, taking into account that at 70 °C, the half life time of the KPS is about 10.5 h, an estimation of the decomposition rate shows that after 2 h of reaction, only 20% of the initiator was decomposed.

In run BM3SK, a stream of an aqueous solution of KPS was added for 2 h, starting after 2 h of reaction. Fig. 7 shows that a substantial increase in monomer conversion was observed. Similar increases were obtained feeding redox systems yielding hydrophilic radicals (APS/SBS; run BM3SAS) and hydrophobic radicals (TBHP/AsAc; run BM3STA). The formulations are given in Table 1. It is worth pointing out that the amount of KPS fed was substantially higher than that used in the regular batch miniemulsion polymerizations (i.e., in run BM3). Similarly, the redox systems generated much more radicals than in run BM3 [20]. Fig. 7 shows that when enough radicals were generated monomer conversion increased, but complete conversion was not achieved. This result further supported the idea that limiting conversion was not due

Fig. 5. Effect of the temperature on the hybrid batch polymerization kinetics; (×) BM3, 80 °C; (○) BM3, 70 °C.
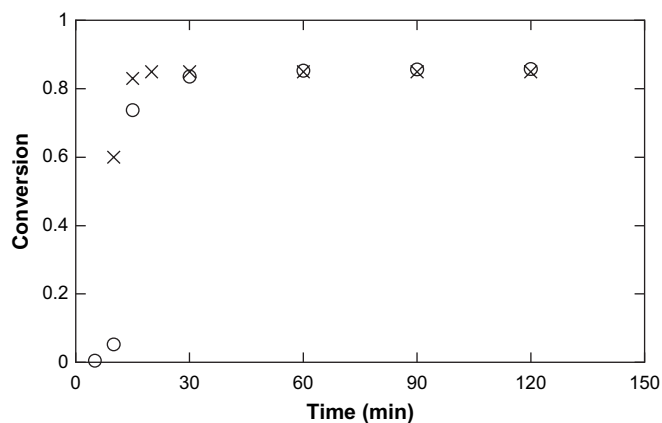

Fig. 6. Effect of the initiator concentration on the hybrid batch polymerization kinetics; (○) run BM3; (×) run BM3K1.4.
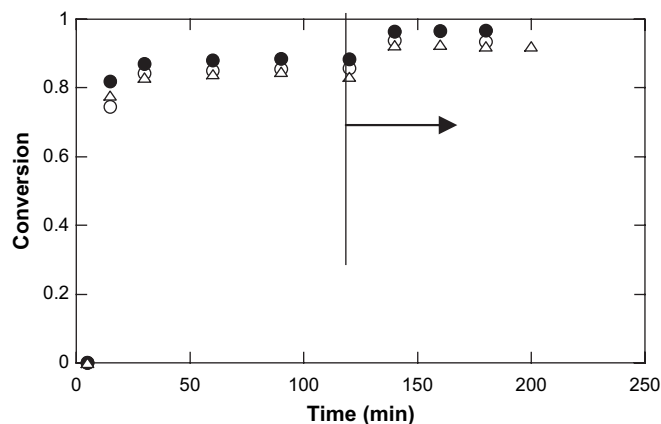
Fig. 7. Effect of feeding additional initiators: (○) KPS (BM3SK); (●) APS/SBS (BM3SAS) and (△) TBHP/AsAc (BM3STA).

to the entrapment of the monomer within the segregated PDMS forming the core of the polymer particle, but to the action of a chemical mechanism that led to inactive radicals. Such a mechanism should involve the vinyl group of the PDMS.

The (meth)acrylic radicals may either abstract a hydrogen from the PDMS or propagate with the vinyl group. However, propagation is much more energetically favoured than hydrogen abstraction from the vinyl group. Moreover, the butyl acrylate radical is more reactive than the MMA radical (this radical was stabilized by the CH_3 that also provides a steric impediment). Therefore, one would expect that most of the reaction with the vinyl groups of the PDMS involved BA radicals, yielding radicals that are strongly stabilized by the hyperconjugation with the electrons of the $Si-CH_3$ bond (Fig. 8). This hypothesis is supported by the late incorporation of PDMS during the batch process, as illustrated in Fig. 9. In fact, because of the reactivity ratios of BA and MMA (Table 2), at the beginning of the reaction mostly MMA reacted (Fig. 10). Therefore, while MMA was present in the system most active chains were MMA terminated, and hence the reaction with DV-PDMS occurred in a very limited extent. However, when most of the MMA reacted, the probability of having BA radicals increased, which favoured the reaction with DV-PDMS, yielding quite inactive radicals.

3.2. Semicontinuous miniemulsion polymerization

Fig. 11 shows the evolution of monomer conversion in the experiments using a miniemulsion feed. It can be seen that the instantaneous conversion (defined as the polymer formed
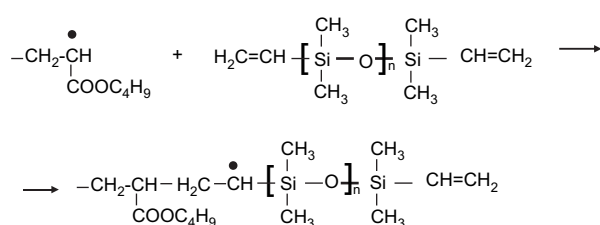

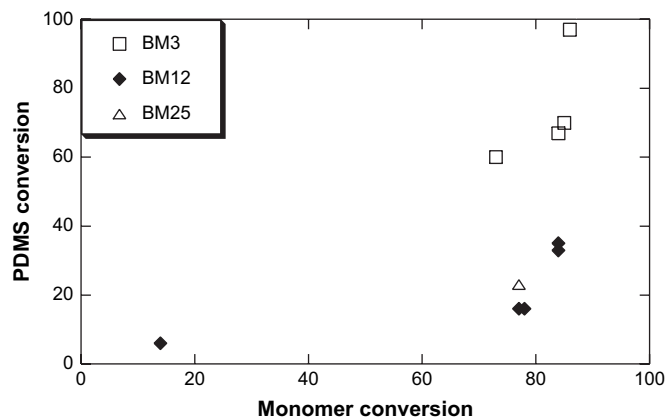Fig. 8. Mechanism of reaction of PDMS chains.

Fig. 9. PDMS incorporation; (□) BM3; (◆) BM12; (△) BM25.

Table 2
Reactivity ratios of the used monomers [21]

r_{ij}	MMA	BA	PDMS
MMA	–	2.47	25.5
BA	0.33	–	5.5
PDMS	0.016	0.098	–

divided by the monomer fed until a given time) decreased as the PDMS content increased. This is in agreement with the mechanism discussed above because for this system the concentration of BA in the reactor was higher than that of MMA, and DV-PDMS was continuously fed into the reactor.

Fig. 12 shows the evolution of the conversion in the semicontinuous process in which the miniemulsion forming the initial charge was polymerized in batch and then a neat monomer addition was used. It can be seen that a very high monomer conversion was reached. In these reactions, the DV-PDMS was included in the initial charge (30 wt% of PDMS) and then the monomers and the redox initiator system were added. There were three factors contributing to the high final conversion. Firstly, the use of a redox system for a rather long period of time [20], which formed a large amount of radicals. Secondly, as both BA and MMA were continuously fed into the reactor, the fraction of BA radicals was lower than that in the last stages of the batch process and hence the
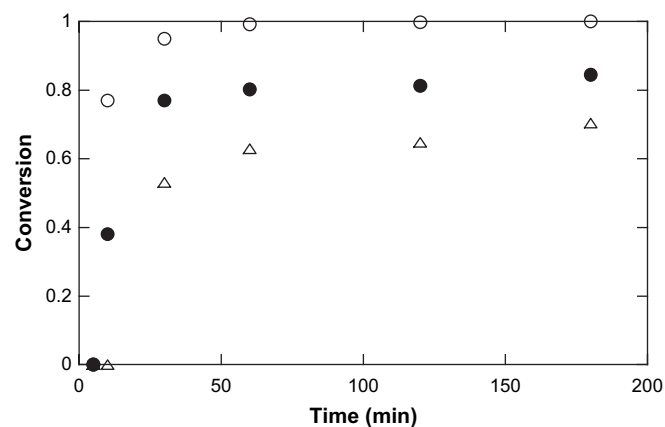

Fig. 10. MMA (○) and BA (△) fractional conversion, and overall conversions (●) for reaction BM3 (70 °C), obtained by GC.
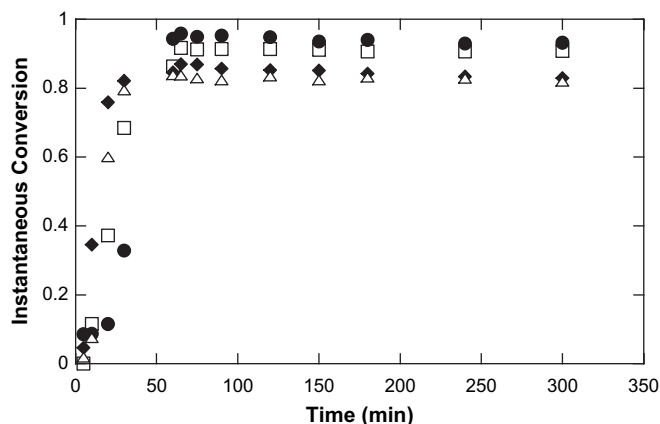
Fig. 11. Effect of the PDMS content on the kinetics of semicontinuous miniemulsion polymerizations using miniemulsion feed; (●) SM0; (□) SM3; (◆) SM12; (△) SM25.
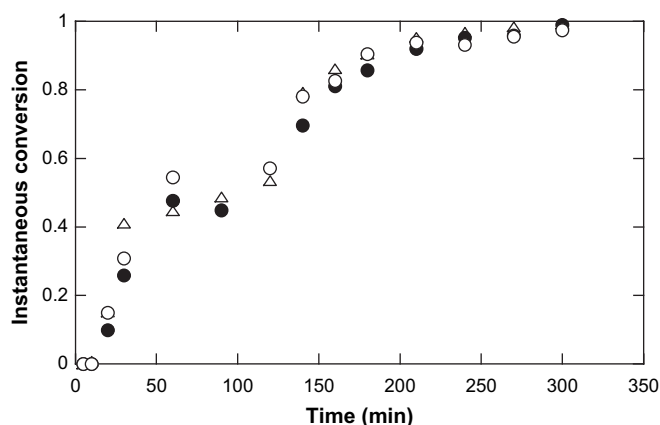

Fig. 12. Kinetics of the semicontinuous polymerization using neat monomer feeding; (●) SNM1; (△) SNM2; (○) SNM3.

reaction with the vinyl groups of PDMS was less likely. Thirdly, new particles (Fig. 13) were nucleated during the semicontinuous operation, which did not contain DV-PDMS, and hence, polymerization in these new particles proceeded unperturbed.
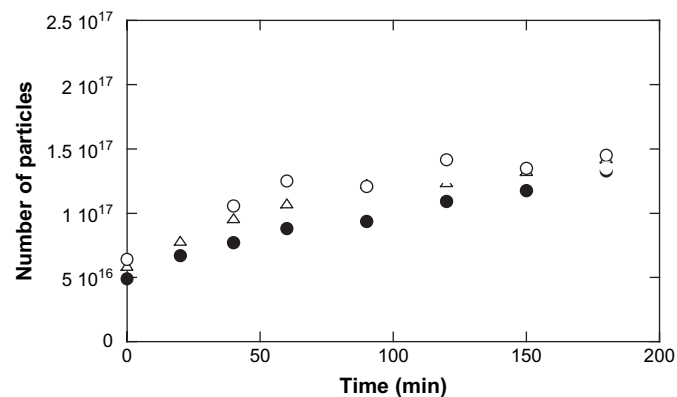

Fig. 13. Number of particles in the semicontinuous miniemulsion polymerizations using neat monomer feeding; (●) SNM1; (△) SNM2; (○) SNM3.

4. Conclusions

In the foregoing, the phenomenon of limiting conversion in the miniemulsion polymerization of reactive PDMS–acrylic systems was investigated. Limiting conversion was found in both batch polymerization and semicontinuous polymerization using miniemulsion feed. Experiments carried out with non-reactive PDMS did not present limiting conversion showing that this phenomenon was not due to monomer retention by the segregated PDMS. Propagation of BA radicals to the vinyl group of the PDMS, which yielded very stable radicals, likely was the cause of the limiting conversion. Complete conversion was achieved by postpolymerization with redox initiators as well as by using a semicontinuous process with monomer feed. In the later case, the factors contributing to complete conversion were: (i) the use of a redox initiator, (ii) the presence of both MMA and BA during the whole process, which favoured the formation of MMA radicals that are less prone to propagate with the vinyl groups of the PDMS, and (iii) the formation of new particles that did not contain PDMS.

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