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ORIGINAL PAPER

Semicontinuous heterophase polymerization of methyl methacrylate in the presence of reactive surfactant HITENOL BC10

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Abstract Semicontinuous heterophase polymerization was used to copolymerize methyl methacrylate (MMA) with reactive surfactant HITENOL BC10 (HBC10) at 60 °C using sodium dodecyl sulfate as pre-stabilizing agent and potassium persulfate as initiator. The mixture of MMA and HBC10 was added at constant rate in continuous mode varying the MMA/HBC10 ratio. High-polymerization rates were observed, decreasing as the MMA/HBC10 ratio decreased. Latexes with polymer content near 20% and polymer to surfactant (P/S) weight ratios between 5 and 15 were obtained. Particle sizes distribution were bimodal in all cases with a tendency to be monomodal as HBC10 concentration increased which was ascribed to enhanced particle stabilization by the presence of HBC10. The average particle diameters at the end of polymerizations for the first and second populations were around 10 and 50 nm, respectively. Very high average molecular weights were observed ($1.4 \times 10^6 \leq M_w \leq 2.1 \times 10^6$ g/mol), which decreased when HBC10 concentration increased. The corresponding polydispersity indexes (M_w/M_n) were in the range of 1.45–2.24.

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Introduction

By micro-emulsion polymerization it is possible to obtain nanoparticles with sizes smaller than those obtained by emulsion polymerization to be used in specific applications. This technique allows high-reaction rates and molar masses due to the compartmentalization [1]. However, a limitation of micro-emulsion polymerization, in general, is the high amount of surfactant needed in formulations ($\approx 10\%$ of total mass [2]). To overcome this problem, some strategies have been developed: polymerizations in Winsor I-like systems (o/w micro-emulsion in equilibrium with an upper oil layer), the use of surfactants with high-monomer solubilization capacity (which increases the micro-emulsion region) and the polymerization in semicontinuous regimes [3].

A simpler variant of semicontinuous micro-emulsion polymerization is the semicontinuous heterophase polymerization (unseeded polymerization), in which the reaction starts from a surfactant solution with concentration higher than the critical micelle concentration (CMC) without monomer charged to the reactor. Thus, only empty micelles are present at the beginning of the reaction. To start polymerization, monomer is added continuously at a constant rate (*Ra*). Ledezma et al. [4] reported the semicontinuous heterophase polymerization of methyl methacrylate (MMA) using a mixture of SDS and Aerosol-OT (AOT) as surfactants and KPS as initiator varying the *Ra* between 0.068 and 0.9 g/min, finding that latexes with high polymer content, $D_p < 40$ nm and narrow PSD can be obtained by this process. Semicontinuous heterophase polymerization can be used to obtain polymeric nanoparticles with tuned morphology. Esquivel et al. [5] used this method to obtain mesoporous polystyrene nanoparticles of approximately 30 nm with narrow PSD.

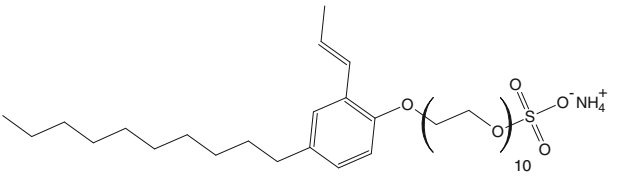
Surfactants play a crucial role in the production and applications of latexes. They strongly influence the nucleation of the latex particles, emulsification of monomer droplets, stabilization of polymer particles during polymerization, and the shelf-life stability of the products [6, 7]. Some negative effects of the presence of conventional surfactants in latex are foaming and migration to interfaces during film formation, giving as a result, water-sensitivity. These deficiencies can be largely reduced or eliminated by chemically incorporating the surfactant into the latex particles [8].

Since the early 1990s the application of reactive surfactants in heterophase polymerization has become a vast topic in its own right [9]. The basic idea is to design surfactants in such a way that they can participate in heterophase polymerizations either as co-monomers (surfmers) or initiators (inisurfs) or transfer agents (transurfs), and finally be completely covalently attached to the polymer. From the application point of view the idea is to use covalent binding to avoid the migration of surfactants in the final application and prevent, for instance, the formation of hydrophilic spots with higher water-uptake in hydrophobic coatings.

The polymerization properties of reactive surfactants have to be tuned carefully in order to avoid undesired effects with regard to stability and/or inhibition of the polymerization reaction. For example, Lai et al. [8] studied the emulsion polymerization of styrene using HITENOL BC20 as reactive surfactant above the CMC. They observed that particle nucleation was similar to that reported using the conventional surfactant SDS. Also, the molecular weight increased with the surfactant concentration as expected for conventional surfactants. The use of reactive surfactants also has been reported in emulsion copolymerization, Huang et al. [10] studied the emulsion copolymerization of methyl methacrylate with octyl acrylate using ammonium sulfate allyloxy nonylphenoxy poly(ethyleneoxy) (10) ether (DNS-86). They obtained latexes with better stability and films with less water absorption than those obtained with conventional surfactants. Also, the synthesis of surfmers with various polymerizable groups, their copolymerization behavior, and their applications has been reported. Guyot [11] has reviewed the use of polymerizable surfactants in polymerization reactions.

Electron beam lithography (EBL) is an important patterning method for nanosystems and devices, such as Coulomb blockade devices, molecular electronics, high-density magnetic storage, mold making for nanoimprint lithography, and high-precision mask making, among others [12]. Since, the introduction of EBL there has been considerable effort in the development of electron sensitive resists of both the positive and negative type. As EBL patterning resolution approaches the molecular region (less than 5 nm) with the availability of improved systems, the key issues now are the properties of the resist and developer combination and pattern transfer. Poly(methyl methacrylate) (PMMA) is the most widely known resist of the positive type still in use in many laboratories primarily because of its superior resolution [13]. During patterning by EBL, interactions of polymer with electrons can conduce to chain rupture, decreasing the molar mass (positive resists) or chain reticulation (negative resists). The electron beam has a wavelength so small that diffraction no longer defines the lithographic resolution. In electron beam lithography, the resolution is limited by electron optic aberrations and, more importantly, scattering of electrons in resist and substrate. These electron scattering effects, often referred to as the proximity effect [14], cause exposure of areas surrounding the area where the electron beam was incident. Any pattern written can suffer significant variation from the intended size because of proximity effect. Using the copolymer of MMA with the reactive surfactant *p*-polyoxyethylene-alkylphenyl ether ammonium sulfate; 10 Units of ethylene oxide (HBC10) or poly(MMA-*co*-HBC10) as positive resist in EBL, will increase the resolution of lines exposed to electrons during pattern due to the chemical structure of HBC10 (Scheme 1) which can act as protective from electron scattering. In addition, the films formed with this polymer will have less water-sensitivity, giving as a result an increased performance in EBL because the surfactant chemically bonded to polymer will not migrate to the film surface.

In this study, the effect of the MMA/HBC10 ratio on kinetics, colloidal characteristics of the latex and polymer molar masses during semicontinuous heterogeneous polymerization has been studied with the objective of developing the optimized conditions to obtain poly(MMA-*co*-HBC10) to be used in EBL.



Scheme 1 Chemical structure of HBC-10

Experimental

SDS was purchased from Hycel (Guadalajara, Mex.) (≥98%), HBC10 was obtained from Dai-Ichi Kogyo Seiyaku Co., Ltd. (Japan) (>98%); all the other reactants were purchased from Aldrich (Toluca, Mex.) (≥99%) and were used as received. Bi-distilled grade water and argon of ultrahigh purity from Infra™ were used. The recipes are given in Table 1. The polymerizations were carried out at 60 °C and 200 rpm in a four-necked 1 l glass—jacketed reactor equipped with mechanical stirring and reflux condenser. The SDS, water, and KPS were charged to the reactor; afterwards, the system was purged with argon for 1 h to remove oxygen. Then, the mixture was brought to reaction temperature and the MMA/HBC10 mixture was added to the reactor using a GasTight 100 ml syringe adapted to a calibrated addition pump (Kd-Scientific®) and using a constant monomer addition rate (*Ra*) of 0.8 g/min. After the semicontinuous addition period, the reactions were allowed to continue for 1 h. Conversion was followed gravimetrically: samples were withdrawn from the reacting system at given times and placed in vials (of known weight) immersed into an ice bath to stop the polymerization. Then, the samples were weighed and dried at 40 °C. Conversions were determined by gravimetry.

Particle size was determined by quasielastic light scattering (QLS) with a Nano S90 (Malvern) apparatus at 25 °C. Polymer samples were purified washing several times with hot water and dried at 40 °C for molar mass determinations. Average molar masses and molar mass distributions (MMD) of polymers (previously dissolved in THF) were determined in a gel permeation chromatograph apparatus (Agilent Technologies) with Ultrastyragel columns (1–40 kDa/103 Å, 40 kDa–4MDa/105 Å, and 400 kDa–40 MDa/106 Å) at 40 °C and a flow rate of 1 ml/min, coupled to a Waters 410 differential refraction index and ultraviolet refractometer. Purified polymer samples also were analyzed by Raman spectroscopy using a high resolution Raman spectrometer (Horiba Jobin–Yvon, LabRAM HR 800).

Table 1 Recipes used in the reactions

Reaction[a]	Water	KPS	SDS	MMA	HBC10
A	250	0.2	4	80	0
B	250	0.2	4	79	1
C	250	0.2	4	78	2
D	250	0.2	4	76	4
E	250	0.2	4	72	8

[a] All the amounts are in grams

Results

The initially clear micellar solution in the reactor turned bluish and translucent at the beginning of monomers addition indicating the start of polymerization. The copolymerization of HBC10 with MMA was proved by Raman spectroscopy. Figure 1 shows the Raman spectra of final polymers obtained in the different runs and the corresponding to HBC10 as monomer. The chemical structure of copolymer is shown in Scheme 2. The signals near 987 cm^{-1} (a) have been assigned to the O–CH_3 rock vibration interacting with the stretch vibrations of the C–O–C group of MMA units [15].

The band near 1,450 cm^{-1} (b) is ascribed to CH_2 symmetric bend vibration involving motion mostly parallel to the long axis of the molecules [16]. The signal around 1,732 cm^{-1} (c) corresponds to the C=O stretching mode. The shift observed at 600 cm^{-1} (d) is due to O–C=O in plane bending. The signal at 2,838 cm^{-1} (e) is due to symmetric stretching of CH_3; the signal at 2,950 cm^{-1} (f) corresponds to CH_3 symmetric stretching of O–CH_3. The strong signal at 1,600 cm^{-1} (g) in the spectrum of pure HBC10 is due to aromatic C=C stretching.

For Run E, in which the amount of HBC10 was the highest, a weak signal at 1,600 cm^{-1} can be appreciated. However, an enlargement of the spectra from Fig. 1 around this region is shown in Fig. 2. It can be seen that the signal of aromatic C=C stretching is absent for Run A (in which only MMA was used), that is, the reactive surfactant HBC10 has already been incorporated into the polymer obtained in runs B, C, D, and E.

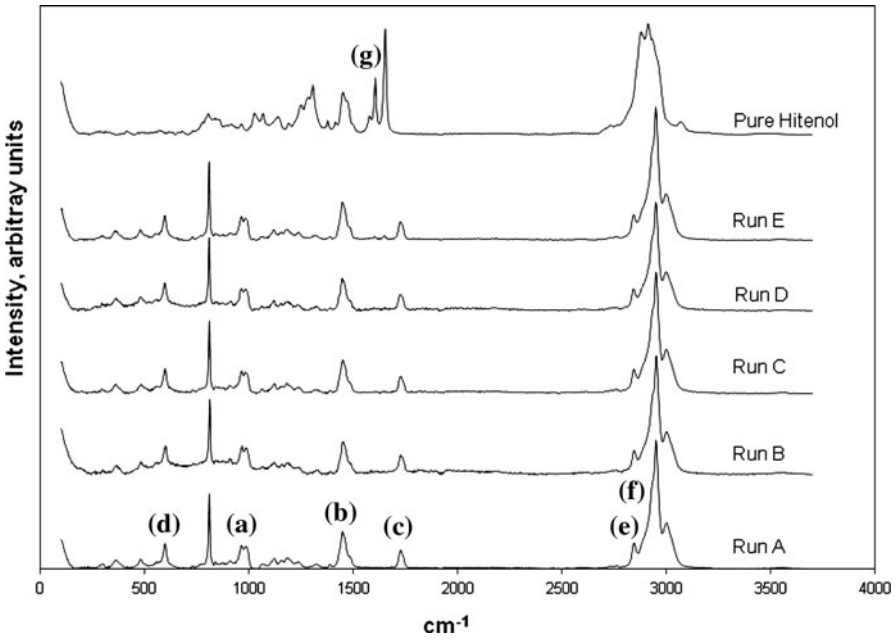


Fig. 1 Raman spectra of final polymers obtained in the different runs and the corresponding to HBC10 pure as a monomer

Scheme 2 Chemical structure of copolymer of MMA and HBC10

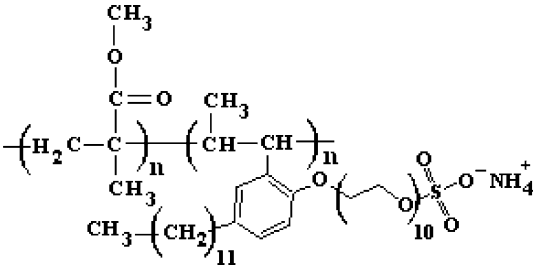
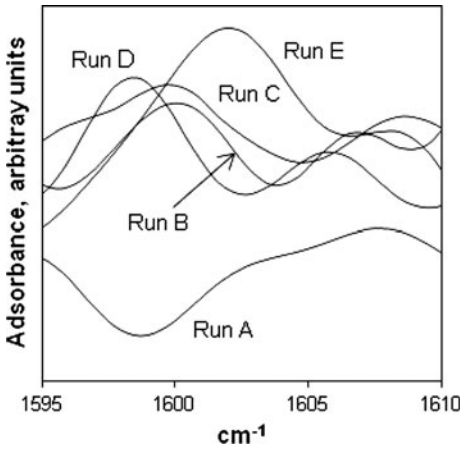


Fig. 2 Enlarged region of Raman spectra of final polymer obtained in the different runs



The kinetic of the different runs are shown in Fig. 3. It can be inferred that polymerization rate decreases when HBC10 content increases, which is contrary to what is typically expected for conventional surfactants, because by increasing the surfactant concentration more particles will be nucleated thus increasing polymerization rate.

However, it has been demonstrated for some reactive surfactants that reactions at the interface control much of the kinetics and the chain transfer reaction to the allyl double bond of reactive surfactants contributes to the reduction of reaction rate [17]. For example, El-Aasser and co-workers [18] studied the kinetics of the emulsion polymerization of vinyl acetate (VAc) in the presence of the reactive surfactant sodium dodecyl allyl sulfosuccinate (TREM LF-40). They showed that the rate of polymerization was slower than in the presence of the hydrogenated version (H-TREM LF-40) and decreased with increasing surfactant concentration despite the fact that the number of particles increased. This suggested that TREM LF-40 does not act only as a surfactant. Solution copolymerization of VAc with TREM LF-40 [19] indicated that the copolymerization rate was slower than the homopolymerization of VAc, this being one of the possible reasons for the "unconventional" behavior. Also, FTIR analysis of the aqueous phase showed the presence of PVAc in the serum of latexes prepared with the reactive surfactant while there was no PVAc detected with the non-polymerizable derivative, H-TREM LF-40, confirming the formation of water soluble copolymers [19].

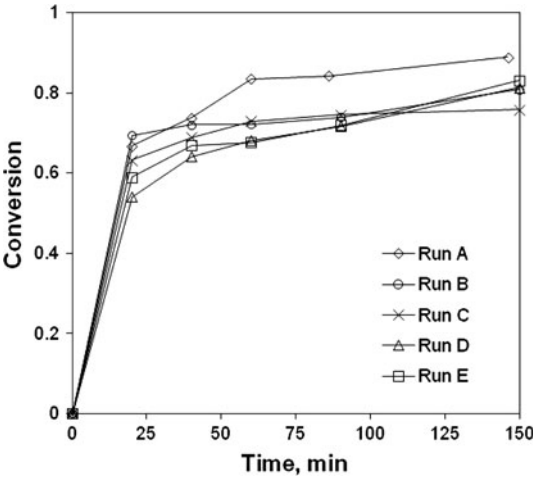


Fig. 3 Instantaneous conversions as a function of time, at different HBC10/MMA ratios in the feed at constant addition rate (*Ra*)

Table 2 shows the final characteristics of the latexes. The copolymer contents (C_p) were near to 20 wt% in all cases. The average particle diameter ranged from 26 to 40 nm, apparently increasing with the HBC10 content. The polydispersity index in sizes (PDI), which were calculated from QLS measurements, remain almost constant near 2.0. Figure 4 shows the corresponding particle-size distributions (PSD). It can be seen that when no HBC10 was used (run A) a bi-modal PSD was obtained. However, by increasing the HBC10 content in the recipe, the shoulder of small particle sizes disappears.

The mode of monomer addition affects the mechanism of particle formation, as well as their growth. For example, a process in which the monomer is added in the pre-emulsified form under monomer-starved conditions, the surfactant associated to the monomer fed can reside in the water or can diffuse to the growing particles to stabilize them. However, if the same process is carried out in flooded conditions, a small part of the surfactant can be adsorbed in the monomer droplets. When surfactant accumulates in the water phase, secondary nucleation can occur (new particles formation) by homogeneous or micellar nucleation. This secondary nucleation contributes to the broadening of the PSD. Although the main locus of HBC10 copolymerization can be considered at the particle/water interface, due to

Table 2 Final characteristics of latexes

Run	D_p (nm)	PDI (D_{pw}/D_{pn})	C_p (wt%)
A	26	2.02	20
B	25	1.96	18
C	26	2.17	17
D	31	2.28	19
E	40	1.83	20

PDI polydispersity in sizes from QLS measurements; D_{pw} and D_{pn} refer to weight and number average particle diameter, respectively; C_p copolymer content

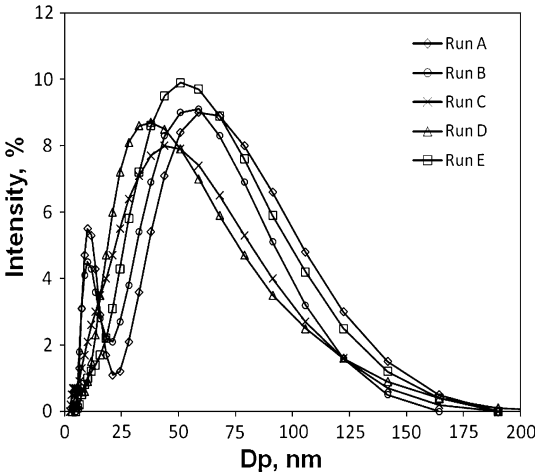


Fig. 4 Particle-size distributions (PSD) of final latexes obtained by QLS at different HB10/MMA ratios in the feed at constant addition rate (*Ra*)

the relatively high-water solubility of MMA (1.5 g/100 ml), homogeneous nucleation are present throughout polymerization, which explains the small particle sizes shoulder in Fig. 4. However, by increasing the HBC10 content, micellar nucleation becomes more important than homogeneous nucleation, thus suppressing the shoulder of small particle sizes.

Figure 5 shows the MMD of the copolymers at the end of polymerization. The MMD are relatively narrow in all cases with polydispersity indexes ($M_w/M_n \approx 1.5$ in Fig. 6) almost independent of HBC10 content, except for the higher HBC10 content ($M_w/M_n \approx 2.2$). It can be observed that runs A and E were almost monomodal while the others were bi-modal. The weight average molar masses at the end of polymerization for all runs are shown in Fig. 6. It can be seen that the molecular weight decreased with increasing HBC10 concentration. This is contrary to what is normally expected for a conventional surfactant. For example, Aguilar et al. [20] used SDS as surfactant to polymerize MMA by semicontinuous heterophase polymerization under monomer-starved condition at constant monomer addition rate. They found molar masses much lower than those expected from termination by chain transfer to monomer, which is the typical termination mechanism in 0–1 emulsion and micro-emulsion polymerization of this monomer. They also observed that molar masses increased slightly with the SDS concentration.

Similar results were observed when the mixture of SDS/AOT (3:1 wt/wt) was used as surfactants [4]. However, Lai et al. [8] using the reactive surfactant polyoxyethylene alkylphenyl ether ammonium sulfate; 20 Units of ethylene oxide (HBC20) in the batch emulsion polymerization of styrene, observed that the molecular weight increased with increasing surfactant concentration. This behavior was explained by the decreased radical entry rate per particle as more particles are produced with increasing surfactant.

These results imply that not only the type of the reactive surfactant affects the characteristics of resulting polymer, but also the nature of monomers and the mode

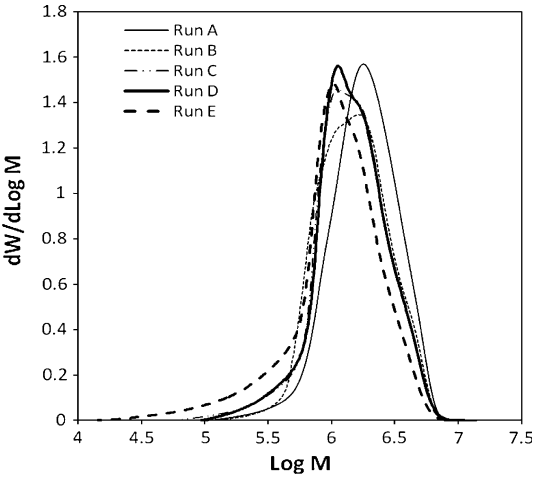


Fig. 5 Molar mass distributions (MMD) of the copolymers at the end of reaction

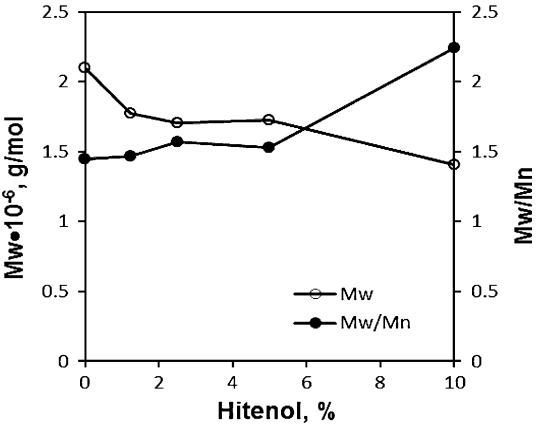


Fig. 6 Weight average molar masses (*empty symbols*) and M_w/M_n of final polymers at the end of polymerizations

of polymerization (batch, semicontinuous, or heterophase polymerization). However, more work is needed to explain the effect observed in this research.

Conclusions

Latexes with nanoparticles of poly(MMA-*co*-HBC10) were successfully obtained by semicontinuous heterophase polymerization. Very high-molar masses were obtained by this technique ($1.4 \times 10^6 < M_w < 2.1 \times 10^6$ g/mol). The D_p were in the range of 25–40 nm with wide PSD, which compare with those obtained in micro-emulsion polymerization. It was also observed that polymerization rate decreases as HBC10 concentration increases, which was ascribed to chain transfer events to the allyl double bond of HBC10.

The polymers obtained here will be used in film formation to study their performance in electron beam lithography.

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References

1. Ovando-Medina VM, Peralta RD, Mendizábal E, Martínez-Gutiérrez H, Corona-Rivera MA (2011) Microemulsion copolymerization of vinyl acetate and butyl acrylate using a mixture of anionic and non-ionic surfactants. Polym Bull 66:133–146
2. Pavel Florentina M (2004) Microemulsion polymerization. J Disp Sci Tech 25:1–16
3. Ovando-Medina VM, Peralta RD, Mendizábal E (2009) Semicontinuous microemulsion copolymerization of vinyl acetate and butyl acrylate: high solid content and effect of monomer addition rate. Colloid Polym Sci 287:561
4. Ledezma R, Treviño ME, Elizalde LE, Pérez-Carrillo LA, Mendizábal E, Puig JE, López RG (2007) Semicontinuous heterophase polymerization under monomer starved conditions to prepare nanoparticles with narrow size distribution. J Polym Sci A 45:1463
5. Esquivel O, Treviño ME, Saade H, Puig JE, Mendizábal E, López RG (2011) Mesoporous polystyrene nanoparticles synthesized by semicontinuous heterophase polymerization. Polym Bull 67:217–226
6. Asua JM (2004) Emulsion polymerization: from fundamental mechanisms to process developments. J Polym Sci A 42:1025–1041
7. Lai Z, Sudol ED, Dimonie VL, El-Aasser MS (2005) Determination of the extent of incorporation of a reactive surfactant in polystyrene latex particles via GPC. J Polym Sci A 43:2675–2678
8. Lai Z, Sudol ED, Dimonie VL, El-Aasser MS (2008) Kinetics of emulsion polymerization of styrene using the reactive surfactant HITENOL BC20. J App Polym Sci 109:2275–2282
9. Guyot A, Tauer K (2001) Polymerizable and polymeric surfactants. In: Texter J (ed) Reactions and synthesis in surfactant systems. Marcel Dekker, New York, pp 547–575
10. Huang H, Lu D, Sheng L, Guan R (2008) Reactive surfactant in the emulsion copolymerization of methyl methacrylate and octyl acrylate. J Macromol Sci A 45:242–247
11. Guyot A (2002) Recent progress in reactive surfactants in emulsion polymerization. Macromol Symp 179:105–132
12. Hu W, Sarveswaran K, Lieberman M, Bernstein GH (2004) Sub-10 nm electron beam lithography using cold development of poly(methylmethacrylate). J Vac Sci Technol, B 22:1711–1716
13. Hailer I, Feder R, Hatzakis M, Spiller E (1979) Copolymers of methyl methacrylate and methacrylic acid and their metal salts as radiation sensitive resists. J Electrochem Soc 126:154–161
14. Fischer PB, Chou SY (1993) 10 nm electron beam lithography and sub-50 nm overlay using a modified scanning electron microscope. Appl Phys Lett 62:2989–2991
15. Allara DL, Baca A, Pryde CA (1978) Distortions of band shapes in external reflection infrared spectra of thin polymer films on metal substrates. Macromolecules 11:1215–1220
16. Zhang JM, Shen DY (2002) Near-infrared SERS study of the adsorption of a PMMA dip-coated onto silver mirror substrate. Chinese Chem Lett 13:563–566
17. Dimonie VL, Sudol ED, El-Aasser MS (2008) Role of surfactants in emulsion polymerization polymers by design. Rev Chim (Bucureti) 59:1218–1221
18. Urquiola MB, Dimonie VL, Sudol ED, El-Aasser MS (1992) Emulsion polymerization of vinyl acetate using a polymerizable surfactant. I. Kinetic studies. J Polym Sci A 30:2619–2629
19. Urquiola MB, Dimonie VL, Sudol ED, El-Aasser MS (1992) Emulsion polymerization of vinyl acetate using a polymerizable surfactant. II. Polymerization mechanism. J Polym Sci A 30:2631–2644
20. Aguilar J, Rabelero M, Nuño-Donlucas SM, Mendizábal E, Martínez-Richa A, López RG, Arellano M, Puig JE (2011) Narrow size-distribution poly(methyl methacrylate) nanoparticles made by semicontinuous heterophase polymerization. J Appl Polym Sci 119:1827–1834