Miniemulsion copolymerization of styrene and gama-methacryloxy propyl trimethoxysilane: kinetics and mechanism

5 AUTHORS, INCLUDING:

Elodie Bourgeat-Lami
CPE Lyon
171 PUBLICATIONS **5,385** CITATIONS

Nida Othman
Claude Bernard University Lyon 1
73 PUBLICATIONS **557** CITATIONS

Gilles Fevotte
Claude Bernard University Lyon 1
104 PUBLICATIONS **1,437** CITATIONS

Miniemulsion Copolymerization of Styrene and γ-Methacryloxypropyltrimethoxysilane: Kinetics and Mechanism

Z. H. Cao,[†,‡,§] G. R. Shan,[‡] G. Fevotte,[∥] N. Sheibat-Othman,[§] and E. Bourgeat-Lami*,[†]

Chimie, Catalyse, Polymères, Procédés, C2P2/LCPP-UMR 5265 CNRS/CPE/UCBL, Bât. 308F, 43 Bd du 11 Novembre 1918-69616 Villeurbanne, France; State Key Laboratory of Chemical Engineering, Department of Chemical Engineering, Zhejiang University, Hangzhou, 310027, Zhejiang, China; LAGEP, CNRS/CPE/UCBL, Bât 308G, 43 Bd 11 Novembre 1918, 69622 Villeurbanne, France; and Ecole Nationale Supérieure des Mines de Saint Etienne, 138 cours Fauriel, 42000 Saint Etienne, France

ABSTRACT: The kinetics of the miniemulsion copolymerization of styrene (St) and γ-methacryloxypropyltrimethoxysilane (MPS) was investigated by studying the effects of the MPS/St weight ratio, the nature and amount of initiator, the suspension pH, and the surfactant concentration on the overall and individual monomer conversions. It was found that the introduction of MPS accelerates the free radical copolymerization reaction due to its higher propagation rate constant and higher water solubility compared to styrene. On the other hand, MPS decreases the copolymerization rate mainly during the second half of the reaction. This is presumed to be due to the formation of alkoxysilane-rich copolymers on the particles surface providing a barrier to radical's entry. The rate of hydrolysis is pH-dependent, and for a given pH, the influence of the surfactant concentration on the hydrolysis rate suggests that the interface between the latex particles and water is the main locus of hydrolysis. ^{29}Si solid-state NMR analysis showed that the hydrolyzed alkoxysilyl moieties did not condense under neutral conditions even for high MPS/St feed ratios. Premature cross-linking could be also minimized under basic conditions but could not be avoided in acidic media.

Introduction

In recent years, latexes incorporating reactive alkoxysilyl moieties capable of undergoing cross-linking during film formation have drawn increasing interest.[1–19] Indeed, the presence of postapplication cross-linking mechanisms in water-borne coatings offers major advantages. It provides films with improved quality and properties in terms of solvent resistance, water repellency, mechanical integrity, and adhesion to inorganic substrates.[1–3,7,11–14] However, previous works on the emulsion copolymerization of vinyl alkoxysilanes and organic monomers have shown that avoiding premature hydrolysis and cross-linking of the silane moiety is challenging due to the high reactivity of the alkoxysilyl groups in the presence of water.[1–9,13,14] Bourne et al.[3] have shown that it is possible to minimize hydrolysis by using sterically hindered alkoxysilanes of greater hydrolytic stability. We[5,6,8,9] and others[4,13] have applied an alternative strategy consisting in the semicontinuous addition of the organoalkoxysilane monomer under pH-controlled conditions. Another approach that looks promising is to carry out a miniemulsion polymerization reaction instead of conventional emulsion polymerization.[15–19] Indeed, this process has recently received great attention due to the fact that in miniemulsion, nucleation occurs primarily within the monomer droplets which are stabilized against coalescence and diffusional degradation.[20–25] Thus, in properly formulated miniemulsions, alkoxysilane monomers are protected from the aqueous phase by the waterproof oil droplets, and hydrolysis and condensation reactions can be better controlled. The first results on the incorporation of alkoxysilanes into latex particles through miniemulsion polymerization were reported by Marcu et al.,[15–17] who copolymerized vinyltriethoxysilane (VTES) and butyl acrylate (BA). However, because of the large difference in VTES and BA reactivity ratios, VTES turned out to be mainly incorporated into the copolymer latex particles via alkoxysilane hydrolysis and subsequent cross-linking rather than by vinyl copolymerization. Using a similar approach, Zhang et al.[19] synthesized Si–OH functionalized latexes via miniemulsion copolymerization of styrene (St) and methacryloxypropyltrimethoxysilane (MPS). The effects of the suspension pH, the MPS/St ratio, and the nature of the initiator on both the copolymer microstructure and the latex surface properties were studied in depth. However, no information on the polymerization kinetics was provided although this is essential to understand the phenomena and reactions occurring in such a complex system. As the free radical copolymerization, the hydrolysis, and the condensation reactions are taking place simultaneously, they should be considered together for a comprehensive interpretation of the overall kinetic process. Recently, we have studied the copolymerization kinetics of styrene and MPS in seeded emulsion polymerization, and for the first time, a model involving both the free radical copolymerization and the hydrolysis and condensation reaction kinetics was presented.[9]

Now, the present work focuses on the kinetic study of the copolymerization of styrene and MPS in miniemulsion. The free radical copolymerization rate of MPS and St and the rate of hydrolysis of MPS were investigated as a function of the MPS/St ratio, the suspension pH, the surfactant concentration, and the nature and amount of initiator.[29] Si solid-state NMR was used to evaluate the condensation reaction while the droplet and particle sizes were determined by dynamic light scattering, which gave insights into hybrid latex particles' formation and stability.

Experimental Section

Materials. γ-Methacryloxypropyltrimethoxysilane (Aldrich) was used as received. Styrene (Aldrich) was purified by vacuum distillation. Typically, styrene, some copper powder, and some

* To whom correspondence should be addressed. E-mail: bourgeat@lcpp.cpe.fr.
† C2P2/LCPP-UMR 5265 CNRS/CPE/UCBL.
‡ Zhejiang University.
§ LAGEP, CNRS/CPE/UCBL.
∥ Ecole Nationale Supérieure des Mines de Saint Etienne.

Table 1. Typical Recipe for Miniemulsion Copolymerization of St and MPS

| water | SDS mM[a] | buffer (wt %)[a] | | KPS (mM)[a] | styrene | MPS | HD (wt %)[b] |
		neutral pH	basic pH				
85 parts	5.5−22.2	0.2	0.38	4.4−8.8	7.5−15 parts	0−7.5 parts	4

[a] Based on the amount of water. [b] Based on the amount of monomer.

Table 2. Summary of Experimental Conditions Used for Miniemulsion Copolymerization of St and MPS

runs	1	2	3	4	5	6	7	8	9	10	11	12	13
MPS/St	0:5	1:4	1:2	1:1	0:5	1:4	1:2	1:1	1:4	1:4	1:4	1:4	1:4
KPS (mM)	4.4	4.4	4.4	4.4					4.4	4.4	4.4	4.4	8.8
AIBN (mM)					4.4	4.4	4.4	4.4					
pH	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0	9.2	3.9	7.0	7.0	7.0
SDS (mM)	11.1	11.1	11.1	11.1	11.1	11.1	11.1	11.1	11.1	11.1	5.5	22.2	5.5

zeolite were introduced in a three-necked flask equipped with a thermometer, a Vigreux distillation column, and a capillary tube. The pressure was maintained at 30 mm of mercury by a pump attached to the outlet of the reflux condenser. The distillate was collected and kept in the refrigerator until use. Potassium persulfate (KPS, Acros Organics) and 2,2′-azobis(isobutyronitrile) (AIBN, Acros Oganics) were used as initiators. Hexadecane (HD, 99%, Acros Organics), sodium dodecyl sufate (SDS, 99%, Acros Organics), ammonium dihydrogen phosphate (99%, Acros Organics), disodium hydrogen phosphate (99%, Prolabo), hydrochloric acid (0.1 N standard solution, Acros Organics), and sodium tetraborate decahydrate (99%, Aldrich) were used as received. The water was deionized on mixed bed resins before use.

Methods. The miniemulsions were prepared by first dissolving the costabilizer (HD) in the monomer mixture. This oil phase was then added to the aqueous solution containing the surfactant and the pH buffer and homogenized to form nanodroplets through sonication (Branson Ultrasonics Corp., model 75042) for 20 min using a pulsed sequence (9 s sonication followed by 6 s break) with an 80% duty cycle under magnetic agitation in an ice bath. The miniemulsion was next introduced into the reactor and purged with nitrogen. The temperature was raised to 70 °C, and the KPS aqueous solution was fed into the reactor to start the polymerization, which lasted for 3 h. During the polymerization process, samples were withdrawn at specific time intervals and divided into three parts for gravimetric, gas chromatography (GC), and particle size analyses. For polymerizations initiated by AIBN, the latter was dissolved in the oil phase prior to the homogenization step required to generate the miniemulsion. A typical recipe for the miniemulsion copolymerization of St and MPS is given in Table 1, while Table 2 summarizes the experimental conditions for each run.

The individual monomer conversions and the methanol concentration were measured by GC. The samples withdrawn during the polymerization were cooled down rapidly in an ice bath and further dissolved in an appropriate amount of THF acting as the internal standard substance for GC calibration. The overall conversion was measured by gravimetry.

Both droplet and particle sizes were measured by dynamic light scattering (DLS, Zetasizer 1000 HSA, Malvern) at 25 °C and a fixed scattering angle of 90°. An estimate of the width of the size distribution, hereafter defined to as the polydispersity index (PDI), was determined from the autocorrelation function using a second-order method of cumulant analysis according to the international ISO13321 standard of dynamic light scattering.[26] The miniemulsion droplets or the latex particles were diluted in a 0.2 wt % SDS aqueous solution before analysis. Five measurements were performed and averaged for each sample. The surface tension of the miniemulsion was characterized by a Krüss K12 processor tensiometer at 25 °C. The final data was the average of 40 measurements, and for each sample, the analysis was repeated four times.

The hybrid copolymers were characterized by infrared and solid-state NMR spectroscopy. The latex was centrifuged and redispersed in deionized water three times in order to remove water-soluble substances. The resulting polymer was then dried at 50 °C overnight before analysis. Infrared spectra were recorded using a Nicolet FTIR 560 spectrometer from powder-pressed KBr pellets. ^{29}Si solid-state NMR spectroscopy was performed on a Bruker DSX-300 spectrometer operating at 59.6 MHz, using cross-polarization of protons. The contact time was 5 ms, the recycle delay was 1 s, which is sufficient for a full relaxation of protons, and the spinning rate was 5 kHz.

Results and Discussion

Effect of the MPS/St Ratio. In miniemulsion polymerization reactions initiated by water-soluble initiators, the polymerization rate depends on the rate of radical entry which, in turn, depends on the propagation rate constants, the water solubility of the monomers, the entry rate coefficient "k_e", and the critical length of entry radicals "z". A rapid estimation of z according to Morisson et al.,[27] for non-hydrolyzed MPS, shows that its critical length of entry radicals is almost the same as styrene (around 3). In addition, k_e (which depends on the diffusion coefficient of the oligoradicals in the water phase) is also the same for both monomers. Therefore, because of the higher water solubility of MPS (14 mM) compared to St (3.65 mM),[9] and given the propagation rate constants and reactivity ratios of MPS (monomer 1) and styrene (monomer 2)—$k_{p11} = 1.44 \times 10^6$ cm³ mol⁻¹ s⁻¹, $k_{p22} = 5.7 \times 10^5$ cm³ mol⁻¹ s⁻¹, $r_1 = 0.9$, and $r_2 = 0.45$[28,29]—the reaction rate should be faster for the copolymerization system than for the homopolymerization reaction.

Nevertheless, the results displayed in Figure 1a show that there is no significant influence of the MPS concentration on the overall reaction rate up to around 45% conversion. Above 45% conversion, in contrast, both the overall reaction rate and the individual monomer conversions depend on the MPS/St ratio (Figure 1a−c). However, the observed evolutions are in disagreement with the above predictions as the reaction rate decreases with increasing the MPS concentration. Indeed, the higher is the amount of MPS, the lower are the styrene and MPS conversions. Therefore, these results suggest that MPS plays an unsuspected role influencing the kinetics and mechanism of radical entry and exit. Several reports in the literature pointed out a decrease in the rate of radical entry due to the formation of an electrosteric layer of polymeric surfactants in conventional emulsion polymerization.[30−33] By analogy with these previous reports, the kinetics profiles shown in Figure 1 can be reasonably ascribed to the formation of a hairy layer around the particles, through which the rate of diffusion of oligomeric z-mer radicals would be significantly reduced. Indeed, given the MPS and styrene reactivity ratios, alkoxysilane-rich oligomers are produced in the earlier stages of polymerization. These oligomers may enter the monomer droplets and further propagate with styrene or may undergo hydrolysis reactions. The amount of hydrolyzed alkoxysilyl groups, estimated by GC titration of released methanol, increases as the MPS concentration increases (Figure 1d). Because the resulting copolymers are highly hydrophilic, they can expand in the water phase and undergo further hydrolysis reactions. The resulting silanols next dissociate into silanolate ions
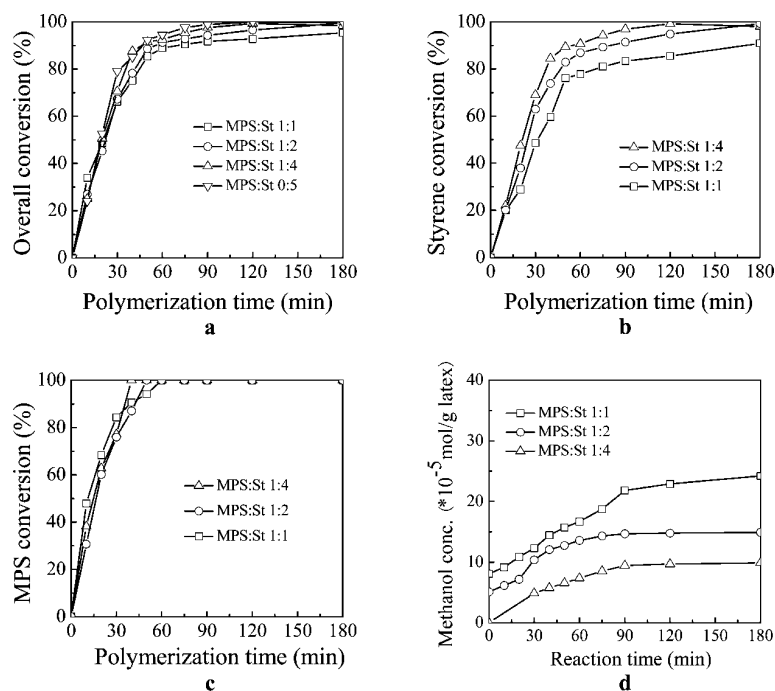
Figure 1. Influence of the MPS/St ratio on the kinetics of the miniemulsion copolymerization of MPS and St initiated by KPS under neutral conditions: (a) overall conversion, (b) St conversion, (c) MPS conversion, and (d) methanol concentration.

depending on pH, giving rise to the formation of an electrosteric layer on the particles surface, which may affect the rate of radical exchange between the aqueous phase and the particles (i.e., adsorption and desorption). The fact that we noticed only a minor influence of MPS on the polymerization rate at low conversions is not in contradiction with the present assumption. Indeed, on the one hand, the reaction rate should increase with increasing the MPS concentration as mentioned previously, but on the other hand, it should decrease due to a decrease of the rate of entry. The hairy layer can also potentially induce a decrease in the rate of exit, but as exit mainly involves monomeric radicals, the barrier effect is presumed to be less important for exiting than for entering oligomeric radicals. A recent work from Gilbert et al.[33] aiming to rationalize the mechanism and kinetics of electrosterically stabilized emulsion polymerization systems involving copolymers of acrylic acid and styrene showed that the electrosteric effect on adsorption is minimal unless the steric barrier is extremely crowded. The authors thus proposed a mechanism postulating that the poly-(acrylic acid) chains on the particle surface can undergo rapid chain transfer, resulting in a radical which is slow to propagate but quick to terminate, thus affecting the overall kinetics. To confirm that the kinetics profiles observed in the present work are due to diffusion limitation and not to chain transfer reactions in the hairy layer, we performed a simple experiment involving styrene, MPS, and AIBN in toluene. The results (details of which are given in the Supporting Information) did not reveal any chain transfer to the alkoxysilane monomer or to the MPS oligomers which supports the assumption that the decrease in the overall polymerization rate is due to a restricted diffusion of z-mer radicals through the hybrid polymeric layer on the particle surface and not to radicals loss by chain transfer. Although the "restricted" diffusion assumption is in agreement with the experimental trends seen in this work, extensive mechanistic studies need to be done to have a more complete understanding of the physicochemical parameters influencing entry and exit rate coefficients in the present system. However, such a mechanistic study is beyond the focus of the current article.

Another important parameter that can have a significant influence on the polymerization kinetics is the droplets and/or particles size. Table 3 summarizes the effect of the MPS/St ratio on the size of the miniemulsion droplets and of the resulting latex particles.

It can be seen that the droplets size varies from 71 to 86 nm and decreases with increasing MPS/St ratio. Although the effect is not very pronounced, it is nevertheless real and can be reasonably attributed to the formation of silanol functionalities consequently to MPS hydrolysis. Indeed, as shown in Figure 1d, hydrolysis starts as soon as the miniemulsion droplets are created by sonication. The higher the MPS/St ratio, the more important is the amount of silanols and, consequently, the smaller is the droplets size. An indirect proof of the presence of silanol groups on the surface of the droplets was provided by measuring the surface tension of the miniemulsions as a function of the MPS/St ratio. Figure 2 shows that the surface tension decreases with increasing MPS/St ratio, which can be interpreted by an increase of the SDS concentration in the water phase consequently to the presence of hydrolyzed alkoxysilane moieties on the droplets/water interface that may promote surfactant desorption. While polymerization of the styrene miniemulsion formed particles of almost the same size as the monomer droplets, suggesting almost 100% droplet nucleation, the latex particles size was systematically larger than the original droplets size when MPS was introduced in the system. The ratio of the number of particles to the number of droplets (N_p/N_d) was thus lower than one whatever the MPS content, indicating that only a fraction of the original droplets have been nucleated. One could also assume that the decrease in the number of particles is due to some instability of the growing latex particles in the presence of the alkoxysilane monomer. Such instability has been discussed in our previous works on emulsion polymerization and was presumed to be due to the formation of water-soluble oligomers carrying silanol groups capable to promote particle–particle interactions.[8,9] This last assumption is supported by the fact that the particle size increases as the MPS content increases.

Table 3. Droplets Size, Particles Size, N_p/N_d Ratio, and Degree of MPS Hydrolysis for Miniemulsion Copolymerization of St and MPS Performed under the Experimental Conditions of Table 2

runs	reaction parameters		D_d (nm)	PDI[a]	D_p (nm)	N_d ($\times 10^{16}$)	N_p ($\times 10^{16}$)	N_p/N_d	MPS hydrolysis (%)
1	MPS/St (KPS)	0:5	85.4	0.16	85.1	5.3	4.7	0.88	
2		1:4	76.1	0.24	89.5	7.3	4.0	0.55	27.5
3		1:2	70.3	0.39	91.3	9.1	3.8	0.42	24.8
4		1:1	71.0	0.40	97.2	8.7	3.2	0.36	26.9
5	MPS/St (AIBN)	0:5	81.5	0.19	84.0	6.1	4.9	0.80	
6		1:4	79.8	0.24	78.1	6.3	6.1	0.97	33.8
7		1:2	72.0	0.37	75.3	8.5	6.8	0.80	30.1
8		1:1	73.0	0.39	79.3	7.7	5.8	0.76	32.3
9	pH	9.2	55.4	0.24	85.9	15.8	4.6	0.29	85.0
2		7.0	76.1	0.24	89.5	7.3	4.0	0.55	27.5
10		3.9	47.8	0.14	72.8	24.5	7.5	0.31	92.4
11	[SDS] (mM)	5.5	97.4	0.25	114.8	3.5	1.9	0.55	19.4
2		11.1	76.1	0.24	89.5	7.3	4.0	0.55	27.5
12		22.2	62.6	0.31	74.5	13.2	7.0	0.53	50.9
2	[KPS] (mM)	4.4	76.1	0.24	89.5	7.3	4.0	0.55	27.5
13		8.8	76.8	0.25	87.2	7.1	4.4	0.61	31.1

[a] Polydispersity index.
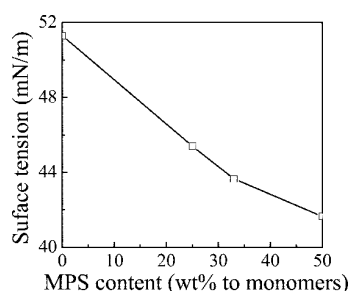
Figure 2. Surface tension of the miniemulsions as a function of the MPS content (in wt % to monomers).

In an attempt to better control the latex stability and confirm the effect of radical entry on kinetics, we have replaced KPS by an oil-soluble initiator: AIBN. Although AIBN is known to distribute between the aqueous and oil phases, Asua et al. have shown that the main locus for radical formation is the oil phase.[34] AIBN radicals created in the monomer droplets may undergo termination (if desorption is not fast enough) or exit. If the termination in the water phase is negligible, the desorbed radical will re-enter the droplets. If termination in water is significant, the desorbed radicals will be lost and, hence, the polymerization rate will decrease. The overall kinetics therefore heavily depend on the radical desorption/termination rate ratio. Asua et al. showed that the radicals produced in the aqueous phase are not efficient in initiating the polymerization as they mainly undergo termination and that, consequently, the main locus of radical formation is the oil phase. The conversion−time curves for the hybrid miniemulsions initiated by AIBN are shown in Figure 3.

It is first noticeable that the overall reaction rate decreased compared to miniemulsions initiated by KPS while the final conversion was again limited. As stated above, this is thought to be due to the tendency of oil-soluble initiators to recombine after initiation. It can also be seen that the copolymerization rate increases as the MPS/St ratio increases until the conversion reaches about 80%. Once more, this can be attributed to the relatively higher MPS propagation rate constant compared to styrene. In contrast to the KPS system, the St polymerization rate is only slightly influenced by the MPS/St ratio. This is again to be related to the initiation locus. As the radicals are mainly produced in the monomer droplets, entry is no longer rate-determining, and therefore, there is no more effect of the incorporation of MPS on the styrene polymerization rate although Figure 3d shows that MPS hydrolysis takes place at almost the same rate as when KPS is used as initiator. The fact

that the styrene polymerization rate is no longer influenced by the presence of MPS when AIBN is used as initiator supports the previous assumption according which radicals desorption is not kinetically significant in the present system.

To gain insights into the effects of the nature of the initiator on condensation, the hybrid copolymers were characterized by ^{29}Si solid-state NMR analysis (Figure 4). According to the conventional T^n nomenclature where n designates the number of Si−O−Si bonds, the sole signal at −43 ppm, corresponding to T^0 (($CH_3O)_3SiR$) species, indicates that no condensation occurred at pH 7 when KPS was used as initiator even for a high MPS/St feed ratio. In contrast, weak resonances at −48, −58, and −68 ppm corresponding to T^1 (($CH_3O)_2Si(OSi)R$), T^2 (($CH_3O)Si(OSi)_2R$), and T^3 species ($Si(OSi)_3R$) appeared when the miniemulsion polymerization was initiated by AIBN under otherwise the same conditions. This was unexpected and can be reasonably attributed to the relatively longer polymerization time required in this case. Most importantly here, Table 3 shows that N_p/N_d is close to one regardless of the MPS/St ratio. This does not only mean that the droplets have been efficiently converted into particles, but it also indicates that the droplets or the resulting particles remained stable and did not undergo coalescence. This is probably because fewer radicals are produced in the water phase when AIBN is used as initiator. Consequently, a minor proportion of oligomers responsible for particles aggregation are produced in comparison to KPS despite similar alkoxysilane hydrolysis rates.

Effect of pH. The mechanism by which alkoxysilanes give rise to the formation of Si−O−Si cross-links has been widely described in the literature.[35,36] The overall process involves a two-step hydrolysis−condensation reaction sequence, and both reaction rates are pH-dependent. The hydrolysis is faster under acidic conditions while condensation is promoted in basic media. Despite the great number of studies in this area, comparatively little research has been carried out on the influence of pH on alkoxysilane/vinyl monomers copolymerization kinetics.[9] However, it is obvious that the latex surface properties and the latex particles size will be influenced by MPS hydrolysis and condensation. The overall kinetic process is therefore also expected to be strongly dependent on the suspension pH. Figure 5 shows the conversion−time curves for polymerizations performed under neutral, basic, and acidic conditions.

It can be seen that the polymerization performed at pH 3.9 is very fast during the first stage of the reaction. This is probably due to the very small droplet size obtained under these conditions as shown in Table 3. As displayed in Figure 5d, the rate of hydrolysis is also very fast, resulting in almost instantaneous MPS consumption (Figure 5c). As MPS conver-
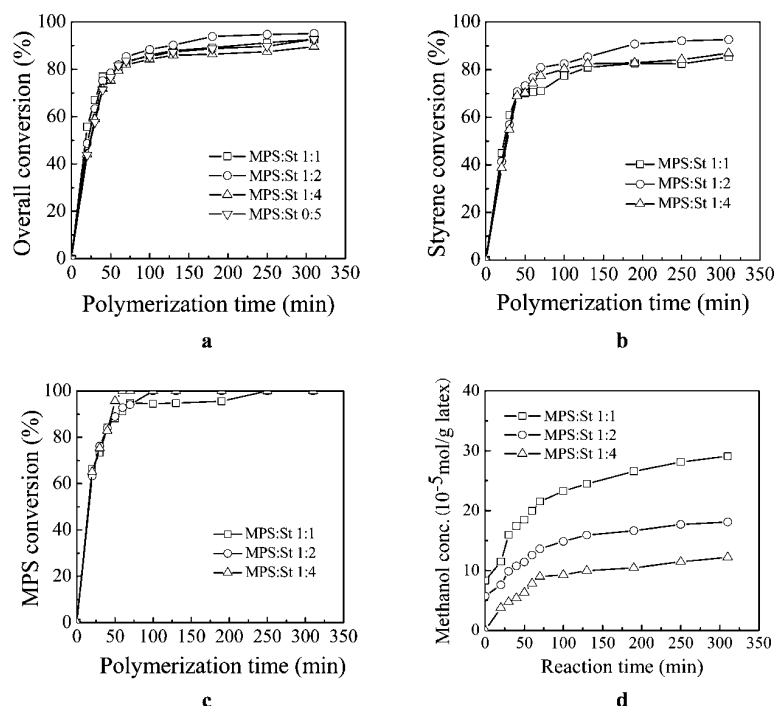
Figure 3. Influence of the MPS/St ratio on the kinetics of the miniemulsion copolymerization of MPS and St initiated by AIBN under neutral conditions: (a) overall conversion, (b) St conversion, (c) MPS conversion, and (d) methanol concentration.
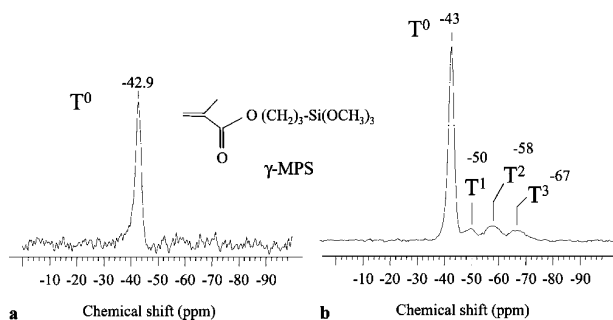

Figure 4. ^{29}Si solid-state NMR spectra of latexes obtained by miniemulsion copolymerization of MPS and St under neutral conditions using KPS (a) and AIBN (b) as initiators. MPS:St = 1:1.

sion is complete at time zero before starting polymerization, it can be concluded that MPS has been consumed by self-condensation of the trimethoxysilyl groups rather than by radical polymerization. When KPS is introduced in the reactor, the cross-linked siloxane oligomers can undergo further reaction with styrene (via the vinyl unsaturation) as attested by FTIR analysis and enter the polymer particles. As the rate of styrene polymerization is not affected by a diminution of the suspension pH, it can be concluded that the cross-linked siloxane oligomers formed in acidic conditions have only a minor influence on the adsorption rate of radicals. This is probably related to the nature of these oligomers which carry only a minor amount of negative charges at low pH values. It is worthwhile to mention that the final conversion is nevertheless lower than under neutral conditions.

As expected, the MPS hydrolysis rate was slower at pH 9.2 than at pH 3.9. Consequently, 40% of MPS was remaining in the reactor just before starting polymerization, indicating that MPS has only partly condensed in these conditions (Figure 5c). In addition, the overall polymerization rate was observed to only slightly increase compared with experiments performed at pH 7.0, despite important differences in droplet size. It can be

reasonably assumed that increasing the pH from 7 to 9.2 promoted the formation of an electrosteric polysiloxane barrier which decreased the rate of radical entry and resulted consequently in a decrease in styrene conversion.

As shown in Table 3, N_p/N_d decreased from 0.5 to around 0.25 when increasing or decreasing the suspension pH. This might be again related to the nature of the polymer chains formed during the earlier stages of polymerization in both acidic and basic conditions. Because of the fast silane hydrolysis, the growing radicals contain a high proportion of SiOH groups that may promote hydrogen bonds between particles, leading to an increase in particles size and thus to a decrease in N_p/N_d.

Figure 6 shows the FTIR spectra of the copolymers synthesized under acidic, neutral, and basic conditions. All the spectra show characteristic vibrations of polystyrene at 1600, 1492, 906, 756, and 697 cm^{-1} as well as absorption bands corresponding to MPS ($\nu_{C=O}$ at 1724 cm^{-1}) and support the formation of the hybrid copolymer. The spectra of Figures 6b and 6c, corresponding to neutral and basic conditions, respectively, show additional bands at 822 and 1087 cm^{-1} attributed to symmetric and asymmetric Si–O–C bonds of non-hydrolyzed MPS. This result is in agreement with GC analysis and supports the conclusion of partial hydrolysis. Under acidic conditions, in contrast, the Si–O–C signal at 822 cm^{-1} can no longer be detected while the signal attributed to the asymmetric Si–O–C bond is shifted to a higher wavenumber (Figure 6a), which again supports the GC analysis data.

Figure 7 shows the ^{29}Si NMR spectra of hybrid latexes synthesized at pH 3.9 and pH 9.2. There are noticeable differences between the two samples. While under acidic conditions most of the hydrolyzed species condensed to form T^1, T^2, and T^3 species (Figure 7a), under basic conditions only T^2 and T^3 signals could be identified in the NMR spectrum presumably due to the fast condensation rate (Figure 7b). In addition, we can also notice a strong signal at −43 ppm belonging to T^0 species, indicating that, in agreement with the kinetics data, only part of MPS was involved in condensation reactions.
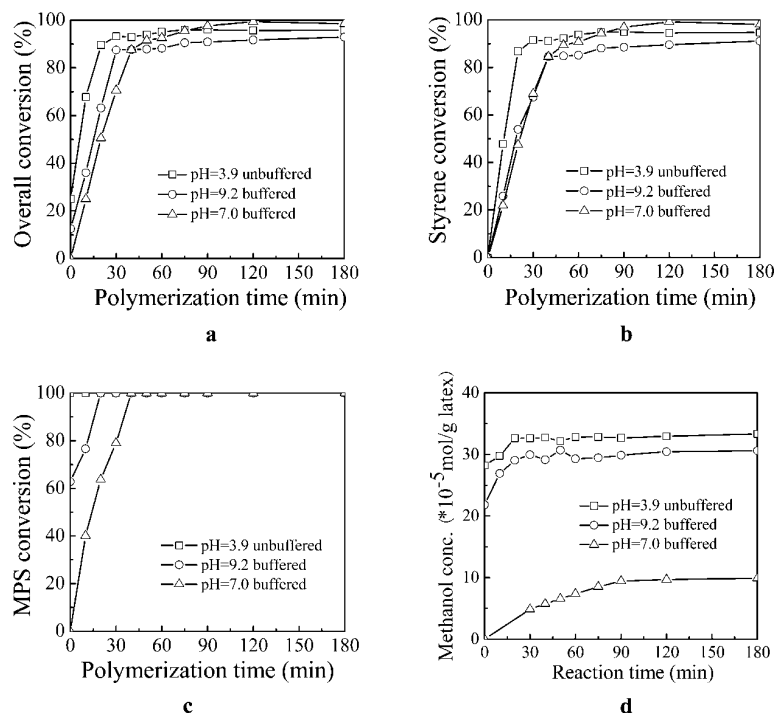
Figure 5. Influence of the suspension pH on the kinetics of the miniemulsion copolymerization of MPS and St initiated by KPS: (a) overall conversion, (b) St conversion, (c) MPS conversion, and (d) methanol concentration. MPS:St = 1:4.
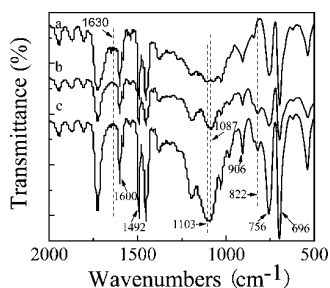

Figure 6. FTIR spectra of latexes obtained by miniemulsion copolymerization of MPS and St initiated by KPS at pH = 3.9 (a), pH = 7.0 (b), and pH = 9.2 (c). MPS:St = 1:4.
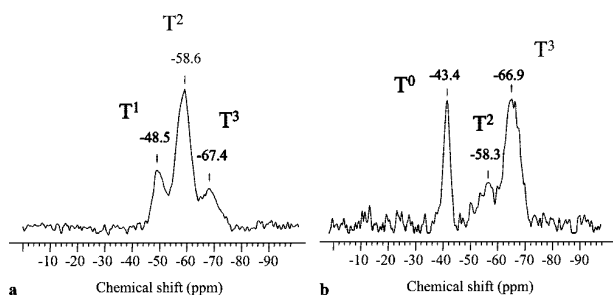

Figure 7. ^{29}Si solid-state NMR spectra of latexes obtained by miniemulsion copolymerization of MPS and St initiated by KPS at pH = 3.9 (a) and pH = 9.2 (b). MPS:St = 1:4.

Effect of the Surfactant Concentration. The concentration of surfactant is a key parameter of miniemulsion polymerization reactions as it controls both the droplets and particles size. The droplets and particles sizes obtained for SDS concentrations of 5.5, 11.1, and 22.2 mM are given in Table 3. As expected, the droplets size decreases with increasing the surfactant concentration. The conversion−time curves of this series of experiments are shown in Figure 8a. It can be seen that the polymerization

rate increases as the droplets size decreases. This is a usual trend in miniemulsion polymerization.[37] In addition, Figure 8b and Table 3 show that the rate of hydrolysis also increases with increasing the surfactant concentration. The strong influence of the surfactant concentration on the hydrolysis rate suggests that hydrolysis takes place at the droplet/water solution interface. Indeed, the smaller the particles size, the higher is the area in contact with water and the faster is therefore the hydrolysis reaction. Marcu et al. also came to the same conclusion for the miniemulsion copolymerization of vinyltriethoxysilane and *n*-butyl acrylate.[17] As a fast hydrolysis reaction promotes the formation of a physical barrier to radical entry in the early stages of polymerization, the kinetics profiles of the polymerizations performed at 22 and 11 mM SDS were found to be quite similar despite significant differences in the droplets sizes. Moreover, as the polymerization was retarded in the former situation, the final conversion was found to be slightly lower for the highest surfactant concentration than for the lower concentration.

Effect of the Initiator Concentration. Figure 9a shows the conversion−time curves of two miniemulsion polymerizations performed with different initiator concentrations. Surprisingly, the copolymerization rate did not appear to be influenced by the amount of initiator in the concentration range investigated. Also unexpectedly, the final conversion was lower for the highest initiator concentration. Again, this can be explained by alkoxysilane hydrolysis. Indeed, as shown in Figure 9b, the hydrolysis rate increases as the KPS concentration increases. The increase in the hydrolysis rate with increasing the amount of initiator is presumably due to a decrease of the suspension pH following the decomposition of KPS, which produces strongly acidic sulfate groups. As a matter of fact, the final pH value was measured to be 6.4 for KPS = 4.4 mM, whereas it was only 5.9 for KPS = 8.8 mM. The faster is the rate of hydrolysis, the higher is the probability of forming a physical barrier to radical entry and the slower is consequently the copolymerization reaction.
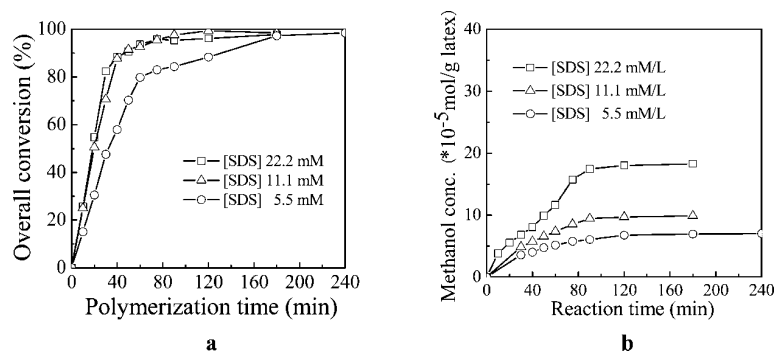
Figure 8. Influence of the surfactant concentration on the kinetics of the miniemulsion copolymerization of MPS and St initiated by KPS under neutral conditions: (a) overall conversion and (b) methanol concentration. MPS:St = 1:4.
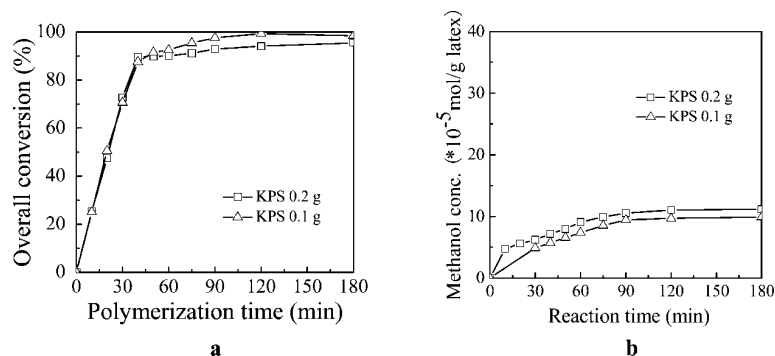

Figure 9. Influence of KPS concentration on the kinetics of the miniemulsion copolymerization of MPS and St under neutral conditions: (a) overall conversion and (b) methanol concentration. MPS:St = 1:4.

Miniemulsion vs Macroemulsion Polymerization. Although miniemulsion and macroemulsion polymerizations exhibit many similarities, they also present obvious differences in the nucleation mechanism which make miniemulsion very attractive. One of the most unique properties of miniemulsion is the lack of monomer transport. Since particle formation takes place in the monomer droplets, miniemulsion polymerization has proven to be advantageous when some control in terms of polymer architecture, morphology, or reactivity is desired. Miniemulsion polymerization thus recently appeared to be an alternative solution in order to avoid premature cross-linking of alkoxysilanes. The advantages of miniemulsion polymerization are twofold. First, this process enables better control over the reactivity of the alkoxysilane monomers to be achieved, which was clearly a major concern in conventional emulsion polymerization. Indeed, it was shown that while the extent of premature cross-linking could be considerably suppressed through the proper choice of pH conditions, the hydrolysis−condensation reactions still proceeded at a finite rate presumably because of poor alkoxysilane incorporation inside of the polymer particles. Moreover, it was shown that increasing the silane content caused a drastic increase in the condensation rate even for seeded emulsion copolymerization processes.[5,8,9] Therefore, the amount of silane that could be incorporated inside the latex particles was limited to relatively low values (typically less than 50% by weight). As in miniemulsion polymerization, monomers are confined into nanodroplets; there is only little mass transfer between the droplets and the aqueous phase. This does not mean that hydrolysis does not take place. On the contrary, the formation of small droplets promotes hydrolysis reactions as clearly demonstrated in the present work. Nevertheless, as soon as KPS is introduced in the reactor, the hydrolyzed silane monomer is incorporated in the polymer chains, thus minimizing the risk of condensation reactions which is a major difference with emulsion polymerization. Another difference is that in

miniemulsion polymerization the amount of hydrolyzed silane is independent of the silane content and only depends on the droplets size (see Table 3). In contrast, in emulsion polymerization, the higher the silane content, the higher is the rate of hydrolysis and, consequently, the higher is the probability of premature cross-linking.

A second advantage provided by miniemulsion polymerization lies in the colloidal stability of the incipient latex. Indeed, previous works on emulsion polymerization have clearly demonstrated the dominant role of the suspension pH on the latex stability. For instance, Bourne et al. reported that polymerizations performed under acidic conditions, without pH adjustment or with the pH adjusted to 9, resulted in coagulation.[3] When emulsion polymerization was carried out, premature gelation, viscosity buildup, and particles aggregation were reported depending on the suspension pH. In contrast, miniemulsion polymerization enables incorporating a high amount of silane without the formation of coagulum. This latter difference is again related to differences in nucleation mechanism. As in miniemulsion polymerization, hydrolysis occurs mainly at the monomer/water interface; the resulting oligomers remain close to the surface of the droplets where they can undergo further reaction with the vinyl monomer and successfully enter the particles. The silane concentration in the aqueous phase is thus very low, which ensures a good colloidal stability of the latex suspension: there is not enough silane available to induce cross-linking and gelation of the suspension medium.

Conclusion

Post cross-linkable organic−inorganic hybrid latexes containing alkoxysilane moieties were successfully synthesized through copolymerization of styrene and γ-methacryloxypropyltrimethoxysilane in miniemulsion. Kinetic experiments were carried out to analyze the effects of the MPS/St ratio, the nature and amount

of initiator, the suspension pH, and the surfactant concentration on the copolymerization rate. At low conversions, an increase in the MPS concentration led to a slight increase in the copolymerization rate due to the higher MPS propagation rate coefficient and its higher water solubility compared to styrene. The copolymerization rate and the styrene and MPS homopolymerization rates decreased at higher conversions, presumably due to the formation of a silane-rich interfacial area near the particle surface which decreased the rate at which oligomers could undergo irreversible entry. The kinetics of the miniemulsion polymerization reaction performed in the presence of AIBN supports such hypothesis. As the radicals were mainly produced in the oil phase, the overall kinetic process was no longer influenced by the presence of the silane monomer. In the case of KPS, the copolymerization rate was found to be nearly independent of the amount of initiator while it was strongly influenced by the surfactant concentration. An increase in the amount of surfactant produced a decrease in droplets size and enhanced the overall reaction rate. Increasing the surfactant concentration also led to an increase in the rate of hydrolysis, indicating that hydrolysis was taking place at the particles/water solution interface. The faster was the hydrolysis reaction, the higher was the probability of forming an electrosteric barrier to radical entry and, consequently, the slower was the copolymerization reaction.

The rate of hydrolysis was moderate under neutral conditions but increased rapidly at high and low pH. Consequently, the miniemulsions prepared under acidic or basic conditions showed small droplets size and high copolymerization rates. While the siloxane oligomers formed under basic or neutral conditions were found to have an influence on the kinetic processes, those formed at low pH seemed to have only a minor effect. This is presumably due to differences in oligomers architecture. Premature cross-linking could be avoided under neutral conditions and minimized in basic conditions, even for high initial MPS/St feed ratios. However, cross-linking could not be avoided in acidic media due to the very fast hydrolysis rate. All the obtained latexes displayed good shelf stabilities compared to conventional emulsion polymerization products, which is one of the obvious advantages of the miniemulsion polymerization process.

Supporting Information Available: SEC chromatograms of polystyrene and poly(styrene-*co*-MPS) showing that MPS and poly(MPS) do not act as chain transfer agents in the polymerization of styrene. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Burzynski, A. J.; Martin, R. E. U.S. Patent 3,449,293, 1969.
(2) Grawe, J. R.; Bufkin, B. G. *J. Coat. Technol.* **1978**, *50*, 67–83.
(3) Bourne, T. R.; Bufkin, B. G.; Wildman, G. C.; Grawe, J. R. *J. Coat. Technol.* **1982**, *54*, 69–82.
(4) Liles, D. T. U.S. Patent 5,932,651, 1999.
(5) Bourgeat-Lami, E.; Tissot, I.; Lefebvre, F. *Macromolecules* **2002**, *35*, 6185–6191.
(6) Tissot, I.; Reymond, J. P.; Lefebvre, F.; Bourgeat-Lami, E. *Chem. Mater.* **2002**, *14*, 1325–1331.
(7) Vitry, S.; Mezzino, A.; Gauthier, C.; Cavaille, J.-Y.; Lefebvre, F.; Bourgeat-Lami, E. *C. R. Chimie* **2003**, *6*, 1285–1293.
(8) Ni, K. F.; Shan, G. R.; Weng, Z. X.; Sheibat-Othman, N.; Fevotte, G.; Lefebvre, F.; Bourgeat-Lami, E. *Macromolecules* **2005**, *38*, 7321–7329.
(9) Ni, K. F.; Sheibat-Othman, N.; Shan, G. R.; Fevotte, G.; Bourgeat-Lami, E. *Macromolecules* **2005**, *38*, 9100–9109.
(10) Huang, S.; Fan, D.; Lei, Y.; Huang, H. *J. Appl. Polym. Sci.* **2004**, *94*, 954–960.
(11) Tamai, T.; Watanabe, M. *J. Polym. Sci., Part A: Polym. Chem* **2006**, *44*, 273–280.
(12) Watanabe, M.; Tamai, T. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 4736–4742.
(13) Guo, T.; Chen, X.; Song, M.; Zhang, B. *J. Appl. Polym. Sci.* **2006**, *100*, 1824–1830.
(14) Zhang, X.-Y.; Sun, Z.-J.; Huang, H.; Li, Y.-J.; Lan, R.-H.; Chen, H.-Q. *J. Cent. South Univ. Technol.* **2007**, *5*, 666–672.
(15) Marcu, I.; Daniels, E. S.; Dimonie, V. L.; Hagiopol, C.; Roberts, J. E.; El-Aasser, M. S. *Macromolecules* **2003**, *36*, 328–332.
(16) Roberts, J. E.; Marcu, I.; Dimonie, V. L.; Daniels, E. S.; El-Aasser, M. *Polym. Prepr.* **2003**, *44*, 277–332.
(17) Marcu, I.; Daniels, E. S.; Dimonie, V. L.; Roberts, J. E.; El-Aasser, M. S. *Prog. Colloid Polym. Sci.* **2003**, *124*, 31–36.
(18) Luo, Y.; Xu, H.; Zhu, B. *Polymer* **2006**, *47*, 4959–4966.
(19) Zhang, S. W.; Zhou, S. X.; Weng, Y. M.; Wu, L. M. *Langmuir* **2006**, *22*, 4674–4679.
(20) Sudol, E. D.; El-Aasser, M. S. In *Emulsion Polymerization and Emulsion Polymers*; Lovell, P. A., El-Aasser, M. S., Eds.; J. Wiley & Sons Ltd.: London, 1997; Chapter 20, p 700.
(21) Guyot, A. *Curr. Trends Polym. Sci.* **2001**, *6*, 47–57.
(22) Capek, I.; Chern, C. S. *Adv. Polym. Sci.* **2001**, *155*, 101–165.
(23) Asua, J. M. *Prog. Polym. Sci.* **2002**, *27*, 1283–1346.
(24) Antonietti, M.; Landfester, K. *Prog. Polym. Sci.* **2002**, *27*, 689–757.
(25) Schork, F. J.; Luo, Y. W.; Smulders, W.; Russum, J. P.; Butté, A.; Fontenot, K. *Adv. Polym. Sci.* **2005**, *175*, 129–255.
(26) (a) Koppel, D. E. *J. Chem. Phys.* **1972**, *57*, 4814–4820. (b) International Standard ISO 13321. Methods for determination of particle size distribution. Part 8: Photon Correlation Spectroscopy, International Organization for Standardization (ISO), 1996.
(27) Maxwell, I. A.; Morisson, B. R.; Napper, D. H.; Gilbert, R. G. *Macromolecules* **1991**, *24*, 1629–1640.
(28) Rao, V. L.; Babu, G. N. *Eur. Polym. J.* **1989**, *6*, 605–609.
(29) Gilbert, R. G. In *Emulsion Polymerization: A Mechanistic Approach*; Ottewill, R. H., Rowell, R. L., Eds.; Academic Press: London, 1995; p 362.
(30) Nomura, M.; Tobita, H.; Suzuki, K. *Adv. Polym. Sci.* **2005**, *175*, 1–128.
(31) Cohen, E. M.; Lyons, R. A.; Gilbert, R. G. *Macromolecules* **1996**, *29*, 5128–5135.
(32) Cheong, I. W.; Kim, J. H. *Colloid Polym. Sci.* **1997**, *275*, 736–743.
(33) Thickett, S. C.; Gaborieau, M.; Gilbert, R. G. *Macromolecules* **2007**, *40*, 4710–4720.
(34) Alduncin, J. A.; Forcada, J.; Barandiarian, M. J.; Asua, J. M. *J. Polym. Sci., Polym. Chem.* **1991**, *29*, 1265–1270.
(35) Sefcik, J.; McCormick, A. V. *Catal. Today* **1997**, *35*, 205–223.
(36) Osterholtz, F. D.; Pohl, E. R. *J. Adhes. Sci.* **1992**, *193*, 2049–2063.
(37) Bechthold, N.; Landfester, K. *Macromolecules* **2000**, *33*, 4682–4689.