Reactive Poly(ethylene glycol)s in Aqueous Radical Heterophase Polymerization

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Received June 6, 2003

ABSTRACT: A comprehensive study is presented of aqueous heterophase polymerization of styrene with two kinds of reactive poly(ethylene glycol)s, each with an average molecular weight of the poly(ethylene glycol) units of 400 g mol^{-1}: symmetrical poly(ethylene glycol)-azo-initiators with either terminal hydroxyl or styryl groups. Two kinds of stabilizers have been employed either sodium dodecyl sulfate or cetyltrimethylammonium bromide. Results are presented with regard to polymerization kinetics (reaction calorimetry), average particle sizes (dynamic light scattering), molecular weights (size exclusion chromatography), particle morphologies (transmission electron microscopy), swelling ratios (in water and tetrahydrofuran), and cross-linking density (analytical ultracentrifugation). These results reveal the exciting possibilities of reactive poly(ethylene glycol)s in heterophase polymerization.

Introduction

Poly(ethylene glycol)s (PEG) of comparatively low molecular weights (below 10^4 g mol^{-1}) represent important building blocks in surfactant chemistry, especially for nonionic, steric stabilizers. One important application is their use as stabilizing moieties in a variety of commercial polymer dispersions.[1] Particularly, they impart to colloidal particles improved resistance against enhanced electrolyte concentrations as well as improved stability during multiple freeze−thaw cycles. Moreover, PEG has many interesting properties such as high biocompatibility, mechanical as well as thermal stability, and stealth properties in the reticulo-endothelial system. Moreover, it has bizarre solubility pattern; that is, it is soluble both in water and in many organic solvents.[2−4]

Particles can be decorated with PEG either via adsorption of surfactants containing PEG moieties as lyophilic block or via reactive binding of PEG with appropriate reactive groups. For polymer particles prepared by radical heterophase polymerization PEG can be covalently bonded to the particle surface by using PEG primary radicals, PEG macromonomers, or PEG transfer agents that are able to initiate or to participate in radical polymerization. Concerning the use of PEG primary radicals and PEG macromonomers in heterophase polymerization, comprehensive descriptions of the state of the art can be found in refs 5, 6, and 7 respectively. Concerning the application of PEG transfer agents in heterophase polymerization, comparatively little has been published (cf. ref 8). Another way to impart reactivity to PEG is the combination of two abilities such as radical formation and copolymerization in so-called macroinimers.[9] These macroinimers offer the additional advantage to prepare in heterophase polymerizations PEG containing gel particles of any size between a few nanometers (in microemulsion polymerizations) and micrometers (in dispersion polymerizations). By a proper choice of the PEG chain length, such particles are dispersible or redispersible after cleaning and drying in any media that are solvents for PEG. Another interesting possibility to use macroinimers is the successive activation of their functionalities. Very recently, microemulsion polymerization of styrene in the presence of PEG macroinimers at 25 °C utilizing a redox initiator system was reported.[10] Such a procedure preserves the azo-functionalities for subsequent modification of the latex particles.

The aim of this contribution is to compare the action of a PEG-azo-initiator and a PEG-azo-styryl macroinimer, each with PEG of molecular weight of 400 g mol^{-1} in emulsion polymerization of styrene in the presence of both anionic (sodium dodecyl sulfate) and cationic (cetyltrimethylammonium bromide) stabilizers with regard to polymerization kinetics and latex particle properties. The structures of the PEG-azo-initiator (PEGA400) and the PEG-azo-styryl macroinimer (PEGAM400) are given in Scheme 1.

Especially, it is interesting to study the influence of cross-linking on polymerization kinetics under compartmentalized conditions with as much as possible identical recipes, which is given by the comparison between PEGAM400 and PEGA400. Moreover, cross-linking via macroinimers should influence heterophase polymerization kinetics in a special way as expressed by eq 1 describing the rate of polymerization

$$r_p = k_p \bar{n} C_M N \quad (1)$$

where k_p is the propagation rate constant, C_M is the monomer concentration inside the latex particle as main reaction locus, $\bar{n}$ is the average number of radicals per particle, and N is the particle concentration. As both C_M and $\bar{n}$ are indirectly and directly dependent on the macroinimer concentration, respectively, a good prediction regarding differences in the dependence of r_p on the concentration of both reactive PEGs is not easy and definitely needs experimental verification.

Furthermore, special emphasis is placed on the question of whether or not the distribution of PEG in both phases, the aqueous continuous and the organic dispersed phase, leads to different reaction products, that is, two kinds of particles with different compositions and

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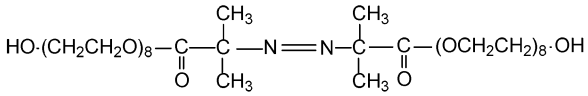
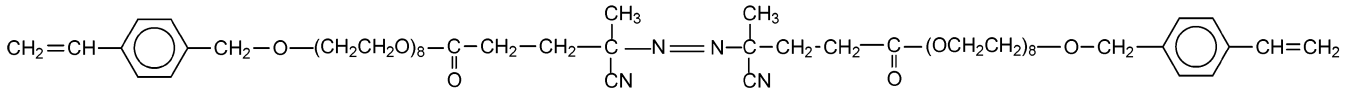
10.1021/ma0303115 CCC: $25.00
Published on Web 10/22/2003

Scheme 1. Structure of the Symmetrical PEG-Azo-Initiator (PEGA400) and the Symmetrical PEG-Azo-Styryl Macroinimer (PEGAM400)



PEGA400



PEGAM400

properties. In a former study on PEGA initiators some first experimental hints were found that the PEG content in polystyrene particles depends on the particle size.[11] In that particular investigation the latexes were separated into fractions with particle sizes below and above about 50 nm by ultrafiltration through membranes of proper pore size. By means of infrared spectroscopy and elemental analysis data, it was proven that the smaller size fractions contain a higher covalently bound PEG content. It might now be expected that this effect be enlarged by the use of PEG macroinimers due to the cross-linking reaction taking place in both phases.

Experimental Data

Materials. Styrene, methanol, and tetrahydrofuran (THF), from Sigma-Aldrich, sodium dodecyl sulfate (SDS) from Karl Roth GmbH (Karlsruhe, Germany), and cetyltrimethylammonium bromide (CTAB) from Ferak (Berlin, Germany) were all, except the monomer used, as received. The styrene was distilled under reduced pressure to remove inhibitors and stored in a refrigerator. Prior to use, the monomer was checked regarding oligomer formation during storage by instilling a drop into an excess of methanol. Only oligomer-free monomer was used. The water was taken from a Seral purification system (PURELAB Plus) with a conductivity of 0,06 μS cm^{-1} and degassed prior to use for the polymerizations.

The symmetrical poly(ethylene glycol)-azo-initiator with an average molecular weight of 400 g mol^{-1} (PEGA400) and the symmetrical poly(ethylene glycol)-azo-styryl macroinimer (PEGAM400) were prepared from PEG with an average molecular weight of 400 g mol^{-1}, as described elsewhere (PEGA400[12,13] and PEGAM400[14,15]). The structure of the reactive PEGs was confirmed by FT-IR spectroscopy (not shown here) and elemental analysis assuming a molecular weight of 907.06 and 1217.46 g mol^{-1} for PEGA400 and PEGAM400, respectively. Theoretical and experimentally found elemental analysis data for PEGA400—C_{theory} = 52.97%, C_{found} = 52.19%, O_{theory} = 35.28%, O_{found} = 35.46%—and for PEGAM400—C_{theory} = 61.67%, C_{found} = 61.02%, O_{theory} = 26.28%, O_{found} = 28.95%—are in good agreement if a structure is assumed as depicted in Scheme 1 (eight ethylene oxide units) and any distribution effects are neglected.

Polymerizations. The batchwise heterophase polymerizations were carried out with styrene as the monomer in a 100 mL all-glass reactor. The reactor was equipped with a stirrer, a reflux condenser, a nitrogen inlet and outlet, a heating jacket to control the temperature, and a valve on the bottom to remove the latex. The standard procedure was as follows: 10 g of the monomer, 35 g of water, and 0.1 g of the stabilizer (either SDS or CTAB) were premixed in the reactor during heating up to reaction temperature (80 °C). Injecting the desired amounts of PEGA400 or PEGAM400 dissolved in 5 g of water started the polymerizations. The sample code used corresponds in the following way to the polymerization recipe. The first capital letter either S or C denotes the surfactant SDS or CTAB, respectively, the number following stands for the initiator or reactive PEG concentration where ascending numbers mean decreasing PEGAM400 or PEGA400 concentration, and the X stands for cross-linked samples prepared with PEGAM400; otherwise PEGA400 was used. For example, sample S1 was prepared with SDS and the highest PEGA400 concentration whereas C5X was prepared with CTAB and the lowest PEGAM400 concentration. The concentrations of both PEGA400 and PEGAM400 were varied between 2.68, 1.34, 0.67, 0.335, and 0.168 g per run. After 2−6 h, depending on the initiator concentration, the polymerizations were complete.

Besides the above standard procedure, some polymerizations were also conducted in a reaction calorimeter CPA200 (ChemiSens AB, Lund, Sweden). Reaction calorimetry is suited to measure directly the polymerization rate by means of the heat flow (HF). Details of reaction calorimetry of heterophase polymerization can be found elsewhere.[16−18] For the runs in the calorimeter the procedure was the same as described for the glass reactors, except that the amounts of all ingredients were doubled.

After the polymerizations and before any characterization of the latexes the coagulum was removed by passing the dispersion through a pore 1 or 2 sintered glass frit. Consequently, the solids content (FG) is not only a measure of the conversion but corresponds much more inversely to the amount of coagulum formed during the polymerization.

Methods. Elemental analysis regarding C, H, N, S, and O was carried out with a vario EL elemental analyzer (Analysensysteme GmbH, Hanau, Germany). All latexes were characterized regarding the solids content with a HR 73 halogen moisture analyzer (Mettler Toledo, Giessen, Germany) and the average particle size with dynamic light scattering (intensity-weighted average particle diameter D_i) with a NICOMP particle sizer (model 370, NICOMP particle sizing systems, Santa Barbara, CA). Molecular weight distributions were determined by gel permeation chromatography (GPC) and used to calculate weight- and number-average molecular weights (M_w, M_n). GPC was carried out by injecting 100 μL of about 0.15 wt % polymer solutions (solvent tetrahydrofuran) through a Teflon filter with a mesh size of 450 nm into a Thermo Separation Products setup being equipped with UV (TSP UV1000) and RI (Shodex RI-71) detectors in THF at 30 °C with a flow rate of 1 mL/min. A column set was employed consisting of three 300 × 8 mm columns filled with a MZ-SDplus spherical polystyrene gel (average particle size 5 μm), having a pore size of 10^3, 10^5, and 10^6 Å. This column set allows a resolution down to molecular weights less than 500 g mol^{-1}. Molecular weights and molecular weight distributions were calculated on the basis of polystyrene standards. Clearly, this procedure results in apparent molecular weights as one might formally consider the PEG-ended polystyrenes as block copolymers. However, both blocks are soluble in THF, and hence aggregation effects, if they ever occur, can be neglected.

FT-IR spectra were recorded with an Impact 400 spectrometer (Nicolet) in a KBr pellet (2 mg of sample in 200 mg of KBr). Transmission electron microscopy (TEM) was used in order to investigate the shape and morphology of the particles as well to determine the particle size distributions of the latexes by enumerating TEM pictures. TEM was performed with a Zeiss EM 912 Omega microscope operating at 100 kV. For TEM the solids content of the latexes was adjusted to

about 0.5%, and a suspension preparation technique was employed to deposit the particles on the grid. To determine the particle size distribution and to calculate average diameters, about 600 particles have been enumerated with an Opton TGZ3 counter (Zeiss, Oberkochen, Germany). The following average diameters were calculated: $D_6 \propto \langle D^6\rangle/\langle D^5\rangle$ and the number-average particle size $D_1 \propto \langle D^1\rangle$. D_1 and D_6 are the average that corresponds to the number-average diameter and to the intensity-weighted average diameter from dynamic light scattering, respectively. Analytical ultracentrifugation (AUC) was performed for cross-linked polymer samples dispersed in tetrahydrofuran with a preparative Optima XL-80K ultracentrifuge (Beckman Coulter, Palo Alto, CA) converted to an analytical one as described in refs 19 and 20. AUC was used to check whether the particles are entirely cross-linked or still contain free polymer molecules employing a procedure as described in ref 21. Preparative ultracentrifugation (30 min at 50 000 rpm) (PUC) with a L-70 ultracentrifuge with a 70-Ti rotor (Beckman Coulter, Palo Alto, CA) was used in order to separate the polymer particles in the original latexes from the serum and the dissolved reaction products mainly surfactants and unreacted PEGA400 or PEGAM400 as well as primary recombination products thereof.

Swelling. The swelling ratio (q_v) or the reciprocal swelling volume being defined as the ratio of the equilibrium swollen volume to the initial polymer volume was determined by gravimetrical standard procedures as described in ref 15 with THF (the cross-linked particles no. 1 only) and water (all particles no. 1 after PUC) as swelling agent, respectively. Briefly, a known amount of dried polymer (about 0.2−0.3 g) was given to about 30 mL swelling agent and kept at room temperature for 24 h. Then the swollen solid was separated from the excess swelling agent by filtration and weighed in order to determine the amount of absorbed swelling agent. The swelling ratios were calculated by the assumption of the additivity of volumes. The molecular weight between to cross-links was estimated with the Flory−Rehner equation.[25]

Results and Discussion

Reaction calorimetry reveals that the rate of polymerization is a function of the concentration of the reactive PEG and that the rate of polymerization is higher for PEGA400 compared with PEGAM400 for all systems studied. A common feature of all heat flow−time curves is the appearance of a sharp maximum within the first third of the overall polymerization duration and the occurrence of a second maximum at conversions above 50%, which is very likely due to the gel effect. The gel effect is more pronounced in the case of PEGA400 and is higher with increasing initiator concentration. (At lower initiator concentrations only a weak shoulder appears in some cases.) The heat flow−time curves put together in Figure 1 compare all systems investigated exemplarily with the medium concentration of the reactive PEGs. Obviously, there are clear differences on one hand between PEGA400 and PEGAM400 at given surfactant but on the other hand also between SDS and CTAB at given reactive PEG. Polymerizations with PEGA400 and CTAB are faster than polymerizations with PEGAM400 and SDS, respectively. The maximum heat flow observed during the un-cross-linked polymerizations is up to a factor of 5 higher than that during the polymerizations in the presence of the macroinimer. The difference between PEGA400 and PEGAM400 reflects the difference between un-cross-linked and cross-linked particles regarding C_M. The monomer concentration in the latex particles as main reaction locus is higher for un-cross-linked than for cross-linked particles.[22−24] The magnitude of the difference depends on the degree of cross-linking and

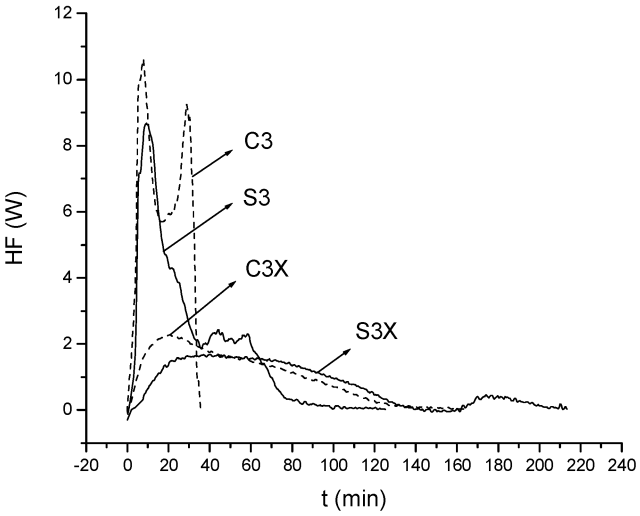


Figure 1. Comparison of heat flow−time curves for PEGA400 and PEGAM400 as reactive PEG during emulsion polymerization of styrene with either SDS or CTAB as stabilizer: S3-SDS, 0.67 g of PEGA400; S3X-SDS, 0.67 g of PEGAM400; C3-CTAB, 0.67 g of PEGA400; C3X-CTAB, 0.67 g of PEGAM400.

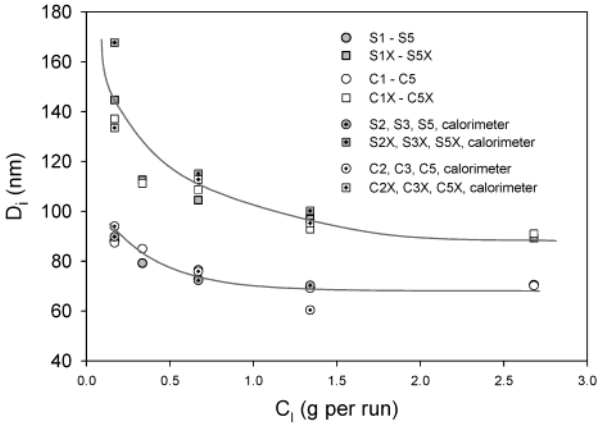


Figure 2. Variation of average hydrodynamic latex particle diameter with the amount of reactive PEG (lines are just for guiding the eyes).

is larger for higher cross-linking densities according to the Flory−Rehner expression.[25]

The slightly but significantly higher rates of polymerization for the CTAB systems compared with the SDS systems are experimental facts that cannot consistently be explained at the moment. On the basis of eq 1, one can assume that differences in either N or $\bar{n}$ or C_M are responsible. Since neither the average particle sizes (cf. Figure 2) nor the particle numbers (not reported here) in the final latexes and hence, also not $\bar{n}$, differ significantly for the polymerizations with both stabilizers, as sole reason obviously remains C_M. Indeed, there is some experimental evidence that the concentration of the emulsifier influences the swelling behavior of latex particles.[24,26] One might now speculate that due to the longer alkyl chain CTAB promotes the uptake of styrene in comparison to SDS more strongly.

Figure 2 shows the dependence of the average hydrodynamic latex particle diameter on the concentration of the reactive PEG, either PEGA400 or PEGAM400. For both types of reactive PEG the hydrodynamic diameters decrease with increasing concentration. This is an expected dependence as with increasing number of radicals more but finally smaller particles can be

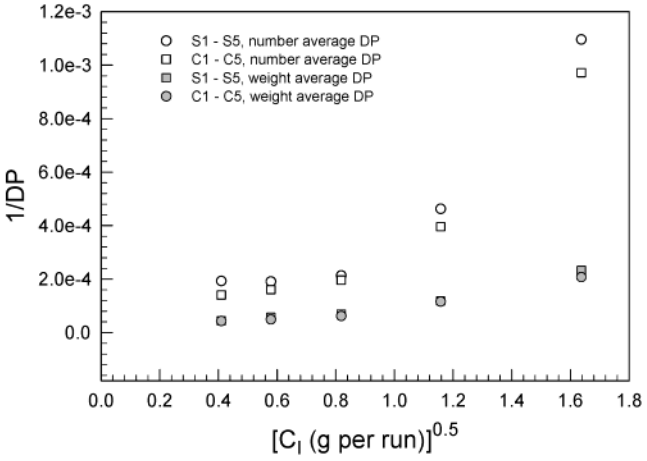


Figure 3. Change of the inverse degree of polymerization with the square root of the initiator concentration.

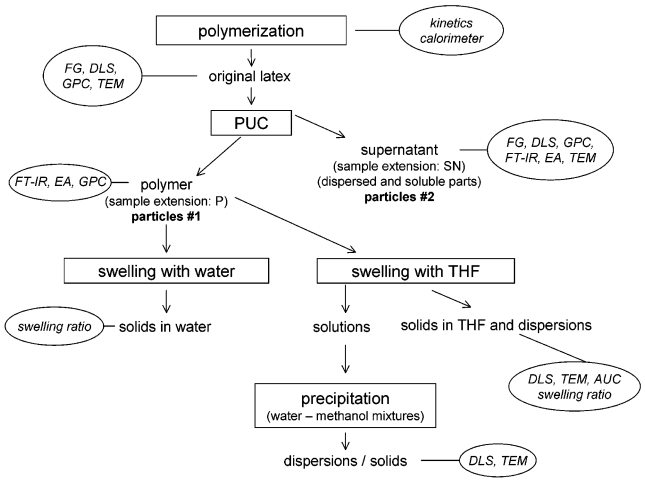


Figure 4. Sample history and characterization techniques employed.

formed. The unexpected behavior is the strong dependence of D_i on the type of initiator, which is much more pronounced than the dependence on the surfactant hydrophobicity (C_{12} vs C_{16}) or the type of reactor. The hydrodynamic diameters of the un-cross-linked particles are in any case smaller. This result is the more surprising as the concentrations of SDS (8.7 mM) and CTAB (6.9 mM) are below and above the critical micelle concentrations, respectively. The critical micelle concentrations have been determined for CTAB as about 2 mM and for SDS as about 11 mM at 80 °C in water saturated with toluene to mimic as much as possible the conditions during the polymerizations.[27] Obviously, the kind of reactive PEG is much more crucial for the final particle numbers than both the hydrophobicity and the concentration of the surfactant with regard to the critical micelle concentration. This result arouses questions regarding the particle nucleation mechanism, which are however beyond the scope of this contribution but will be considered in forthcoming publications.

Another interesting result in dependence on the concentration of the reactive PEGs is displayed in Figure 3 showing the change of the inverse degree of polymerization (1/DP) with the square root of C_I. This plot together with eq 2 is suited to check whether or not chain transfer to either monomer or initiator takes place during the polymerization (cf. ref 28).

$$\frac{1}{\mathrm{DP}} \propto C_{\mathrm{I}}^{1/2} + \frac{k_{\mathrm{tr,M}}}{k_{\mathrm{p}}} + \frac{k_{\mathrm{tr,I}}}{k_{\mathrm{p}}}\frac{C_{\mathrm{I}}}{C_{\mathrm{M}}} \qquad (2)$$

In eq 2, $k_{tr,M}$ and $k_{tr,I}$ are the chain transfer rate constant to monomer and initiator, respectively. The initial portions of the plots are linear, but at higher PEGA400 concentrations they deviate from linearity as the contribution of transfer to initiator increases. This is an important experimental result as it allows a kinetic explanation of the former observed effect of increased PEG content in smaller particles (cf. above and ref 11).

The results discussed so far are attributed to the original latexes as obtained after the polymerization. To gain information with regard to the influence of the distribution of the reactive PEGs on both phases on latex and polymer properties, preparative ultracentrifugation (PUC) was used to separate the latex particles from the serum. Figure 4 clarifies by means of a kind of "family tree" the sample history for the further characterizations. PUC revealed the astonishing result that the latexes obviously composed of two kinds of particles (particles no. 1 and particles no. 2) as it was impossible to separate even after 30 min at 50 000 rpm an optically transparent serum from the particles. For all latexes treated with PUC (S1, S1X, S5, S5X, C1, C1X, C5, C5X) the serum phase remained turbid so that from the eight latex samples selected 16 samples were obtained for further characterization. With the particular equipment used for PUC, one might expect that polystyrene particles (density 1.05 g cm^{-3}) with an average diameter of 50, 100, and 200 nm at 50 000 rpm should reach the bottom of the cell within about 17, 4, and 1 min, respectively. In contrast, for a water-soluble PEG molecule with an average size of about 2 nm, it takes about 90 h to reach the bottom of the cell. Having these data in mind, two conclusions are justified. First, as complete sedimentation does not take place within 30 min, the dispersions contain particles with different densities and hence different compositions. Second, the polymer on the bottom of the cell should contain only minor parts of water-soluble products, which could have been only dragged with sedimentating particles. Note, the sedimentation coefficient, s in time units, depends according to eq 3 on the particle size (D), the difference between the particle density (ρ_p) and the density of the dispersion medium (ρ_0), and the dynamic viscosity of the dispersion medium (η). For particles swollen with the dispersion medium the density difference becomes lower and dominates the behavior compared to the size increase at high swelling ratios.

$$s = \frac{(\rho_{\mathrm{p}} - \rho_0)D^2}{18\eta} \qquad (3)$$

Using appropriate mass balances, it is possible to calculate after PUC the weight percent of polymer present in the sediment (particles no. 1) and in the supernatant (particles no. 2). The amount of particles in the sediment increases with decreasing PEGA or PEGAM concentration and is for the highest concentrations above 90 wt %, independent of the kind of surfactant (samples S5, S5X, C5, and C5X). For the samples S1 and S1X the amount of particles in the supernatant is about 30 wt % whereas for sample C1 it is 55 wt % and for sample C1X only 8 wt %. Note that these values are only estimates as after PUC the border

Table 1. Elemental Analysis, Molecular Weight, and Particle Size Data for Samples Obtained after PUC[a]

sample	C (%)	H (%)	N (%)	O (%)	M_w (g/mol)	M_n (g/mol)	D_i (nm)	D_6 (nm)	D_1 (nm)
S1-P	87.44	8.29	0.034	4.34	4.58E+05[b]	1.08E+05	70.5	63.8	61.3
S1-SN	59.08	9.55	0.083	27.91	3.89E+05	1.04E+04	64.9	83.8	78.6
S5-P	85.29	8.23	0.0075	0.816	1.81E+06	6.35E+05	88.1	66.5	61.2
S5-SN	89.4	9.285	0.016	2.366	1.82E+06	6.55E+05	81.3	83.1	78.7
C1-P	86.37	9.162	0.053	5.306	5.03E+05	1.47E+05	70.2	53.7	50.6
C1-SN	79.31	9.532	0.06	12.51	3.70E+05	8.80E+04	63.2	70.6	66.9
C5-P	91.62	9.12	0.026	0.635	2.28E+06	8.65E+05	87.4	78	59.4
C5-SN	90.32	7.65	0.048	1.189	1.39E+06	4.60E+05	86	71.4	60.8
S1X-P	85.6	9.4	0.013	6.077	(630) gel	(430) gel	89.3	76.2	66.9
S1X-SN	83.64	9.386	0.023	9.126	(400) gel	(220) gel	73.6	72.1	60.2
S5X-P	91.48	9.33	0.006	1.04	(1100) gel	(830) gel	144.8	137.4	118.8
S5X-SN	88.31	9.531	0.016	2.992	(10700) gel	(970) gel	120.1	113.8	83.4
C1X-P	86.41	9.16	0.037	5.695	(620) gel	(540) gel	109.4	100.6	88.7
C1X-SN	70.31	9.361	0.096	18.44	(400) gel	(330) gel	68.2	77.9	72.8
C5X-P	91.78	9.18	0.026	0.515	(780) gel	(600) gel	137.1	124.1	94.7
C5X-SN	89.35	8.906	0.055	2.101	(2100) gel	(420) gel	117.2	106.1	59.6

[a] The particle sizes (D) of the samples with extension P refer to the original latexes. [b] Read as 4.58×10^5.

between sediment and supernatant is rather diffuse, and hence, a quantitative separation of both fractions is impossible. Nevertheless, these data show the expected dependence on the concentration of reactive PEG; that is, higher concentrations cause higher weight fractions of products in the supernatant.

Table 1 summarizes the analytical data of particles no. 1 and particles no. 2 with regard to elemental analysis, molecular weights, and average particle sizes from both dynamic light scattering and enumeration of TEM pictures. These data reveal a few remarkable features of the particular aqueous heterophase polymerization with reactive PEGs investigated. The elemental analysis data confirm the existence of two kinds of particles as the elemental composition is quite different for the sedimentated (extension P) and dispersed (extension SN) fractions. The carbon content and the oxygen content of the P samples are higher except (S5) and lower (in all cases), respectively, than for the SN samples. Thus, the SN samples contain more PEG than the P samples. As the carbon and the oxygen content of the SN samples are higher and lower, respectively, in comparison with the reactive PEGs in all cases investigated, the SN samples clearly also contain styrene units. On the other hand, the oxygen content of all P samples is much higher than one would expect for polystyrene with only two PEG end groups supposing dominating termination by combination. For example, for sample S1-P with the lowest M_n of about 10^5 g mol^{-1} the C, H, and O content should be 91.94, 7.75, and 0.3%, respectively. FT-IR spectra as depicted in Figure 5 confirm the difference in the composition of the P and SN samples, especially by means of the intensity ratio of the bands at about 1100 cm^{-1} (asymmetric stretching vibrations of ether groups) and about 700 cm^{-1} (out-of-plane bending vibration of the phenyl rings). Clearly, these data do not allow to distinguishing between physically entrapped and covalently bonded PEG. It is to mention that the GPC traces of samples S1-SN and C1-SN prepared with the highest PEGA400 concentrations clearly show peaks eluting in the same region where also PEGA400 elutes whereas the other SN and P samples do not show peaks in this region. From the GPC data it can be calculated that about 15% of these two samples elute at molecular weights below 1000 g mol^{-1}. But there are good arguments supporting the conclusion that at least larger parts of PEG400 are also covalently attached. First, the data depicted in Figure 3 clearly suggest that chain transfer to PEGA might

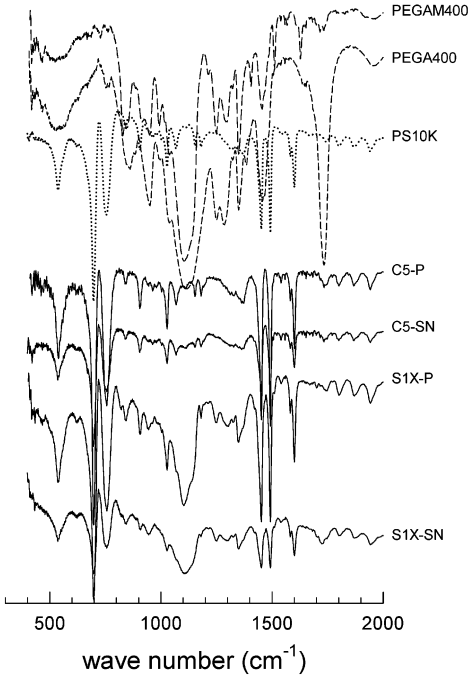


Figure 5. FT-IR spectra of samples separated by PUC. Sample assignment: cf. Table 2. PS10K: anionically prepared polystyrene with an average molecular weight of 10^4 g mol^{-1}.

take place. Second, the oxygen content is only slightly higher in the cross-linked samples, but one might expect a much higher difference as PEGAM400 is bifunctional compared to PEGA400 and in two of eight samples (S1-SN and C5-P) is even the reverse order observed. Third, in former studies it was found that polystyrene and PEG phase separate with increasing conversion and during storage due to incompatibility.[13,29] Fourth, a higher PEG content was observed in the smaller size particle fractions in former investigations (cf. above and ref 11) despite that after fractionation of the polystyrene latexes prepared with PEGA200 by ultrafiltration all unreacted PEGA200 was removed.

The different composition of the P and SN samples is also reflected in the appearance of the particles on TEM photographs, as illustrated for example in Figure 6. For both kinds of reactive PEG the particles of the SN samples look less compact, appear much more grainy than the particles in the original samples, and resemble rather core−shell type particles than homogeneous polymer particles. It is interesting to note that this effect

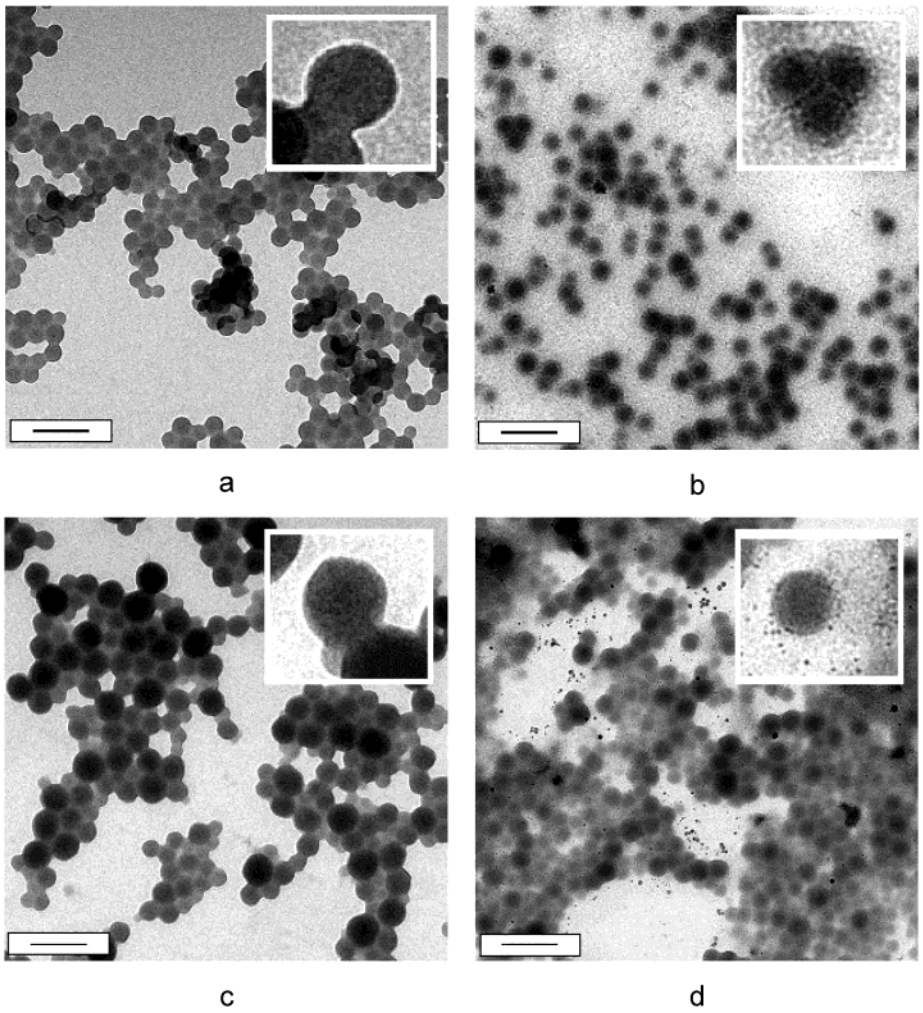


Figure 6. TEM pictures of original latexes and corresponding SN-samples after PUC: (a) S1, (b) S1-SN, (c) C1X, (d) C1X-SN.

is more pronounced for latexes prepared with PEGA400 (cf. Figure 6b,d), indicating that it is presumably caused by phase separation between the PEG and the polystyrene blocks which is hindered in the cross-linked samples.

With regard to the average particle sizes summarized in Table 1 the following facts are worth mentioning. In any case the D_i values for the original samples are larger than those for the SN samples. However, looking at the average diameters determined by enumerating TEM pictures, which in contrast to the D_i values characterize the dried samples, there are clear differences to recognize between cross-linked and un-cross-linked particles. For the latexes prepared with PEGAM400 both the D_6 and D_1 average values are lower for the SN samples than those for the original latexes. The latexes prepared with PEGA400 show, except for sample C5, the opposite behavior. These results indicate that the cross-linked samples shrink during drying whereas the un-cross-linked particles increase their apparent size, which means they flatten and, hence, appear optically larger. This effect occurs possibly due to phase separation between the PEG and the polystyrene blocks, which should be more pronounced for the SN samples than for the original samples as the PEG content is higher. This idea is also supported by the fact that in the case of the un-cross-linked SN samples the D_6 values are larger than the D_i values.

In conclusion concerning the data in Table 1, it should be emphasized that the molecular weights of the un-cross-linked SN and original samples almost coincide although a tendency might be recognized that the SN samples have slightly lower molecular weights. The molecular weight distributions above 10^3 g mol^{-1} are in any case monomodal. Also, for the cross-linked SN and P samples the molecular weights given in Table 1 in parentheses represent the very minor parts in the products that are just able to pass through the 450 nm filter with molecular weight distributions showing 2 or in many cases even three distinct peaks. These products are either initiator residues, or products of side reactions in the aqueous phase, or surfactants.

The sedimentated polymers (particles no. 1) obtained after PUC have been dried, and the polymer powder was subsequently used to carry out swelling experiments with both THF and water as swelling agent. The results are summarized in Table 2 and show a clear dependence on the concentration of the reactive PEG in the expected direction; that is, higher PEG concentrations lead to lower swelling ratios. Both the un-cross-linked and cross-linked polymers are capable of swelling with water, and the swelling ratio is practically independent of whether or not the polymer is cross-linked. While the ability of the polymers to swell with water was expected for the cross-linked samples prepared with PEGAM400, q_v values on the same order of magnitude for the un-

Table 2. Summary of Swelling Experiments

sample	m_1 (%)[a]	swelling ratio, q_v water	swelling ratio, q_v THF	M_c (g mol^{-1})[b]	remarks
S1-P	26.80	1.81			
S1X-P	26.80	1.73	7.20	9 475	for swelling of polystyrene gels prepared by bulk polymerization with PEGAM400 $q_v \sim 5$ [ref 14]
S5-P	1.68	2.00			
S5X-P	1.68	2.00	14.60[c]	37 300	for swelling of polystyrene gels prepared by bulk polymerization with PEGAM400 $q_v \sim 88$ [ref 14]
C1	26.80	1.91			
C1X-P	26.80	1.87	8.00	11 570	for swelling of polystyrene gels prepared by bulk polymerization with PEGAM400 $q_v \sim 5$ [ref 14]
C5-P	1.68	2.06			
C5X-P	1.68	2.37	n.m.[d]	n.m.[d]	for swelling of polystyrene gels prepared by bulk polymerization with PEGAM400 $q_v \sim 88$ [ref 14]

[a] Amount of reactive PEG with respect to the monomer mass. [b] Molecular weight (M_c) between two cross-linkages. [c] Sample partly redispersed in THF. [d] Determination was not possible because the sample completely redispersed in THF.

cross-linked polymers are surprising. This fact indirectly confirms once more that also the P samples prepared with PEGA400 contain excess PEG as the ability of swelling with water is only caused by PEG and not by polystyrene blocks. Moreover, the inverse dependence of q_v on m_1 for the un-cross-linked samples, even if only slightly but observed in any case, is puzzling. In THF the un-cross-linked samples are completely soluble, thus indicating that the excess PEG is not incorporated via cross-links. Contrary to the un-cross-linked polymers, the cross-linked samples swell in THF and the samples prepared with lower PEGAM concentrations even form spontaneously, that is, without any stirring, dispersions. For instance, sample C5X-P completely forms a dispersion with an average particle size D_i of some 130 nm, whereas of sample S5X-P only minor parts are redispersed down to particle sizes of some 220 nm. In the latter sample the particles in the bulk material swell to a size and arrange in a lattice, allowing the observation of iridescence. This indicates that also in the bulk material the latex particles, although not redispersed, keep their identity, and hence, the q_v values might expect to be lower than for macroscopic gels formed in homogeneous bulk polymerizations. The lower swelling ability compared with that of bulk material is a consequence of the colloidal nature of this particular samples (cf. discussion above concerning swelling of latex particles). Consequently, the lower q_v value of sample S5X-P (low PEGAM concentration) compared with that of the corresponding sample from bulk polymerization does not necessarily indicate a so much higher degree of cross-linking but is to some extent caused by the colloidal nature of the sample. Taking into account the pretty large experimental scatter of q_v for these powdery and redispersible samples, the values obtained for S1X-P and C1X-P (high PEGAM concentration) might be considered to be similar to that obtained for bulk polymerization (cf. Table 2). However, comparison between homogeneous bulk and heterophase polymerization is faulty anyway due to the different nature of both systems. The concentration of PEGAM as well as the ratio to monomer at the reaction loci is clear for bulk polymerizations, but it can only hardly be estimated under heterophase conditions as any PEG distributes between both phases. For example, for PEG-*b*-poly(propylene glycol)-*b*-PEG triblock copolymers it was determined that at 70 °C only 38% and 62% are dissolved in the aqueous and organic phase (ethylbenzene), respectively.[30]

The completely redispersed sample C5X-P, that is, the dispersion in THF, was used to check by means of AUC as described in ref 21 whether the particles are entirely cross-linked or still contain free polymer molecules. The sedimentation coefficient distribution given in Figure 7 clearly shows that both the dispersion in THF, which is a good solvent for polystyrene, and the particles contain obviously no single polymer chains as in the range below 300 Sv no sedimentation is detected. Typically, free polymer molecules have sedimentation coefficients clearly below 10 Sv (cf. ref 21). This is an interesting result as it proves that the cross-linking efficiency under compartmentalized reaction conditions is much higher than in homogeneous systems as for styrene bulk polymerization with PEGAM400 at 70 °C no gel fraction was formed at m_1 values below 5%.[15]

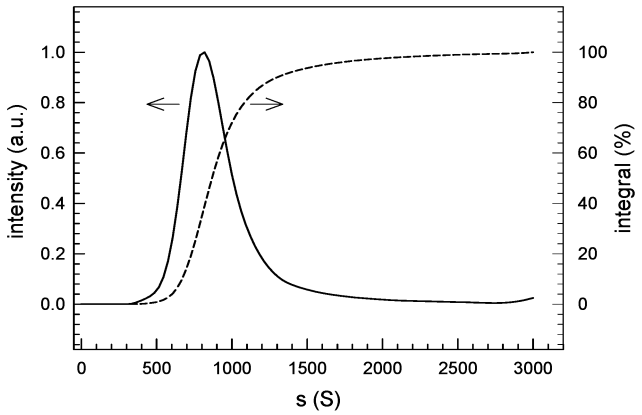


Figure 7. Differential (solid line) and integral (dashed line) distribution of sedimentation coefficient of sample C5X-P in THF.

The comparison of the particle size distribution (PSD) of the different kinds of dispersions obtained for the samples C5X and S5 as depicted in Figure 8 once more reveals that the original latex just after polymerization is at least composed of two types of particles (cf. also Figure 4). For sample C5X the PSD of the original latex covers the whole size range whereas the particles no. 2 (C5X-SN) concentrate in the small size region and the particles no. 1 (C5X-P) in the large size region. As discussed in connection with Table 1 (cf. above), for sample S5 just the opposite behavior is observed as the particles no. 2 are shifted toward larger sizes compared with the PSD of the original sample. Note that the PSD in both figures allow only to compare the size ranges and not the relative number of particles (N_j) for a given size (D_j) between the different portions of the samples.

Finally, the THF solutions of the un-cross-linked samples S1-P and C1-P when tried to precipitate in

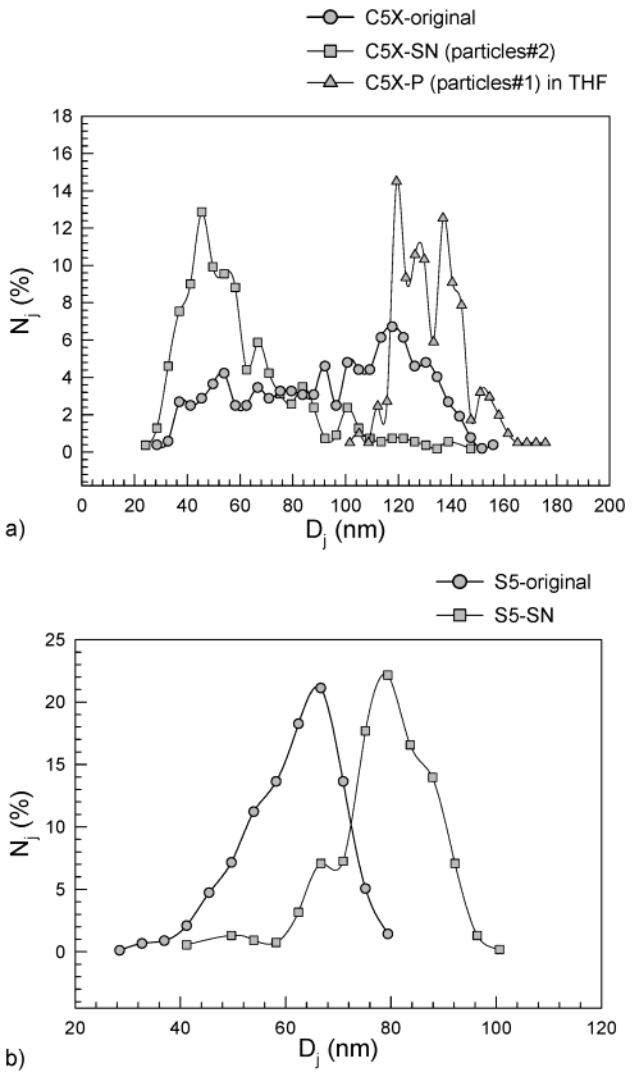


Figure 8. Particle size distribution of the various dispersions of sample C5X (a) and sample S5 (b) determined by enumerating TEM pictures (*j* is the size index).

methanol or methanol/water mixtures (1:1 by volume) do not form a macroscopic precipitate but a dispersion. The size of the particles depends on both the precipitant and the surfactant used to prepare the samples. Figure 9 illustrates this behavior by means of TEM pictures. These pictures reveal clear differences between SDS and CTAB as stabilizer used during the polymerizations regarding the shape and morphology of the precipitated particles. Dynamic light scattering of the samples precipitated in methanol gives D_i values of 550 and 310 nm for samples S1-P and C1-P, respectively. As the THF solutions of S5-P and C5-P treated in the same way form macroscopic precipitates, this points to an influence of the PEG concentration in stabilizing the particles. The influence of the kind of surfactant is not completely understood but in any case very interesting.

Summary

The above results revealed some special features concerning the application of PEG-azo-compounds, either the neat PEG-azo-initiator (PEGA400) or the styryl modified PEG-azo-macroinimer (PEGAM400), in emulsion polymerization. Generally, the advantage of reactive PEGs is that they can be applied in both aqueous and nonaqueous polymerization systems due to the solubility properties of PEG. In particular, in aqueous heterophase polymerizations any kind of stabilizer (anionic, cationic, or uncharged) can be used without the necessity to consider electrostatic interactions.

The most astonishing results of these investigations is the experimental proof that both types of reactive PEGs lead to two kinds of particles with different PEG content, obviously reflecting the monomer swollen particles and the aqueous phase as the main reaction loci. The first kind of polymer particles arises from propagation reaction in the hydrophobic monomer−polymer particles and contains a lower PEG content than the second kind of particles containing a much lower polystyrene content.

The average particle size (hydrodynamic diameter) obtained in aqueous emulsion polymerization with two kinds of emulsifiers, the cationic CTAB and the anionic SDS, is primarily determined by the concentration and kind of the reactive PEG and not by the kind of stabilizer. It is decreasing with increasing PEG concentration and in any case higher for PEGAM. However, there are also some distinct differences between CTAB and SDS. First, the cationic CTAB leads to higher rates of polymerization. Second, the cationic cross-linked particles show a much higher tendency to redisperse spontaneously in THF. Third, the un-cross-linked polymer prepared with the highest PEGA concentration does not form a macroscopic precipitate when a THF solution is dropped into excess of methanol or methanol/water mixture but redisperses whereby the polymer prepared in the presence of CTAB forms spherical colloidal particles and the one prepared with SDS nonspherical aggregates. These data point out specific interactions between the different surfactants and PEG. Such interactions are well-known and an ongoing topic in colloid research (cf. refs 31−33). The complex formation is mainly driven by the ionic headgroup interaction with the ethylene oxide groups and has been found to be much more marked for anionic than for cationic surfactants. A detailed discussion is beyond the scope of this paper and reserved for future works.

Another remarkable result to note is with regard to the elemental composition of the particles prepared with both kinds of reactive PEG. There is only a slightly higher PEG content in the particles prepared with PEGAM400, but one would expect a much larger difference due to the two possibilities how PEG from PEGAM can be incorporated into the polymer. The molecular weight data clearly prove that chain transfer to PEGA400 takes place. But these data cannot explain the higher PEG content as they only prove a stronger decrease in the average molecular weight than alone caused by the higher radical concentration with increasing PEGA concentration. This finding is not surprising as there are several reports in the open literature with regard to chain transfer reactions to PEG either as block in nonionic surfactants[34] or to neat PEG.[35] Obviously, another mechanism is responsible for the high PEG incorporation. It is known that aromatic azo-compounds cause a retardation of radical styrene polymerization due to the formation of triarylhydrazyl radicals, which are much more stabilized by resonance than the growing polystyrene radicals (cf. ref 36 and references therein). For the PEG-azo-compounds investigated here an analogous reaction might take place (cf. Scheme 2), leading to less stabilized PEG hydrazyl radicals, which do not cause retardation but only the increased PEG content.

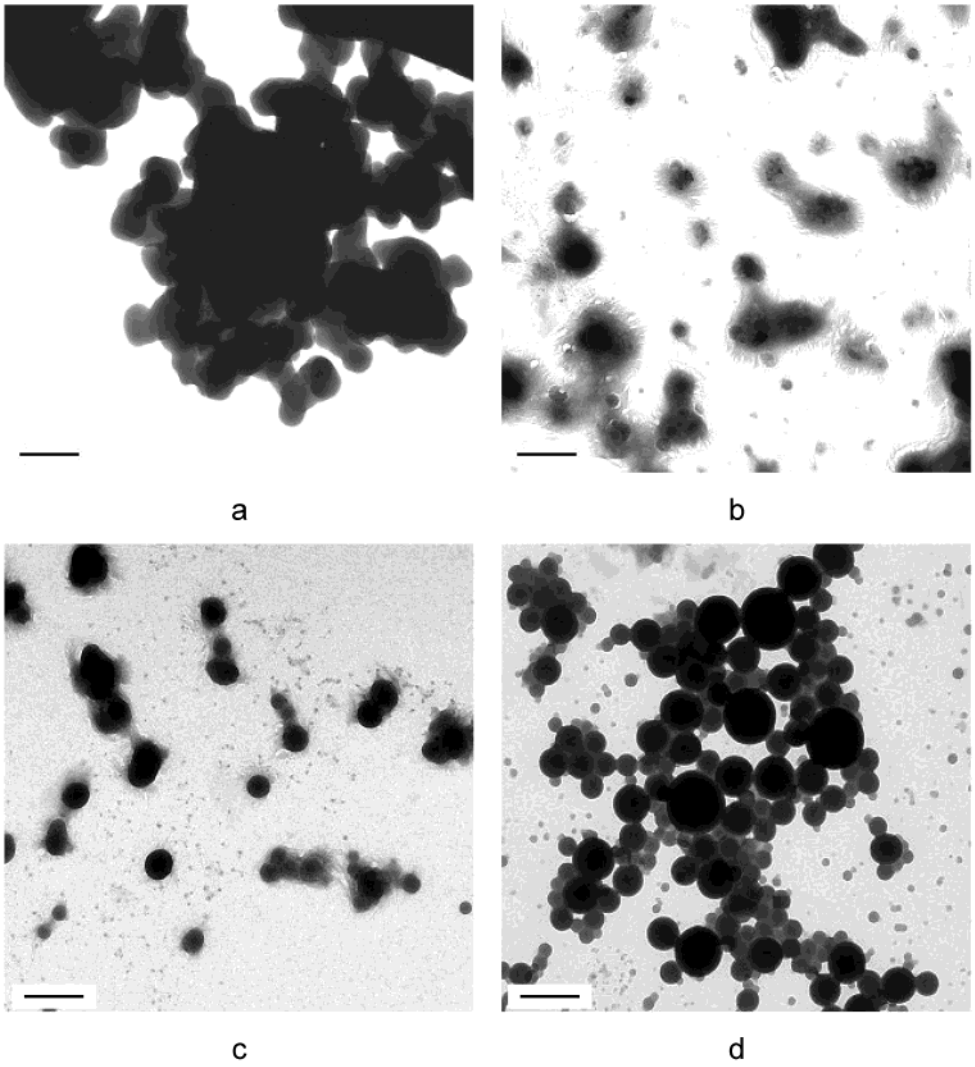
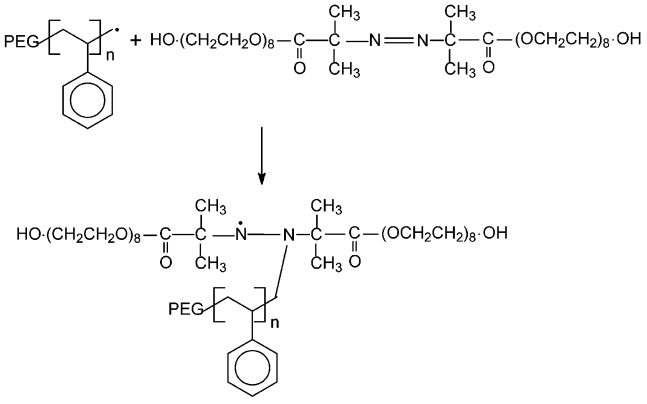


Figure 9. TEM pictures of dispersions formed during precipitation of THF solution un-cross-linked samples S1P and C1P; the bar indicates 500 nm for pictures a, c, and d and 1000 nm for picture b. (a) S1-P precipitated in methanol, (b) C1-P precipitated in methanol/water mixture (1:1 volume), (c) C1-P precipitated in methanol, and (d) C1-P precipitated in methanol/water mixture (1:1 volume).

Scheme 2. Addition of Growing Polystyrene Radicals to Azo Groups Adopted from Ref 34



Swelling as well as AUC experiments prove experimentally that in comparison to bulk polymerization of styrene with PEGAM400 the compartmentalized nature of heterophase polymerization causes at given PEGAM400 to monomer ratio considerably higher degrees of cross-linking. In fact, complete cross-linking of the polymer formed in the monomer−polymer particles is observed for all PEGAM concentrations investigated. There might be at least two reasons for this effect. First, the heterogeneous nature causes not only a higher PEGAM to monomer ratio; it also increases with conversion, as the monomer concentration inside the particles is the lower the higher the cross-linking density. Second, the above-discussed attack on the azo-group increases the concentration of pending styryl groups along the chain.

In conclusion, PEG-azo compounds are an interesting alternative to persulfate initiators for aqueous heterophase polymerizations. Depending on the particular type of PEG compound, either un-cross-linked, high molecular weight polymer particles with a high amount of PEG covalently attached (PEGA) or completely cross-linked particles without any leakage of polymers (PEGAM) are accessible. The polymerization mechanism is characterized by a complex interaction of features typical for heterophase polymerizations, PEG chemistry, and azo-group chemistry.

Acknowledgment. The authors gratefully acknowledge preparative and analytical assistance by Mrs. U. Lubahn, Mrs. J. Brandt, and Mrs. S. Pirok. For pre-

parative and analytical ultracentrifugation the authors thank Mrs. A. Völkel, for discussions Dr. H. Cölfen, for the TEM pictures Mrs. R. Pitschke, and for the GPC measurements Mrs. M. Gräwert. U.Y. thanks the Max Planck Institute of Colloids and Interfaces for a financial grant during a postdoctoral fellowship.

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MA0303115