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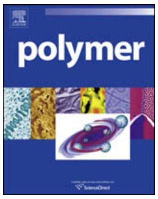

Polymer Communication

Miniemulsion polymerization of styrene in the presence of macromonomeric initiators

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ABSTRACT

Macromonomeric azo initiators (macroinimers, MIM) which have the properties of macromonomers, macrocrosslinkers and macroinitiators in a macrostructure were used in miniemulsion polymerization of styrene in the presence or absence of any other stabilizer and initiator. MIMs were prepared from the reaction of 4,4′-dicyano-4,4′-azovaleryl chloride, with poly(ethylene glycol) (PEG) of different molecular weights (400 and 2000 g/mol) and with 4-vinylbenzyl chloride. The stabilizing and initiator efficiency of MIMs and the effect of the chain length of PEG units were evaluated.

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1. Introduction

Miniemulsion polymerization is an efficient way to synthesize polymer nanoparticles in the size range of 40–500 nm with high uniformity and chemical stability [1,2]. The major interest in miniemulsion polymerization processes is to avoid the step of micellar nucleation. Therefore, polymerization occurs in the polymer droplets that are nucleated directly either upon capturing the (oligo) radicals transferred from the water phase, or because of the presence of an oil-soluble initiator inside the droplets. The size of the polymer particles after polymerization should therefore be identical to that of the monomer droplets. Thus the monomer droplets must be stable enough and contain a very hydrophobic compound, which is almost completely insoluble in water phase. This hydrophobe inhibits Ostwald ripening of the monomer molecules from the smaller droplets to the larger ones. If properly stabilized the droplets have a long shelf up to several months before the beginning of coalescence [3].

Conventional surfactants are held on the particle surface by physical forces. Thus, an adsorption/desorption equilibrium always exists, which may not be desirable since the surfactant molecules can be easily desorbed when for example subjected to higher shear or to freeze–thaw cycles. Then flocculation occurs and a peptization of the flocculated particles is often not easily possible. Furthermore, the surfactants can interfere with adhesion to a substrate and may be leached out upon contact with water. Furthermore, surfactant migration affects film formation and their lateral motion during particle–particle interactions can cause a destabilization of the colloidal dispersions. When films are formed from the latexes, the major part remains as hydrophilic domains buried inside the films. These hydrophilic domains are then responsible for accumulation of water when the films are exposed to high humidity conditions. Furthermore, conventional non-ionic surfactants are small and mobile and these surface-active molecules can migrate to the surface layer of a polymeric film. This kind of action can have a negative effect on the application properties (e.g. adhesion water resistance of pressure-sensitive adhesives). One approach to alleviate the surfactant migration problem is to use a polymerizable surfactant, which has a carbon–carbon double bond and can be chemically incorporated into the latex particles during a radical polymerization process. An interesting alternative arises with the use of unsaturated macromonomers as reactive amphiphilic surfactants. Amphiphilic poly(ethylene oxide) (PEO) macromonomers and the PEO graft copolymers present all the typical properties of conventional non-ionic surfactants, such as micelle formation, critical micellar concentration (CMC), emulsifying activity, craft-point, interfacial tension reduction, etc. In addition, reactive surfactants contain a polymerizable group, thus, they can overcome some of the difficulties encountered with conventional surfactants and can function not only as surfactants, but can also be

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incorporated into the surface layer of the latex particles by polymerization or copolymerization with low molecular weight comonomers. In such a way, desorption of the anchored surfactants is no longer possible. The incorporation of PEO group into the particle surface (and into the polymer matrix) can be performed by several ways. If the PEO amphiphiles include an initiator group or a transfer agent group, the surfactants can be incorporated to the polymer matrix via the initiation and chain-transfer processes. In the former case, the initiating radicals formed by decomposition of the initiator contained PEO unit. In the latter case, the chain-transferred radicals, that contained EO units, can either re-initiate the polymerization or terminate growing radicals. Furthermore, the most efficient way of incorporation of EO units into the polymer matrix is via propagation of unsaturated PEO macromonomer or copolymerization with comonomer. In these manners, the reactive surfactants are prevented from subsequent migration [4]. On the other hand, PEO segments are not only hydrophilic, but also nonionic and crystalline [5]. Macromonomeric azo initiators (macroinimers, MIM), which were first reported by Hazer [6,7] and used in different polymerization systems for different purposes by Yildiz [8–13], have the properties of ***macro***crosslinker, macro***ini***tiators, and macromono***mer***s in a macrostructure. A typical macroinimer can be synthesized by the reaction of 4,4′-dicyano-4,4′-azovaleryl chloride (ACPC), polyethylene glycol (PEG), and 4-vinylbeznyl chloride as described in Ref. [9]. MIMs based on PEG-400 and PEG-2000 (number refers to molecular weight of PEG) were prepared and characterized.

In the current study, we describe the use of MIMs in the miniemulsion polymerization of styrene not only as initiators but also as sole surfactants, or as additional surfactants in the presence or absence of another stabilizer and/or initiator. SDS as an additional stabilizer and the hydrophilic KPS, or the hydrophobic AIBN and V59 were used as additional initiators. It will be the first attempt in the literature to use MIM in the miniemulsion polymerization of sytrene.

2. Experimental

2.1. Materials

Commercially available styrene (St, from Aldrich) was purified by usual methods. Analytical grade poly(ethylene glycol)s (PEG-400 and PEG-2000), 4,4′-dicayano-4,4′-azovaleric acid (ACPA), potassium peroxodisulfate (KPS), α,α′-azoisobutyronitrile (AIBN) were supplied by Fluka AG. 2,2′-Azobis(2-methylbutyronitrile) (V59) was supplied from Wako Chemicals. 4-Vinylbenzyl chloride and hexadecane were supplied from Aldrich. All these chemicals were used without further purification. 4,4′-Dicyano-4,4′-azovaleryl chloride (ACPC) was prepared by the reaction of ACPA and PCl_5. In all miniemulsion experiments, double distilled water was used as a continuous polymerization medium.

2.2. Synthesis of macroinimer

A typical macroinimer (MIM) can be synthesized by the reaction of 4,4′-dicyano-4,4′-azovaleryl chloride (ACPC), polyethylene glycol (PEG), and 4-vinylbenzyl chloride as described in Ref. [9].

2.3. Miniemulsion polymerization procedure

A typical recipe is given in the following: 6 g of styrene and 250 mg of hexadecane were mixed and added to a solution of SDS (or SDS + MIM, or sole MIM) in 24 g of water. After stirring for 1 h, the miniemulsion was generated by ultrasonicating the emulsion for 120 s at 90% amplitude with a Branson Sonifier W450 Digital. To avoid any polymerization due to heating of the sample, the mixture was ice-cooled during the homogenization. For polymerization, the temperature was increased up to 72 °C (for 22 h) and the water-soluble initiator (KPS or MIM) was added to initiate the polymerization. In the case of using the hydrophobic AIBN and V59 as initiators, 100 mg of AIBN or V59 were added to the monomer phase prior to miniemulsification. In the absence of any other initiator and stabilizer, the MIMs were added to the continuous phase prior to miniemulsification.

2.4. Characterization

The particle size of the latexes was analyzed by dynamic light scattering (DLS) with a Nicomp particle sizer (model 370, PSS Santa Barbara, USA) at a fixed scattering angle of 90°.

Transmission electron microscopy was performed with a Zeiss 912 Omega electron microscope operating at 100 kV. The diluted colloidal solutions were applied to a 400-mesh carbon-coated copper grid and left to dry. No further contrasting was applied.

Infrared (IR) spectroscopy was performed on a Biorad FTS 600 spectrometer in the spectral range between 4000 and 400 cm^{-1}.

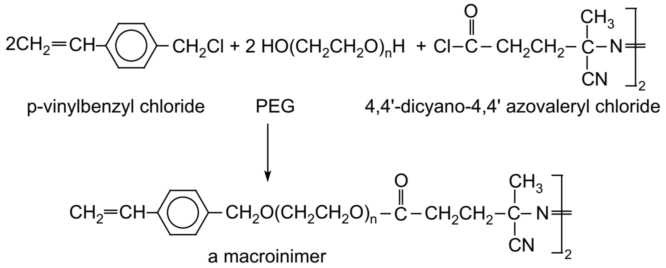
The molecular weights of the MIMs were determined by gel permeation chromatography (GPC) analysis. GPC was carried out by injecting 100 μl of about 0.15 wt.% polymer solutions (solvent tetrahydrofuran) through a Teflon-filter with a mesh size of 450 nm into a Thermo Separation Products set-up being equipped with UV (TSP UV100) and RI (Shodex RI-71) detectors in THF at 30 °C with a flow rate of 1 ml min^{-1}. A column set was employed consisting of three 300 × 8 mm columns filled with a MZ-SD *plus* spherical polystyrene gel (average particle size 5 μm) having a pore size of 10^6, 10^5 and 10^3 Å, respectively. This column set allows a resolution down to molecular weights of less than 500 g mol^{-1}. Molecular weights and molecular weight distributions were calculated based on polystyrene standards. The molecular weights, M_w, of the MIMs were determined by GPC as 9.2×10^2 ($M_w/M_n = 1.04$) and 3.9×10^3 g/mol ($M_w/M_n = 1.07$) for MIM400 and MIM2000, respectively.

^{1}H NMR spectra were recorded with a Bruker DPX-400 MHz spectrometer at 40 °C in D_2O using TMS as standard.

3. Results and discussion

3.1. Macroinimer synthesis

Macromonomeric azo initiators (macroinimers, MIMs), MIM400 and MIM2000 (numbers refer to molecular weight of PEG which was used in preparation) were synthesized as shown in Scheme 1 and characterized by IR and NMR spectroscopy and GPC chromatography methods. The IR spectra of MIMs show all characteristic peaks: at 1100 (CH_2-etheric bonds of PEG), 1620 (vinyl and benzyl groups), 1750 (carbonyl of ester group), 2250 cm^{-1} (bond of C≡N). The ^{1}H NMR spectra of MIMs exhibit characteristic signals at $\delta = 3.6$



Scheme 1.

(C**H**$_2$C**H**$_2$O groups in PEG), 4.5 ppm (*s*, C**H**$_2$ group in vinylbenzyl group), 5.2 and 5.7 ppm (*m*, C**H**$_2$=CH– group in vinylbenzyl group), 6.7 ppm (CH$_2$=C**H**– group in vinylbenzyl group) and 7.3 ppm (*s*; phenyl group in vinylbenzyl group). All these characteristic signals of MIMs in their IR and NMR spectra confirmed their structure. The molecular weights of MIMs were determined by GPC to be 920 and 3900 g mol^{-1} for MIM400 and MIM2000, respectively.

MIMs can thermally homopolymerize by themselves or copolymerize with another vinyl monomer. In each case, the polymerization reactions give cross-linked polymers. The gelation behavior of MIM can be explained as follows: at the beginning, a small amount of the azo bonds of the MIM decomposes into macroradicals which initiate the free radical copolymerization of styrene and the vinylic part of the undecomposed MIM in the reaction media, and a cross-linked copolymer is formed. In that case, the undecomposed MIM behave as a macrocrosslinker. As the polymerization proceeds, azo groups in the network cleave to produce radicals ends, and the network structure gets denser.

In the current study, MIMs were used in the miniemulsion polymerization of styrene not only as initiators but also as sole surfactants, or in combination with other surfactants. One advantage of MIMs is that, they are electrically neutral and hence, they can be used for any kind of surfactant or stabilizers. In this connection, at the beginning we have carried out some experiments with MIM400 to see whether it has any effect or not on the miniemulsion polymerization of styrene. For this purpose, a standard miniemulsion (reference latex) was prepared and polymerized using KPS as initiator. The final particle size was 97 nm. The same experiment was carried out again but at that time with the addition of MIM400. The miniemulsion before polymerization was stable and showed particle sizes of about 100 nm. After polymerization, a stable latex was obtained. ^{1}H NMR spectra showed the absence of double bonds indicating that full conversion of the MIM occurred. The final particle size was 75 nm (MIM400-B2). After obtaining such effective result, we have decided to evaluate the effect of the MIM and also the molecular weight of PEG unit on the colloidal stability of the latexes and we have performed five types of polymerization of St in the presence of MIMs:

(A) Miniemulsion polymerization of St with MIMs in the presence of SDS and in the absence of initiator,
(B) miniemulsion polymerization of St with MIMs in the presence of surfactant and initiator; KPS,
(C) miniemulsion polymerization of St with MIMs in the absence of surfactant and initiator,
(D) miniemulsion polymerization of St with MIMs in the absence of SDS but in the presence of initiator; V59,
(E) miniemulsion polymerization of St with MIMs in the absence of SDS but in the presence of initiator; AIBN.

In the first step, we compared the MIMs in the presence of stabilizer, SDS, but in the absence of any initiator (series A). The results can be seen in Tables 1 and 2. MIM400 leads to stable miniemulsions and after polymerizations to stable and narrowly distributed latex particles as well as MIM2000. An increasing amount of both MIMs at a fixed SDS amount yields smaller particles since MIMs can also function as surfactant and thus the increasing amount of MIMs decreases the particle size. The smallest particle sizes were 98 (MIM400-A4 and A5) and 139 nm (MIM2000-A5) for MIM400 and MIM2000, respectively. In the case of MIM400, smaller particles are obtained. The smaller particle size is attributed to lower molecular weight of the PEG units in MIM400. The higher the molecular weight of the PEG, the larger the particle size. An increasing amount of MIM causes smaller particles (Tables 1 and 2, MIM400 and MIM2000-A series) since an increasing amount of MIM enhances colloidal

Table 1
Characteristics of the latexes obtained with MIM400; if SDS is used, the amount is 72 mg, if an initiator is used, the amount is 100 mg.

Run no	SDS +/−	Initiator	MIM400 (g)	Particle size (nm)	Solid. con. (wt.%)
Reference	+	KPS	–	97	17.69
MIM400-A1	+	–	0.050	151	19.60
MIM400-A2	+	–	0.110	120	20.45
MIM400-A3	+	–	0.200	113	20.87
MIM400-A4	+	–	0.400	98	21.65
MIM400-A5	+	–	1.000	98	22.50
MIM400-B1	+	KPS	0.050	103	17.75
MIM400-B2	+	KPS	0.110	75	18.74
MIM400-B3	+	KPS	0.200	91	18.94
MIM400-B4	+	KPS	0.400	92	19.56
MIM400-B5	+	KPS	0.550	86	20.30
MIM400-B6	+	KPS	1.000	89	22.60
MIM400-C1	–	–	0.200	–[a]	–[a]
MIM400-C2	–	–	0.400	453	9.61
MIM400-C3	–	–	0.800	132; 451	2.01
MIM400-C4	–	–	1.000	133; 445	3.49
MIM400-C5	–	–	1.500	129; 451	6.14
MIM400-C6	–	–	2.000	98; 452	4.63
MIM400-C7	–	–	4.000	430	6.70
MIM400-D1	–	V59	0.050	46; 373	5.79
MIM400-D2	–	V59	0.110	165; 355	5.30
MIM400-D3	–	V59	0.200	110; 334	7.71
MIM400-D4	–	V59	0.400	281	8.06
MIM400-D5	–	V59	1.000	38; 449	1.44
MIM400-D6	–	V59	2.000	107; 404	3.08
MIM400-E1	–	AIBN	0.050	435	0.01
MIM400-E2	–	AIBN	0.110	292	6.08
MIM400-E3	–	AIBN	0.200	268	7.48
MIM400-E4	–	AIBN	0.400	79; 291	9.67
MIM400-E5	–	AIBN	1.000	453	2.24
MIM400-E6	–	AIBN	2.000	171; 448	4.96
MIM400-F1	–	KPS	0.200	154; 509	5.30

[a] Aggregation during polymerization.

Table 2
Characteristics of the latexes obtained with MIM2000; if SDS is used, the amount is 72 mg; if an initiator is used, the amount is 100 mg.

Run no	SDS +/−	Initiator	MIM2000 (g)	Particle size (nm)	Solid. con. (wt.%)
Reference	+	KPS	–	97	17.69
MIM2000-A1	+	–	0.050	223	14.93
MIM2000-A2	+	–	0.110	252	15.69
MIM2000-A3	+	–	0.200	234	10.73
MIM2000-A4	+	–	0.400	157	14.90
MIM2000-A5	+	–	1.000	139	21.35
MIM2000-B1	+	KPS	0.050	90	6.42
MIM2000-B2	+	KPS	0.110	115	7.08
MIM2000-B3	+	KPS	0.200	92	4.46
MIM2000-B4	+	KPS	0.400	155	16.87
MIM2000-B5	+	KPS	0.550	113	12.08
MIM2000-B6	+	KPS	1.000	127	18.55
MIM2000-C1	–	–	0.200	1048	4.34
MIM2000-C2	–	–	0.400	642	17.58
MIM2000-C3	–	–	0.800	453	18.70
MIM2000-C4	–	–	1.000	453	22.24
MIM2000-C5	–	–	1.500	462	24.12
MIM2000-C6	–	–	2.000	372	25.46
MIM2000-C7	–	–	4.000	268	33.45
MIM2000-D1	–	V59	0.050	299	3.69
MIM2000-D2	–	V59	0.110	380	4.13
MIM2000-D3	–	V59	0.200	100; 450	5.87
MIM2000-D4	–	V59	0.400	549	11.81
MIM2000-D5	–	V59	1.000	449	21.16
MIM2000-D6	–	V59	2.000	102; 367	22.30
MIM2000-E1	–	AIBN	0.050	262	3.17
MIM2000-E2	–	AIBN	0.110	97; 394	4.19
MIM2000-E3	–	AIBN	0.200	402	5.99
MIM2000-E4	–	AIBN	0.400	444	9.19
MIM2000-E5	–	AIBN	1.000	452	21.94
MIM2000-E6	–	AIBN	2.000	297	22.85

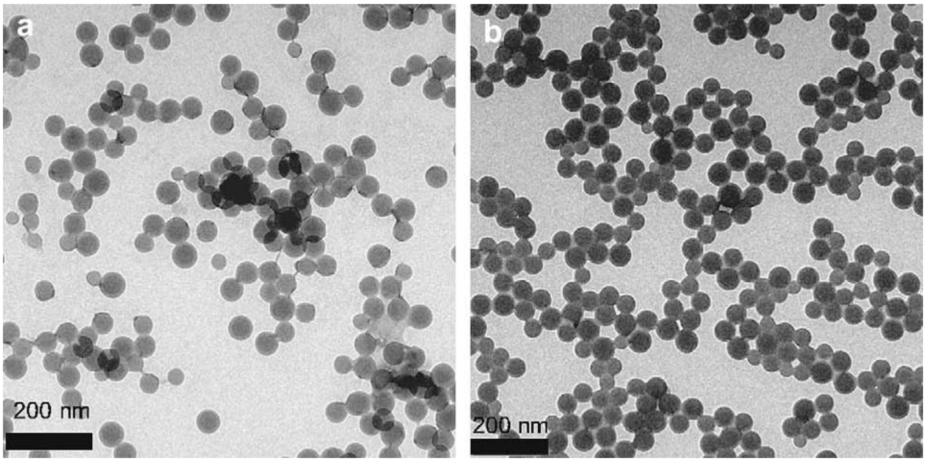


Fig. 1. Latex prepared (a) with SDS, KPS, and 110 mg MIM400 (MIM400-B2); (b) with SDS, KPS, and 550 mg MIM400 (MIM400-B5).

stability due to retardation of diffusional degradation of monomer droplets and prevention of surfactant desorption. MIM has hydrophilic and hydrophobic parts, thus MIM closely packed between SDS molecules and also cover the oil–water interfacial area which has not been occupied by SDS. The cmc of MIM2000 is about 0.520 g/l, whereas for MIM400 it is about 0.30 g/l. The resulting state at the oil–water interface imparts a low interfacial tension and high resistance to droplet coalescence into miniemulsion. Even though the EO chain is quite long in MIM2000, the amphiphilic behavior is still strong. The amount of free chains in the aqueous phase is therefore minimized and most of the MIM molecules are indeed located at the interface. As shown by ^{1}H NMR experiments, the double bonds of MIM disappear indicating the formation of a copolymer with styrene.

In the second step, MIMs were used in the presence of SDS and an additional initiator, KPS. The results are summarized in Tables 1 and 2. Smaller particles were obtained in the second step (B series) than that of the first step (A series). This was an expected result, because MIM acts as initiator and also takes part in the stabilization of the particles simultaneously. Additional initiator will assist in initiating the polymerization and decrease the consumption of MIM for initiation and thus there will be more MIM for stabilizing the particles. Therefore, additional initiator increases the stabilizing effect of the MIMs.

In the third step (C), MIMs were used in the absence of any other stabilizer and initiator. The run without SDS clearly shows the influence of the SDS absence on the particle size. Larger particles were obtained for the C series than those of the A and B series; 453 and 642 nm (MIM400-A4 and MIM2000-A4) in the case of with SDS, 98 and 157 nm (MIM400-C2 and MIM-2000-C2) without SDS for MIM400 and MIM2000, respectively. In the absence of stabilizer and initiator, the MIMs have to stabilize the particles and also initiate the polymerization simultaneously. So, it is a reasonable result to find larger particles in the absence of SDS. Moreover, MIM2000 was more effective than MIM400. Poly(ethylene glycol) chains arising from MIM400 alone are not able to stabilize polymer particles. Whereas in the case of MIM400 even at higher concentration due to the formation of coagulum only a low solid content was obtained, the MIM2000 leads to stable particles without the formation of coagulum at concentrations of >0.2 g MIM2000. As reported by Tauer [14], PEGA initiators which have very similar chemistry with MIM lead to stable PS particles if the average molecular weight of the PEG chain is equal or higher than 2000 g/mol. Due to the longer PEG chain, MIM2000 has a higher stabilizing power than MIM400 which is not suited to stabilize the particles in the absence of any other stabilizer and/or initiator even at larger quantities.

In the last two steps (D and E series), the MIMs were used in the absence of stabilizer but in the presence of different hydrophobic initiators, V59 and AIBN. Oil-soluble initiators, such as 2,2′-azoisobutyronitrile (AIBN) and 2,2′-azobis(2-methylbutyronitrile) (V59), decompose in monomer droplets to generate new radicals but it is known that V59 has more hydrophobic character compared to the AIBN. Thus, the effect of the hydrophobic character of the initiator on the miniemulsion polymerization of styrene in the presence of MIM can be evaluated.

In the case of MIM400, stability of the particles was limited even in the presence of initiators and therefore only solid contents of less than 10% were found. Low solid content and large particle size mean that the stabilizing ability is lower. In the case of MIM2000, higher solid content and smaller particle size were obtained. As explained above, the chain length of the PEG has an influence on the particle size and stability; the longer the PEG chain higher is,

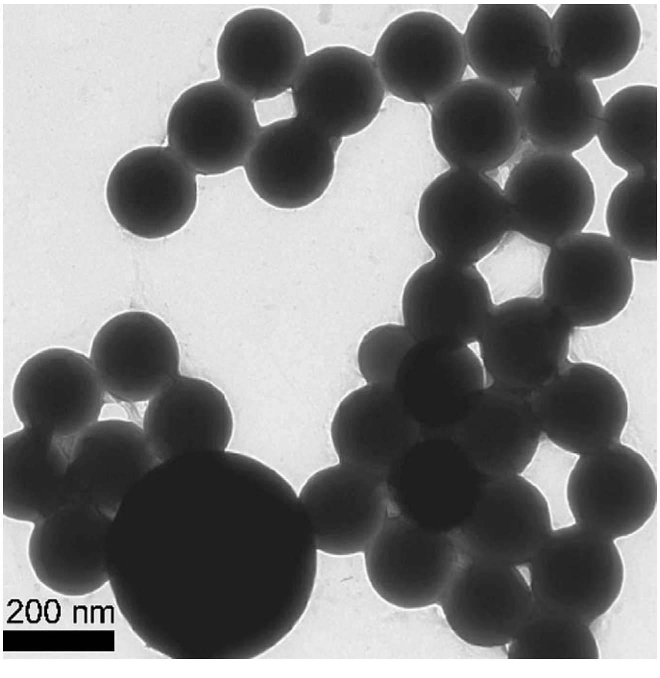


Fig. 2. Latex prepared (a) without SDS, with KPS, and 200 mg MIM400 (MIM400-F1).

the higher the stability of the latexes. The reduced stability of MIM400 might be explained by the short chain of PEG with a hydrophobic core which may strongly associate among the droplets under elevated temperature due to a cloud point in nonionic amphiphiles.

On the other hand, it was seen that the hydrophobicity of the initiator affects the stability and particle size. In the case of AIBN, more stable particles with smaller particle sizes were obtained than those of V59 with a higher hydrophobicity due to the additional CH_2 groups. This is most probably due to the partly water-soluble property of AIBN (the solubility of AIBN is about 0.06 g/ml [15]). AIBN is a partly water-soluble initiator while V59 is only oil soluble. MIM is mainly located at the interface acting as a surface-active initiator and stabilizing agent, AIBN can more effectively initiate the polymerization than V59 due to its partly water solubility and the compatibility with the origin of MIM. However, we need more experiments and data to explain the different initiator efficiency between two neutral initiators: AIBN and V59. In the presence of using the hydrophobic and neutral initiators AIBN or V59, more stable latexes with high solid contents (and no coagulum) could be only obtained with high amounts of MIM2000. Also the use of the hydrophilic KPS (see MIM400-F1) could not lead to more stable nanoparticles.

On the other hand, it must be emphasized that MIM-A and MIM-B series (see Tables 1 and 2 and Fig. 1) are almost more monotonic than other series in relationship between MIM mass and particle size. This is most likely due to the absence of additional stabilizer and the presence of additional initiators which makes the initiation and polymerization process more complex. One example of bimodal distribution in the other series as seen exemplarily in Fig. 2 shows that the particles of the small size are quite monodisperse; the larger size particles are formed due to the limited stability of the latexes. Additionally coagulation takes place (see low solid content in the tables).

In summary, nanoparticles with covalently bonded PEO at the particle surface can be obtained by polymerizing a hydrophobic monomer with macromonomeric azo initiators, MIMs, bearing suitably PEG chains with a molecular weight of 2000 $g\,mol^{-1}$. MIMs can also boost the stabilizing ability of surfactants. Under present experiments and collected results in tables we can conclude that MIMs offer very interesting alternatives as not only initiators but also as sole surfactants or additional surfactants for miniemulsion polymerization. On the other hand, it is for sure that we need more experiments and data for entire evaluation of the effect of the MIM for the miniemulsion polymerization process.

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