Colloid Polym Sci (2007) 285:1455–1462
DOI 10.1007/s00396-007-1705-x

ORIGINAL CONTRIBUTION

Polymer–silica hybrids obtained by microemulsion polymerization

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Received: 28 March 2007 / Revised: 12 April 2007 / Accepted: 29 May 2007 / Published online: 29 June 2007

Abstract The styrene (St), butyl acrylate (BuA), and methyl methacrylate (MMA) polymerization in microemulsion in the presence of sodium dodecylsulfate is studied. This process is conducted in the presence of some comonomers having groups that can participate in sol–gel processes: 3(trimethyloxysilyl) propyl methacrylate (MPTS), triethoxy vinylsilane (VTES), and a comonomer with a sulfate group, styrene sodium sulfonate ($StSO_3Na$). It has been observed that stabile latexes are obtained by radical polymerization at pH = 7, followed by a sol–gel process in the presence of ammonia. Latex particles sizes and zeta potential grow with MTPS concentration and in $StSO_3Na$ presence. VTES effect depends on its reactivity in St, MMA, and BuA copolymerization. Glass transition temperature and thermal decomposing temperature are influences by functional comonomer concentration and chemical structure. The Fourier transform infrared spectrum and inorganic residue growth after organic part thermal decomposition shows the presence of silica in obtained latexes.

Keywords Sol–gel process · Microemulsion · Polymer–inorganic hybrids · Silica networks · Nanomaterials

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Introduction

Polymer–inorganic hybrids obtained by sol–gel processes in disperse systems presents a remarkable interest for nanomaterial field researchers [1–3]. The large number of studies dedicated to radical polymerization in disperse, emulsion, and miniemulsion media have stimulated the researches to realize new hybrids materials [4–16]. The presence of some polymerizable monomers containing side groups able to participate in the sol–gel process or to interact with preformed silica ensures the appearing of covalent or ionic bonding between the polymers formed by radical polymerization and inorganic networks formed by sol–gel processes. The dispersed polymeric particles can be templates in sol–gel processes or can be the place in which these processes happen [1–3].

Inside disperse systems, where copolymerization of some vinyl or acrylic monomers with precursors of sol–gel processes of comonomers takes place, the hybrid particle morphology can be modeled, a function of the initial pH of the reaction medium [11, 12], through the comonomers introduction sequence [13]. Under the condition of radical polymerization occurring in the presence of some silica nanoparticles, the morphology of hybrid particles depends on the formed polymers' nature [14].

In previous works [15], we studied the possibility of forming hybrid nanoparticles through both, simultaneously realized, sol–gel processes and microemulsion radical polymerization. The latex stability was highly dictated by the nature of sol–gel process precursors, having a polarity depending on the selective interaction with the surfactants.

We consider interesting the continuation of the mentioned studies by diversification of polymers used in microemulsion polymerization and consider pursuing by increasing the concentration of sol–gel process precursors,

along with the influence of initial pH (in which a complex synthesis process took place). Because of this reason, we study styrene (St), butyl acrylate (BuA), and methyl methacrylate (MMA) polymerization in microemulsion, in the presence of sodium dodecylsulfate (SDS) and various reactive comonomers in the sol–gel process.

Experimental section

Materials

The St, BuA, and MMA (commercial products) were purified by vacuum distillation. SDS (Merck/Suchardt), ammonium persulfate (APS; Loba Feinechemie), methyl triethoxysilane (MeTES), vinyl triethoxysilane (VTES), teraethoxy orthosilicate (TEOS), 3(trimethoxysilyl) propyl methacrylate (MPTS) (Merck/Suchardt), and styrene sodium sulfonate ($StSO_3Na$; Fluka) were used as is.

Procedures

Microemulsion polymerization was deployed in more variants by initial pH and monomer nature variation (Table 1). The general process was in water. Inside a glass reactor, under magnetic agitation, 40ml of water and 8g of SDS are mixed together. After room temperature dissolution, 4ml of the monomer in which the chosen comonomer is dissolved is introduced. The obtained mixture is purged with nitrogen for 30min, and 0.15g of APS is added, after heating to 65 °C. The entire mixture is maintained under agitation and nitrogen for 3h. After cooling, 0.2ml of NH_4OH (25%) is added to the mixtures with initial pH = 7, to increase the pH to 10. It is maintained for a supplementary hour under agitation and then transferred in vials, and these were flame sealed to observe the latex stability in time.

Table 1 Composition of initial mixtures: 8 g SDS, 40 cm^3 water, 4 cm^3 monomer, 0.15 g APS, 3 h, T=65 °C, 0.2 cm^3 NH_4OH 25%

Number	Initial pH	Comonomers/(g)
A	5	MPTS/0.4
B	11	MPTS/0.4
C	11	MPTS/0.8
D	7	MPTS/0.4
E	7	MPTS/0.8
F	7	MPTS/0.4 $StSO_3Na$/0.4
G	7	MPTS/0.4 (413)/0.4
H	7	VTES/0.8
I	7	–

MPTS 3(trimethoxysilyl) propyl methacrylate, *VTES* vinyl triethoxysilane, *SDS* sodium dodecylsulfate

An amount of latexes was transferred in open vases of polyethylene for air drying. The obtained products are three times washed under agitation in distilled water at 70 °C and separated by centrifugation. The polymers purified in this way are dried in a vacuum at 40 °C for further analyses.

The preparation of siloxanic oligomers was made as in Seog et al. [17]. A mixture formed by 20g of TEOS and 20g of MeTES reacts at room temperatures for 2h, in the presence of 5.6ml of distilled water. After this time, the formed volatile derivate from the sol–gel process is distilled at 78–82 °C. Viscous transparent oligomers were obtained and were kept inside flame-sealed vials. The used oligomers' accorded symbol was 413 (Table 1).

Analyses

The final conversions were gravimetrical established. Conversions more than 98% were obtained in all the cases. The zeta potential was determined using a Malvern ZEN 3600 Zetasizer Nano ZS (Red badge) instrument. Measures on undiluted latexes (Table 3, a) and 1 of 250 diluted latexes in a 0.001N NaCl solution (Table 3, b), were made. The particle sizes for diluted (Table 2, a) and undiluted (Table 2, a) latexes were also obtained on the Zetasizer Nano ZS. The view mode of the particles size distribution is by intensity.

The thermal analyses were made using a DuPont 2000 instrument with 5 °C/min heating rate to estimate the bonded water, 10 °C/min (for differential scanning calorimetry [DSC]) and 20 °C/min (for thermogravimetric analysis [TGA]).

The Fourier transform infrared (FTIR) spectra were registered with a Bruker TENSOR 37 instrument, the samples being mixed with KBr and compressed into pellets.

The scanning electron microscopy (SEM) images were obtained using an FEI QANTA 200 electronic microscope

Table 2 A comparison of the diameters of PSt, PMMA, and PbuA latex particles, for the final microemulsions (a) and for the diluted microemulsions (b), respectively

Sample	PSt		PMMA		PBuA	
	Final a	Diluted b	Final a	Diluted b	Final a	Diluted b
A	–	–	–	–	Gel	Gel
B	–	–	–	–	105	30
C	–	–	–	–	639	46
D	58	26	120	58	54	30
E	50	30	410	123	55	31
F	57	25	585	37	171	24
G	55	30	143	80	94	44
H	46	26	71	41	87	89
I	52	27	100	48	91	37

without previous coatings of the samples, using a low-vacuum working mode. The dialyzed samples were analyzed.

Results and discussions

The first experiments were made using BuA, as mentioned in Table 1. The mean particle average diameters are shown in Table 2, a. Taking in consideration that the initial pH was 5, after 3h of polymerization, the entire reaction mixture had a gel aspect (A variant). In this case, the conditions to realize a high rate for MPTS hydrolysis are provided, assuring in this way the possibility of associations' formation through uncondensated SiOH bonds. These results are in a very good concordance with previously published data [12, 15].

If the polymerization process in the presence of MPTS is realized at pH = 11 (through ammonium addition), stable latexes are obtained, having dimensions that grow along with the reactive comonomer concentration (Table 2, a—var. I, B, and C like in Table 1). In this case, the conditions for an increased condensation rate of SiOH bonds are ensured and consequently for the formation of aggregates, with more copolymerizable methacrylic groups [18].

This suggestion is demonstrated by the size distribution of the particles shown in Fig. 1. The latexes obtained in the presence of MPTS at pH = 11 (C) have a bimodal distribution and a higher medium diameter because of these aggregates.

To decrease the influence of the reactions that can appear by the sol–gel process, all the other experiments were made at pH = 7, through a buffer system addition as in Tissot et al. [12]. The particles' diameter sizes of nanolatexes obtained with BuA are showed in Table 2, a (var. D-I like in Table 1). The latex used as blank, without reactive comonomer, is the corresponding sample I. It can be remarked that along with the increase in MPTS (D, E) concentration, the latex particle diameters do not grow. A monomodal size distribution of particles was observed (E), similar to the one of the PBuA latex (I). By addition of $StSO_3Na$, a high polar monomer with dissociated sulfate groups (F) and higher diameters were obtained. This modification can be ascribed to the particle polarity growth, a fact that permits a rapid access of the water for sol–gel [16] and a bigger quantity of surfactant for stabilization [19].

The addition of the TEOS and MeTES obtained oligosiloxanes [17] was used for the observation of the microencapsulation possibility of polymer particles. Through the distillation of the perhydrolysis-eliminated alcohol, we obtained viscous oligomers in a doubled quantity compared with the theoretical one, corresponding to a total sol–gel process. This result sustains in good concordance with Seog et al. [17] that formed oligomers have enough SiOEt bounds able to cocondensate with MPTS to form a covalent bond with a polymeric chain. The diameters of particles obtained in this experimental way (G) are a little smaller than the blank (I), a fact which shows a polarity modification [19].

In the case of VTES, a monomer having low BuA copolymerization capacity [11] and the most hydrophobic chain bonded on Si and smaller particles were obtained (H) compared with the blank sample case (I).

The latexes with PMMA (Table 2, a), the most polar polymer, have particle sizes varying in function of comonomer nature, the same as in the case described before. The sizes of these particles are bigger than PBuA because of the low stabilization ensured by the polarity because of SDS [19]. The increase in MPTS (D, E) concentration determines the increase in the particles sizes like in Table 2, a and similar to the results from Jun et al. [16]. The higher average particle diameter (comparing with the blank sample) is obtained for MPTS and $StSO_3Na$ copolymerization (F) and the smallest for VTES copolymerization (the most hydrophobic monomer).

In microemulsion polymerization, taking place like in Table 1, the polystyrene (Table 2, a) generates the smallest particles. This polymer is the most hydrophobic from the

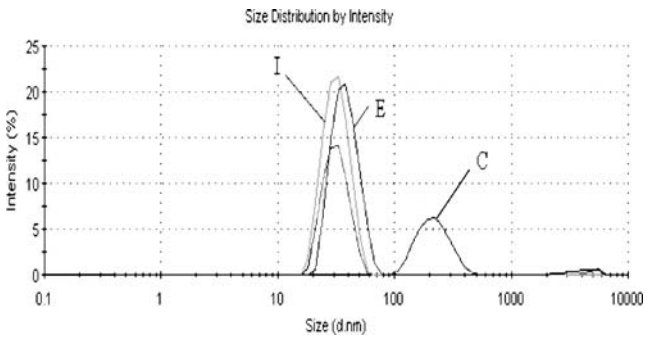

Fig. 1 Dynamic light scattering—intensity size distribution for PBuA (*C*, *E*, and *I*—Table 1) diluted latexes

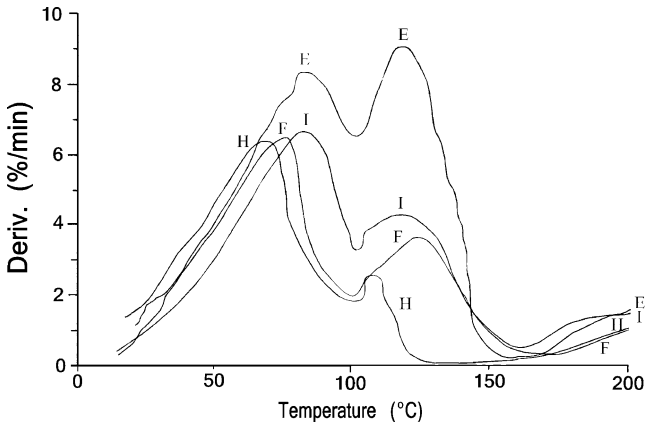

Fig. 2 DTG curves for: PBuA latexes (*I*), copolymer BuA–MPTS (*E*), copolymer BuA–MPTS–$StSO_3Na$ (*F*), and copolymer BuA–VTES (*H*)

Table 3 Zeta potential for PSt, PMMA, and PBuA latexes (for the final microemulsions and for the diluted microemulsions, respectively)

Sample	PSt		PMMA		PBuA	
	Final	Diluted	Final	Diluted	Final	Diluted
A	–	–	–	–	Gel	Gel
B	–	–	–	–	−34.4	−43
C	–	–	–	–	−40.7	−61
D	−33.2	−32	−31.5	−47	−35.9	−40
E	−42.4	−40	−32.6	−54	−42.7	−34
F	−44.6	−37	−40.2	−37	−38.7	−52
G	−39	−41	−32.1	−39	−38	−27
H	−53.1	−35	−29.5	−44	−47	−67
I	−33	−40	−33.5	−42	−42	−35

three ones analyzed in this paper. The comonomers types do not anymore have a high importance like in the previous cases. The effect can be assigned to a better stabilization [19] and to the low penetration of the water to finalize the sol–gel process [16]. A high importance element is that all the obtained latexes are stable, without visible agglomerations or precipitations for 1year.

The determined dimensions for the final microemulsions (Table 2, a) refer to the hydrodynamic diameters that include the high quantities of surfactant. For a better verification of results, measures on diluted latexes were made (Table 2, b). In this case, the value of the average diameter size is smaller with respect on the observation made for the undiluted variant: PMMA latexes have the biggest diameters; the increase in the MTPS concentration increases the mean diameter.

In the previous studies [20], we demonstrated that in copolymer latexes, the bounded water depends on the comonomer structural units' polarity. To verify if this observation is valid in the case of hybrids described in this paper, we observed some latexes' behavior when heating with a rate of 5 °C/min in the 0–170 °C range (Fig. 2). The differential curves (DTG) show two distinct maxima, like in the copolymers case [20]. The biggest amount of water, which exists in the free-state in latexes, is lost in the 0–100 °C interval. The water bounded with particles and SDS from the dispersion medium will evaporate in the 100–170 °C range.

From the quantitative analyses, the amount of bonded water from the latex can be determined. This bonded water was estimated for 1g of polymer. In the results from the analyses we made, in the case of PBuA (var. I, Table 1), the bonded water is 1.4g per 1g of the polymer. The hybrid latex obtained by copolymerization with 0.8g of MTPS (var. E, Table 1) contains 3.2g of water per 1g of the polymer. The increase in the bounded water amount can be assigned to the increase in the particles polarity and to the existence of some SiOH bounds because of the fact that the sol–gel process did not totally get to the silica network formation [16, 21].

BuA–MTPS (0.4 g)–$StSO_3Na$ (0.4 g) ternary copolymers (var. F, Table 1) contain 1.45g of bounded water for 1g of the polymer. The smallest quantity of bounded water (0.9g water per 1g polymer) is contained in BuA–VTES (H) copolymer latexes in which the comonomer is the most hydrophobic one.

The analyzed systems are very complex. The previous estimation brings forward some global modifications without having the certitude that the bounded water interacts only with latex particles. It is known that the SDS molecules are partially hydrated. Through the selective interaction with polar monomers or sol–gel process precursors, these forms can enter in competition [15]. From this reason, we estimated the ratio of bounded water from the entire water existing in the system. The increase in the

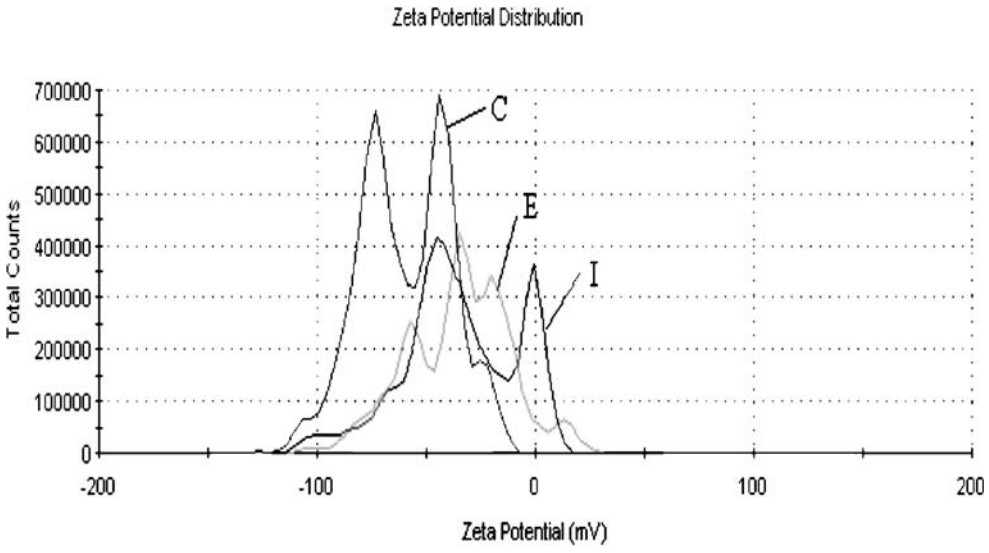

Fig. 3 Zeta potential for PBuA diluted latexes (*C*, *E*, and *I*—Table 1)

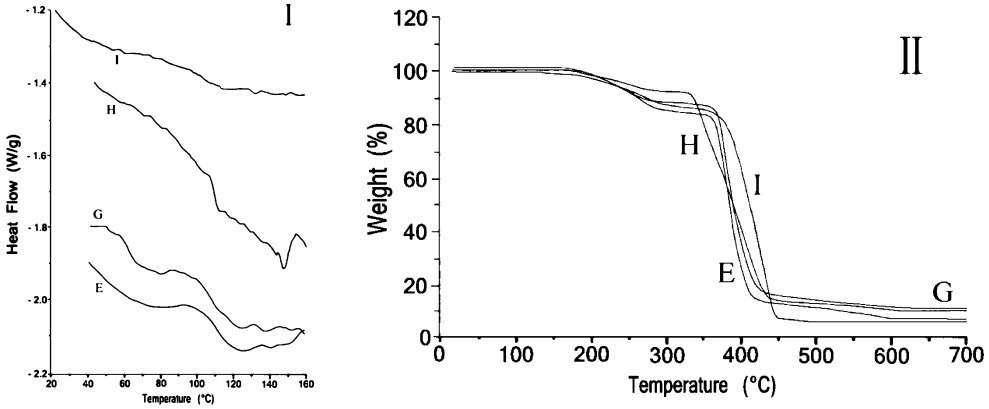

Fig. 4 *I*—DSC thermograms for: PSt (*I*), copolymer St–MPTS (*E*), copolymer St–VTES (*H*), and copolymer St–MPTS–413 (*G*); II—TGA thermograms of: PSt (*I*), copolymer St–MPTS (*E*), copolymer St–VTES (*H*), and copolymer St–MPTS–413 (*G*)

gravimetric ratio of the bounded water is 0.0976 (cop BuA–VTES [0.8] [H]) < 0.135 (PBuA [var. I]) < 0.138 (cop BuA–MTPS [0.4]–$StSO_3Na$ [0.4] [var. F]) < 0.138 (cop BuA–MTPS [0.8] [var. E]).

This increasing order is the same with those mentioned to be reported for 1g of the polymer. This reveals more accurate the changes that occur in the system during hybrid latex synthesis.

The zeta potential variation reflects the PSt particle surface modifications in the presence of functional groups induced by comonomer units. The results from Table 3 are in a good concordance with latexes obtained by emulsion St–MTPS copolymerization, with the addition of MTPS when the conversion of the main monomer exceeds 80% [13]. When compared with the homopolymer (var. I), the growth of MTPS concentration (0.4g—var. D, 0.8g—var. E) leads to the increase in the zeta potential.

The increase in zeta potential is caused by the increase in the concentration of dissociated groups of silanol at pH = 11 (var. D). This modification brings forward the fact that the sol–gel process is not in the final phase; not all the SiOH groups are condensed. Under these conditions, the interaction with SDS modifies (Fig. 3).

The presence in the system of siloxane oligomers along with MTPS (var. G) ensures a zeta potential growth but not more than in the case of the maximum amount of MTPS (var. E). The oligomers have a cyclic structure [21] and a big number of condensed silanol bounds, offering fewer groups ionizable at the latex particle surface. The anionic comonomer $StSO_3Na$ (var. F) determines a growth of the concentration, more than MPTS at the highest level used (var. E). The sulfonic group is much more dissociated than silanolic groups.

The higher zeta potential is remarked in the case of latexes obtained using St, BuA, and VTES (var. H). Because of the poor capacity of polymerization with St [22], after 3h of reaction, unpolymerized VTES can be found to react with the ammonium ions from the polymeric particles surface. Because the vinyl group is shorter, the quantity of silanolic groups is bigger than MPTS.

In the case of MMA polymerization (Table 3, a), the zeta potential varies the function of the comonomer nature. The growth of MTPS concentration (var. D, E) determines the zeta potential increase. The presence of $StSO_3Na$ (var. F) indicates a bigger increase in these potential like in the case of silane olygomers (var. G). A very special aspect can be observed in the case of VTES (var. H). The smaller value of the zeta potential compared with the one of the blank sample (var. I) can be explained by the higher reactivity of the siloxanic comonomer in copolymerization with MMA [22].

The results obtained for BuA are similar with those obtained when St is used (Table 3, a). The results obtained when the copolymerization with MPTS at initial pH = 11 is performed (Table 3, a—var. B, C) are very important. Comparing with the case where the sol–gel process is favored after particles formation (var. D, E), for B and C samples, a smaller zeta potential was obtained. In this case, the dissociable silanolic groups are in a lower number.

The sol–gel process of MPTS is complex, with oligosilane formation, which determines the silanol groups' reduction [21]. These resultants, containing methacrylic groups, cause the appearing of growth centers for monomer–polymer particles, in the polymerization in microemulsion by monomers absorption. This is the reason why in this case, bigger dimensions of latex particles (Table 1, a—var. B, C) are also obtained. A better estimation of the modifications suffered by the zeta potential can be made by studying 1 of 250 diluted latexes in a 0.001N NaCl solution (Table 3, b).

Table 4 The modification of T_g and T_{max} for PST and PMMA

Sample	PSt		PMMA	
	T_g (°C)	T_{max} (°C)	T_g (°C)	T_{max} (°C)
D	104.5	380	125	410
E	111.6	384	121	398
F	109.6	396	109	417
G	109	389	119.9	405
H	108.6	398	126	401
I	104	419	126	402

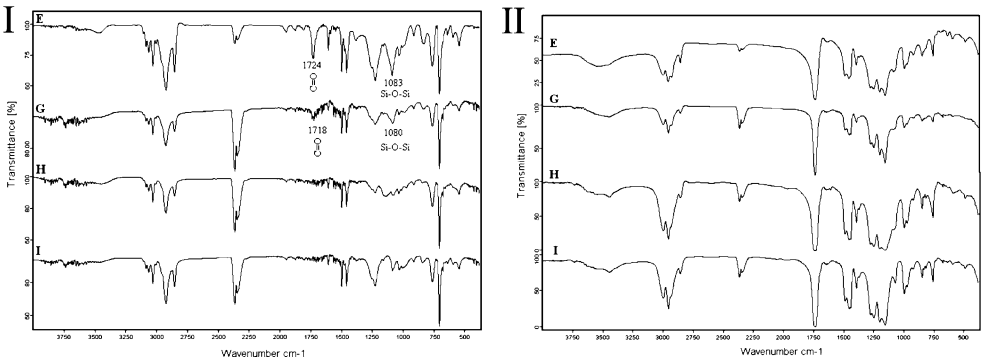

Fig. 5 FTIR spectra of: *I*—PSt and *II*—PMMA

Except measured numerical values, the observations made on final microemulsions are respected.

From our experience, we can say that these effects were not brought forward until now. To elucidate the influence of sol–gel processes on hybrids, the solid products—resulted after water evaporations and SDS elimination by repeated extractions—were analyzed.

The DSC curves for PSt and some hybrids are presented in Fig. 4, I. The shown results are in a good concordance with those published in Jun et al. [16] referring to St–MPTS copolymers obtained by dispersion polymerization. Specific transitions of PSt are remarked without being present the SDS melting endotherm; this indicating clearly its efficient removal without phase separation.

After the sol–gel process, the T_g value is increased in the presence of MPTS [16]. The same remark can be formulated for polymers obtained in the presence of VTES (var. H) or oligosiloxans in MPTS (var. G, Table 1). The change of T_g values for the products obtained by St and MMA polymerization is represented in Table 4. It can be seen that all hybrids containing PSt have bigger values of T_g than the homopolymer (var. I).

In the case of PMMA hybrids (Table 4), this affirmation is no longer valid. It is possible to get lower T_g values by copolymerization, and, under the conditions in which the sol–gel process is not in an advanced state, to get the SiOEt groups to play a plasticizer role [16]. In MMA–MPTS copolymerization in the homogeneous medium, these

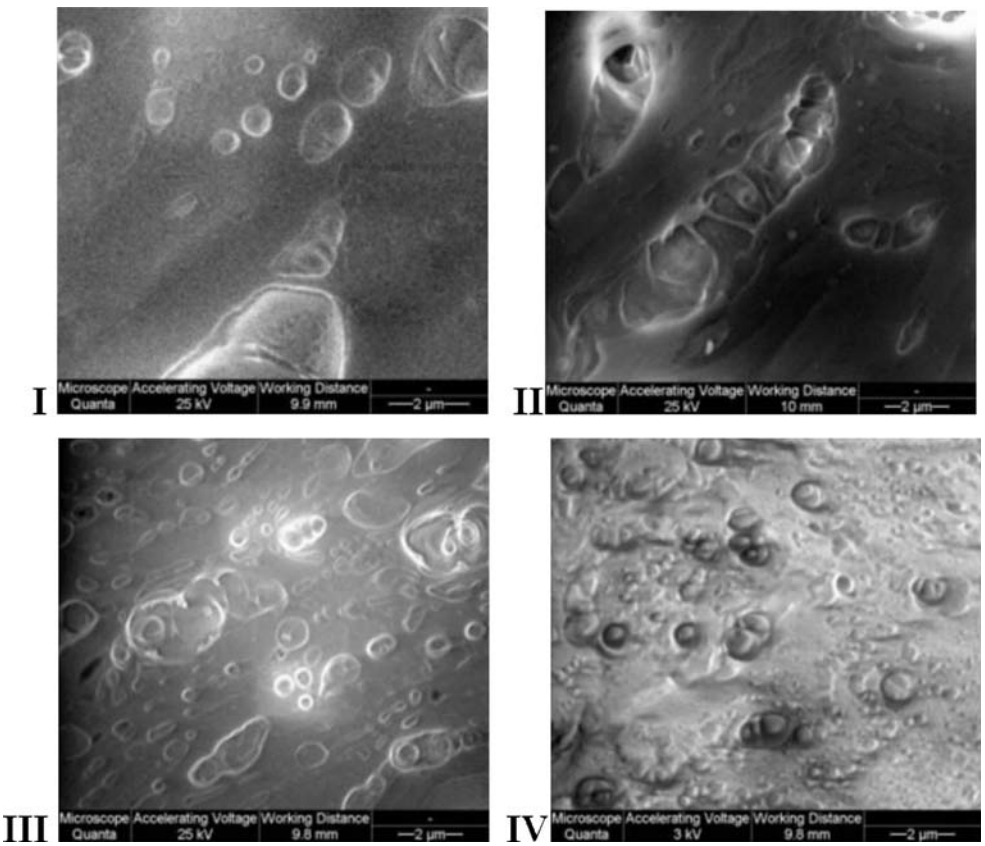

Fig. 6 SEM images of the PBuA films: copolymer BuA–MPTS (0.4 g) at pH=11 (*I*); copolymer BuA–MPTS (0.8 g) at pH=11 (*II*); copolymer BuA–MPTS (0.8 g) at pH=7 (*III*); PBuA (*IV*)

observations cannot be founded. The MMA chain mobility is reduced in the presence of highly cross-linked silica networks [23].

A very important property that can be modified in the presence of polymer–inorganic hybrid networks is the thermal stability [24, 25]. TGA curves for some materials synthesized in this paper are given in Fig. 4, II. Three zones of temperatures can be remarked with big losses of weight. The first interval with weight loss appears around 250 °C. Totally uncondensed alcoxy groups from siloxanes and some unextracted SDS marks are lost in this interval.

The most important domain for weight losses is 350–450 °C and corresponds to polymeric chain thermal degradation. From the DTG curves, the temperatures where the decomposing rate is maximum (T_{max}) were measured. The remarked modifications for T_{max} function of synthesis conditions are presented in Table 4.

For PSt, we can observe a decrease in T_{max} values in the presence of inorganic networks, probably because of the catalytic effect induced by silanol groups (Table 4).

In the PMMA case, this phenomenon is not remarked. The decomposing temperature (T_{max}) is minimally modified for PMMA hybrids (Table 4), in opposition with those with a high content of silica [25]. The third domain of weight loss appears in the 500–600 °C range and corresponds to a final condensation of silica networks with SiOH groups [24].

The growth of the inorganic residue after thermal decomposition until 700 °C is a proof of the inorganic networks existence and therefore of the hybrid polymer–inorganic materials formation (Fig. 4, II).

FTIR spectra for the polystyrene copolymers are presented in Fig. 5, I. The characteristic bands of MPTS units are in the 1,717–1,724cm^{-1} domain for the C=O group. The characteristic bands of aromatic rings from the St units can be observed at 1,602, 1,493, and between 1,452 and 1,455cm^{-1} [12].

Compared with the blank, after addition of the reactive comonomers in the sol–gel process, the analyzed samples present an increase in the intensity in the 1,000–1,200cm^{-1} range [12]. Comparing with the homopolymer, for MMA copolymers, differences (attributed to Si–O–Si bonds) in the mentioned zones (1,000–1,200cm^{-1}) can be remarked (Fig. 5, II). The infrared spectra modification represents another proof of the hybrid polymer–inorganic materials formation.

The SEM images obtained on PBuA and hybrids films are shown in Fig. 6. The analyzed samples were initially dialyzed to eliminate the surfactant. PBuA was chosen because it is a film-forming polymer at room temperature.

Compared with the PBuA film (Fig. 6, IV—var. I from Table 1), the three hybrids present different morphology, materialized by extended association domains. The increase in MPTS concentration from 0.4 g (Fig. 6, I—var. B from Table 1) to 0.8 g (Fig. 6, II—C variant) for syntheses at pH=11 induces the increase in association domains. It can be admitted that these associations owe to nanodomains of modified silica present in the latex particles.

The reaction at pH=7 (Fig. 6, III—var. E) determines a movement of the associated domains because of the fact that the sol–gel process takes place after BuA–MPTS copolymerization. Under these conditions, the associations of the silica domains can be reduced by structural units' inclusion into the polymeric chain.

The autoaggregation phenomenon of the same film was also brought forward in the case of poly vinyl acetate copolymers, grafted on some polar polymer chain [26].

Conclusions

By St, BuA, and MMA copolymerization with MPTS, VTES, and $StSO_3Na$, stabile latexes were obtained through microemulsion polymerization at pH=7. The sol–gel process takes place finally by ammonia addition. The latex particle dimensions and the zeta potential are growing with MPTS concentration and in the presence of $StSO_3Na$. The VTES effect is related with its capacity of copolymerization with the main monomers.

The effect of the presence of the functional copolymers is the growth of the amount of bonded water from latex particles. The glass transition temperature and thermal decomposing temperature are influenced by the concentration and chemical structure of the functional comonomers. FTIR spectra and inorganic residuum growth, after thermal decompose of the organic part, show the silica presence in the obtained latexes. The SEM images bring forward the morphology modification of PBuA films, obtained in the presence of MPTS.

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