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Structural control in radical polymerization with 1,1-diphenylethylene. Part 3. Aqueous heterophase polymerization

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Abstract

Results on aqueous heterophase polymerization in the presence of either 1,1-diphenylethylene or water-soluble precursor polymers containing an α,p-dimer unit of 1,1-diphenylethylene are reported. The precursor polymers are bound covalently to the particles due to a special kind of chain transfer reaction showing on the one hand some features of controlled radical polymerization and leading on the other hand to the formation of block copolymers. Moreover, the covalently bound precursor molecules act as very efficient colloidal stabilizers of the final dispersion and thus, they can be considered as reactive surfactant with the additional ability to control radical polymerization (controlsurf). Under optimum conditions the precursor polymer molecules are almost completely covalently attached to polymer particles. Results are presented regarding block copolymer yields, solids content, and particle diameter in dependence on the polymerization conditions, particularly the precursor polymer concentration, the monomer as well as the initiator concentration, and the initiator type. Under optimum conditions the attainable block copolymer yields and the solids content of the final latexes can be above 95 and about 40%, respectively. Based on experimental results the mechanism of this special kind of controlled radical polymerization under the peculiarities of aqueous heterophase polymerization is discussed.

Keywords: 1,1-Diphenylethylene; Heterophase polymerization; Controlled radical polymerization

1. Introduction

Controlled radical polymerization (CRP) has become one of the most rapidly growing topics in the field of polymer research in the last decade of the 20th century [1–4]. The use of CRP strategies in aqueous heterophase polymerization techniques is nowadays an actual topic of polymer research as it promises to be potentially of enormous practical importance [5–7].

From the mechanistic point of view almost all activities are based on either a reversible termination or a reversible chain transfer process [8]. Regarding reversible termination the activities are mainly focusing either on the utilization of stable nitroxide radicals (NMP—nitroxide mediated polymerization) or redox systems on the base of halogen compounds (ATRP—atom transfer radical polymerization). Dithio-compounds in combination with classical initiators for radical polymerizations play the central role in CRP via the route of reversible addition–fragmentation chain transfer (RAFT). Additionally to these techniques the degenerative chain transfer with iodine [9–12] and catalytic chain transfer [13] were also tested in aqueous systems. Recently, another method of controlling radical polymerizations based on 1,1-diphenylethylene (DPE) has gained some interest [14–24].

Typically, CRP is characterized by the two the features of livingness and control [25–27]. According to these criteria and in a strict sense the DPE method does not belong to the above mentioned CRP techniques as it only allows diblock copolymer formation but shows no real features of controllable chain extension (predictable molecular weight increase with conversion) and livingness regarding multi-block copolymer formation.

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Despite these peculiarities the DPE method appears to be an interesting alternative to the other methods if only block copolymer formation is the goal of controlling free radical polymerizations. In this sense it is the only technique based on entirely hydrocarbons, where no other ingredients such as halides, nitroxides, or metal ions are needed. Moreover, it can be applied easily under both hydrophobic and hydrophilic conditions as well as in industrial scale in bulk, solution and heterophase polymerizations ([14,17,22, 24]). Another difference to the other CRP-techniques is the fact that the DPE-method is a two-step procedure requiring in a first step the preparation of a precursor polymer in the presence of DPE. This precursor polymer is then used as the active species in a second polymerization, where block copolymer formation takes place. The activity of the precursor polymer is based on its unique structure which is the so-called α,*p*-dimer (Fig. 1) formed by combination termination of two DPE-ended radicals as experimentally proven and discussed extensively in Ref. [20].

Depending on the particular composition of the main monomer mixture the precursor polymer can be eventually either hydrophilic or hydrophobic. Including the precursor preparation the DPE method is a two-step procedure that can be carried out either as one pot reaction with consecutive monomer additions or spatially and timely separated. Especially the two-step one-pot procedure is economically interesting as it allows the adaptation of widely used semi-batch feeding procedures [28].

The precursor polymer can also be amphiphilic in nature and then it acts as both control agent and stabilizer during heterophase polymerization. Consequently, this type of amphiphilic precursor polymers might be considered as new class of reactive surfactants [29] specifically as controlsurfs. It is to mention that besides amphiphilic DPE precursor polymers also control agents for NMP, ATRP and RAFT can be prepared as controlsurfs. Moreover, there are several examples known, where surface active oligomers, which might be considered also as controlsurfs, are formed in situ during aqueous phase polymerizations controlled with hydrophilic RAFT agents [30–34]. However, the dithioester and the trithiocarbonate functional groups of the RAFT agents are prone to hydrolysis in aqueous media especially at basic pH and elevated temperatures [35–39]. Even though, the trithiocarbonates are less susceptible to hydrolysis than the dithioesters as experimentally proven in Ref. [37] the long-term stability during storage remains an issue. This susceptibility to hydrolysis might limit the application of RAFT agents in aqueous media, whereas it is no issue for DPE precursor polymers.

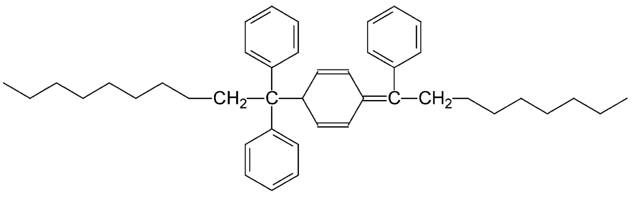


Fig. 1. α,*p*-Dimer unit.

The aim of this contribution is to report experimental results on the behavior of both the DPE during the precursor polymer preparation and the water-soluble precursor polymer during the second stage heterophase polymerization. Special emphasis is placed on polymerization results and on understanding the influence of all active species. After a brief description of the peculiarities of the behavior of DPE as well as of DPE-containing precursor polymers in radical polymerization deduced from the application of hydrophobic precursor polymers in solution polymerization of methyl methacrylate [20,22] the application of hydrophilic precursor polymers in styrene emulsion polymerization is discussed.

2. Experimental section

2.1. Materials

Methyl methacrylate (MMA, 99% purity), styrene (STY, 99% purity), and acrylic acid (AA, 99% purity) all from Sigma-Aldrich were distilled under reduced pressure before use. 1,1-Diphenylethylene (DPE, 99% purity, Acros Organics), potassium peroxodisulfate (KPS, purity ≥ 98%) and ammonium peroxodisulfate (APS, purity ≥ 98%) both from Sigma-Aldrich, 4,4′-azobis(4-cyano pentanoic acid) (ACPA) from Wako, 2,2′-azoisobutyronitrile (AIBN, pure) from Fluka, sodium dodecylsulfate (SDS) ultra pure from Roth, NH_3 solution 25 wt% from Roth, and carbon tetrabromide from Sigma-Aldrich were used as received. The symmetrical poly(ethylene glycol)-azo initiator with a molecular weight of the poly(ethylene glycol) chains of 200 g mol^{-1} (PEGA200) was prepared as described elsewhere [40]. The water for all experiments 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 polymerization.

2.2. Emulsion copolymerization with DPE

Batch-wise emulsion copolymerizations of STY and MMA with DPE were conducted either in a 250 ml all-glass reactor or in a reaction calorimeter. The glass reactor was equipped with stirrer, reflux condenser, nitrogen inlet and outlet, and a valve on the bottom to take samples during polymerization. The reaction calorimeter is a CPA200 (ChemiSens AB, Lund, Sweden) made of a material combination of glass (reactor walls) and stainless steel (316 SS for bottom, lid, and stirrer) and the polymerizations were conducted according to standard procedures ([41]). The polymerizations were carried out as follows: 53 g of degassed water and 0.33 g of SDS, 28.58 g of distilled monomer (either MMA or styrene), 1.53 g of DPE, and 10 g of ammonia solution buffer were charged under stirring and purged with nitrogen then, the mixture was heated to reaction temperature of 70 °C and the reaction was started by the addition of 2.26 g of APS dissolved in 5 g of water.

2.3. Preparation of hydrophilic precursor polymers

The polymerizations were carried out batch-wise in a 2000-ml all-glass reactor equipped with stirrer, reflux condenser, nitrogen inlet and outlet, a valve on the bottom to take samples during polymerization and a dropping funnel to charge the initiator solution. In particular, 525.5 g of degassed water were introduced under nitrogen in the polymerization reactor. Then 102 g of the main monomer, 183.1 g of AA, 15.3 g of DPE, and 99.1 g of ammonia solution buffer ($\geq 25\%$ in water, p.a, Roth) were charged under stirring and purged with nitrogen. The mixture was heated to reaction temperature of 70 °C. After at least 30 min the temperature was equilibrated, and the polymerization was started by dropping slowly over a period of time of 10 min 22.6 g of APS dissolved in 52.5 g of water. After 8 h the polymerization was stopped. The obtained latex was carefully purified by tangential flow ultrafiltration against distilled water through a low protein-binding modified poly(ether sulfone) membrane with a cut-off of 5000 g mol^{-1} (Minisette™ OMEGA 5Kd from Pall Gelman Laboratory). Distilled water was renewed and the ultrafiltration continued until the conductivity of the filtrate was constant. Then, freeze–drying was used to isolate the polymer from its solution.

2.4. Thermal polymerization

The polymerizations were carried out in glass vials placed in a rotation thermostat VLM20 (VLM GmbH, Leopoldshöhe, Germany) at 80 °C for 15 h. The agitation of the reaction mixture is due to an end-over-end rotation of the glass vials. About 10 rpm provide sufficient agitation. The following recipe was used: 7 ml of water, 1 ml of monomer, 0.04 g of AA–MMA–DPE terpolymer and 0.6 ml of ammonia solution. All ingredients were charged in the glass vials and purged with argon before placing them in the rotation thermostat and start heating to reaction temperature. The use of the rotation thermostat allows polymerizing simultaneously 24 samples.

2.5. Second step heterophase polymerization

The polymerizations were conducted in glass vials with the rotation thermostat at 80 °C for 8 h with styrene as main monomer with varying recipe components, which are detailed at corresponding positions in the text. Generally, solutions of the precursor polymer and the initiator in water were prepared separately. The total volume of the reaction mixture was 8.6 ml. Before placing the vials in the rotation thermostat the reaction mixtures were purged with argon. At the end of polymerization the polymer formed was analyzed with regard to the amounts of homopolymer and copolymer formed by the following procedure. In order to characterize the polymeric products regarding the copolymer content the following separation procedure was employed. Acetone acts twofold: As coagulation aid to break the parental latex and as poor solvent for polystyrene with a Flory–Huggins interaction parameter close to one [42]. In detail, 1 ml of the latex was dropped into 50 ml of acetone causing both the coagulation of the latex and the precipitation of the polystyrene homopolymer, which was then isolated, dried, and calibrated. The remaining solution was evaporated to dryness, and the remaining solid was mixed with water in order to dissolve the unreacted precursor polymer, whereas the copolymer of the precursor with styrene is insoluble in water. The precipitate was isolated, dried in vacuum at 50 °C, and calibrated.

2.6. Polymer characterization

The surface tension measurements were carried out with a tensiometer TD1 (Lauda) according to the Du Nouy ring method at room temperature.

Membrane osmometry was performed with an Osmomat 070/090 (Gonotec, Berlin, Germany) using a two-layer cellulose triacetate membrane with a molecular cutoff of 5000 g mol^{-1} in water at room temperature.

The molecular weight distributions of the water-soluble precursor polymers were determined by size exclusion chromatography (SEC) consisting of degasser, pump 515, column heater and a RI-detector (DRI 2410). SEC was carried out at 35 °C with water/acetonitrile (50/50 vol/vol) mixture as eluent at a flow rate of 1 ml min^{-1} and a column set consisting of two Suprema columns (PSS, Mainz, Germany) of hydroxylated PMMA with a pore size of 1000 and 3000 Å. The molecular weights were estimated from a calibration curve based on polyethylene oxide standards (PSS, Mainz, Germany).

SEC in dimethyl acetamide (DMA) was performed for the characterization of the block copolymers using a P1000 pump from thermo separation products (TSP), equipped with a RI-detector (Shodex RI-71) and UV2000 detector (270 nm, TSP) at 70 °C and an eluant flow rate of 1 ml min^{-1}. A column set was employed consisting of four 10 μm $4\times300\ \mathrm{mm}^2$ PSS-Gram columns having pore sizes of 30, 30, 1000 and 3000 Å from PSS (Mainz, Germany). Molecular weight distributions were calculated from a calibration curve based on polystyrene standards.

Molecular weight distributions of polystyrene polymers prepared in the presence of DPE were determined by SEC in THF. That was carried out by injecting 100 μl of about 0.15 wt% polymer solutions in a thermo separation products set-up being equipped with UV (TSP UV1000) and RI (Shodex RI-71) detectors in THF at 30 °C with a flow rate of 1 ml per minute. A column set was employed consisting of three $300\times8\ \mathrm{mm}^2$ columns filled with a MZ-SD plus spherical polystyrene gel (average particle size 5 μm) having pore sizes of 10^3, 10^5, and 10^6 Å, respectively. This column set allows a resolution down to molecular weight less than 500 g mol^{-1}.

2.7. Latex characterization

The latexes were characterized regarding the solids content (SC) with a HR73 Halogen Moisture Analyzer (Mettler Toledo, Gieβen, Germany) and average particle size (D_i, intensity weighted average particle size) with dynamic light scattering (NICOMP particle sizer model 370, particle sizing systems, Santa Barbara, CA, USA). Additionally some latex samples were investigated with transmission electron microscopy (TEM) with a Zeiss EM 912 Omega microscope operating at 100 kV.

3. Results and discussions

3.1. DPE in radical heterophase polymerization

Due to its molecular structure and the ability to stabilize radicals and ions DPE behaves peculiarly in polymerization processes as by any chain growth mechanism homopolymerization to higher molecular weights is practically impossible [43]. But it can be used as comonomer in anionic polymerizations to prepare for instance copolymers with styrene possessing an increased glass transition temperature [44,45]. Also, it is confirmed that it is impossible to get homopolymers of DPE by radical polymerization mechanism [46] but it can participate in copolymerizations [47–54]. The presence of two phenyl groups at the radical carrying carbon atom causes not only steric hinderance for further monomer addition but also stabilizes the radical by electron delocalization. The reactivity ratios of DPE estimated from copolymerization results confirmed the inability of DPE to homopolymerize [48,49,52,55] and in the cases of acrylonitrile, methacrylonitrile, and acrylamide as comonomers the reactivity ratio for DPE was found to be very close to zero [48,52].

In a preceding publication [20] it was shown that DPE acts also in aqueous emulsion copolymerization with MMA as typical degradative chain transfer agent causing a decrease in both the rate of polymerization and the average molecular weight. Moreover, the presence of DPE leads to a considerable narrowing of the molecular weight distribution. Under the particular experimental conditions the cumulative molecular weight distributions were characterized by $M_w/M_n = 1.975$ ($M_n = 4\times10^3$ g mol^{-1}) and 91.2 ($M_n = 3.4\times10^4$ g mol^{-1}) in presence and absence of DPE, respectively. Beside the effects on polymerization rate, final conversion, and molecular weight distribution the emulsion copolymerization of MMA with DPE proceeds without any other conspicuousness. Contrary, the emulsion polymerization of styrene under identical experimental conditions is much more influenced. The conversion of the styrene polymerization levels off at about 50% after 24 h, whereas it is already about 80% for MMA after 15 h. Moreover, a rapid phase separation is observed during the styrene polymerization after stopping the stirrer, where the upper organic phase is of yellowish color. The color of the organic phase becomes more intense and the turbidity of the aqueous latex phase lowers with increasing polymerization time. The cumulative average molecular weight of the polymer in both phases is identical with M_n and M_w values in the range of 1000–2000 and 4000–7000 g mol^{-1}, respectively. Moreover, after particle nucleation the molecular weight decreases continuously during the following 6 h before it increases until the polymerization was stopped after 24 h. These rather unusual effects are still under further investigation and will be considered in detail in a forthcoming publication.

3.2. Preparation of the hydrophilic precursor

For the following study a hydrophilic precursor polymer made by surfactant-free terpolymerization of MMA, acrylic acid, and DPE was exclusively utilized. The polymerization starts with a monomer in water emulsion but the final state is a polymer solution due to the fact that the terpolymer is under the basic pH conditions soluble in water. However, the data summarized in Table 1 reveal that the polymerization recipe is obviously well balanced as any modification led to the formation of dispersions. Even if NH_3 was omitted and only added after the polymerization it was not possible to dissolve the polymer. Also replacing DPE by carbon tetrabromide as chain transfer agent caused the formation of water-insoluble polymer.

The structural analysis of the amphiphilic precursor by MALDI-TOF and NMR spectroscopy as it was successfully done for the hydrophobic precursor [20,22] with only PMMA homopolymer chains attached to the α,*p*-dimer unit turned out to be not unambiguously possible. Obviously, the statistical copolymer chains impede invincible problems regarding a clear analysis of the terpolymer structure. Suppose a DPE radical is equally inactive for either type of penultimate units (MMA or acrylic acid) the assumption seems fair that the hydrophilic precursor has an analogous structure as determined for the hydrophobic precursor [20, 22] and depicted in Fig. 2. Furthermore chain transfer to polymer might be neglected under the particular

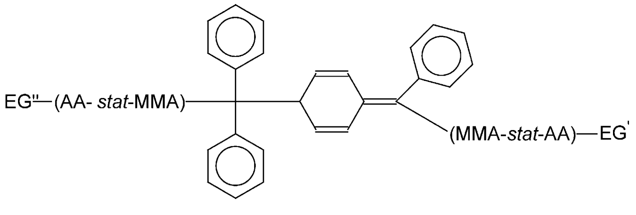


Fig. 2. Sketch of the structure of the hydrophilic precursor polymer with MMA-*stat*-AA copolymers attached to the α,*p*-dimer unit, EG′, EG″-end groups.

Table 1
Influence of modifications of the recipe components on the state of the reaction mixture at the end of the polymerization (S, solution; D, dispersion)

MMA	AA	DPE	CBr_4	NH_3	SDS	State
y	**y**	**y**	**n**	**y**	**n**	**S**
y	y	y	n	n	y	D
y	y	n	n	y	n	D
y	y	n	y	y	n	D
y	n	y	n	n	y	D

The bold line corresponds to the standard recipe for the production of the hydrophilic precursor polymer; y, applied; n, not applied; recipe: 57.5 g of water, 10.2 g of AA, 18.3 g of MMA, 1.5 g of DPE, 9.9 g of NH_3 (25%), 2.25 g of APS, 80 °C.

polymerization conditions as it was observed to poly(acrylic acid) homopolymers during bulk polymerization [56].

Exactly, like described for the hydrophobic precursor, also the hydrophilic precursor polymer causes the decoloration of a bromine solution [20]. This decoloration is a characteristic reaction to prove the presence of the semiquinoid structure as none of the corresponding polymers including the DPE–styrene copolymers react in the same way.

According to its structure the hydrophilic precursor possesses some surface activity at pH conditions, where the acrylic acid groups are deprotonated as proven by the surface tension–concentration plots shown in Fig. 3.

It is interesting to note that the surface tension–concentration plot shows no sign of a critical concentration up to concentration of 20 g l^{-1} but the surface tension steadily decreases.

Due to the surface activity of the precursor polymer the determination of its molecular weight is not an easy undertaking as both adsorption and association processes might influence the measurements. However, the determination of a value for the number average molecular weight was possible by membrane osmometry in aqueous solution at room temperature and resulted in 7300 g mol^{-1}. SEC of the amphiphilic terpolymer was possible with water/acetonitrile (50/50 vol%) mixture. The chromatograms depicted in Fig. 4 show that the amount of DPE in the monomer mixture has only minor influence on the elution behavior. Supposed the copolymer composition has no influence on the hydrodynamic volume or the terpolymer composition does not change significantly with the DPE concentration, the SEC-data indicate that a higher amount of DPE in the monomer mixture causes a decrease in the molecular weight.

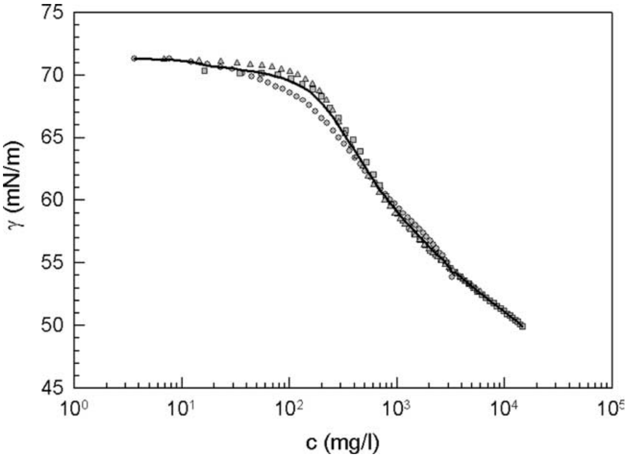


Fig. 3. Surface tension–concentration plots of aqueous solutions of the hydrophilic precursor polymer prepared with 5 wt% DPE relative to the overall amount of monomer, symbols represent three repeats and the line represents the averaged curve.

3.3. Heterophase polymerization with amphiphilic α,p-dimer precursor polymers

According to the mechanism of structural control in radical polymerization with DPE-precursor polymers as discussed in Ref. [22] a common reaction scheme for aqueous heterophase polymerization with hydrophobic monomers can be deduced as shown in Fig. 5.

The concentration of all active species (precursor polymer, initiator, monomer), the nature of the primary initiator radicals (R), the polymerization as well as copolymerization behavior of the second stage monomer, and the monomer combination of the precursor polymer are all of crucial importance for the obtainable degree of control expressed as block copolymer yield.

In brief, the polymerization reaction starts conventionally by initiator decomposition and addition of monomer molecules to primary radicals. Subsequently, the addition of

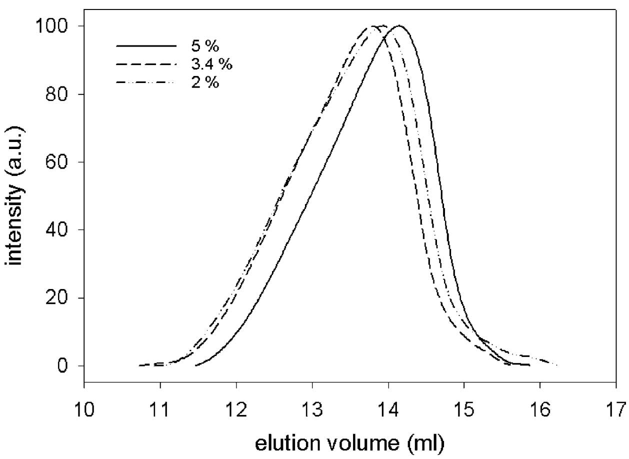


Fig. 4. SEC chromatograms of amphiphilic (MMA-*stat*-AA) precursor copolymers prepared with various amounts of DPE in the monomer mixture, solid line 5, dashed line 3.4, and dashed-dotted line 2 wt% DPE.

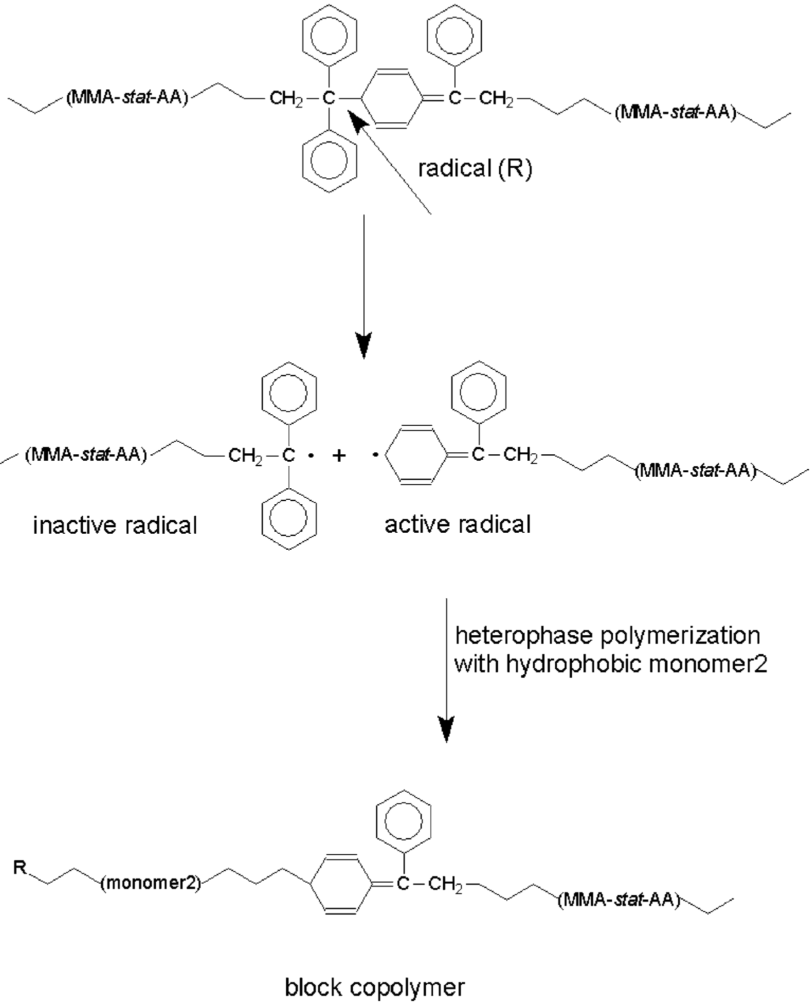


Fig. 5. General scheme of the action of amphiphilic precursor polymers and block copolymer formation in aqueous heterophase polymerization.

monomer molecules is continued until a DPE-containing precursor polymer is met. After the attack of a growing or a primary radical upon the semiquinoid structure at least two possibilities exist. If the initiator concentration is high in comparison to the precursor polymer, side reactions between the polymeric, DPE-terminated radical (denoted as inactive radical in Fig. 5) and primary radicals are favored. Contrary, if the PMMA–DPE copolymer is in excess in comparison with primary initiator radicals, the recombination reaction between two DPE terminated polymeric radicals becomes more and more likely leading to a recovery of the α,p-dimer unit and hence, the control ability is preserved. If, however, a monomer molecule or a growing radical reacts with the active precursor radical with a cyclohexadienyl moiety block copolymer formation takes place. According to the presented mechanism each α,p-dimer unit, that is each precursor polymer molecule, allows at maximum the formation of only one diblock copolymer molecule and hence, there is obviously no chance to get multi block copolymers.

In heterophase polymerizations the amphiphilic precursor polymer influences both the kinetics of the polymerization process and the colloidal properties of the resulting polymer dispersion. In particular, it directly participates in the particle nucleation process as the properties of the initially formed block copolymers determine the precipitation. Moreover, the adsorption behavior of the unreacted amphiphilic precursor polymer contributes to particle stabilization.

For an unseeded, ab initio emulsion polymerization the conditions regarding the structural control with amphiphilic precursor polymers differ before and after particle nucleation. Due to the amphiphilic nature of the precursor polymer the additional use of normal emulsifiers is not necessary. This means for the (MMA-*stat*-AA) copolymer precursor that initially no micelles are present (cf. surface tension data, Fig. 3) but the molecules of the controlsurf are mainly distributed between the aqueous phase and the monomer droplet interface. Hence, the reaction starts in the aqueous phase as solution polymerization, where the control efficiency is governed by the probability of encounter between a free radical and an α,p-dimer unit. Particle formation takes place via precipitation of either block copolymers or homopolymers of the second stage monomer.

The portion of each on the nucleation depends on the particular concentration ratios of all active components as discussed for homogeneous polymerizations in Ref. [22]. After the particle nucleation both the (MMA-*stat*-AA) copolymer parts of the formed block copolymers and the remaining precursor polymer molecules are located predominantly at the particle water interface acting as electrosteric stabilizer. Hence, a situation is created, where the structural control in the further course of the polymerization depends on the transfer of growing radicals through the interface and the probability of meeting an α,*p*-dimer on that passage. Contrary, any free radical entering the particles without contacting an α *p*-dimer control unit leads to the formation of homopolymer of the second stage monomer. The situation after particle nucleation is sketched in Fig. 6. Accordingly, under the heterogeneous reaction conditions after particle nucleation, the surface to volume ratio of the monomer swollen polymer particles is, additionally to the control criteria for homogeneous systems [22], another crucial parameter.

3.4. Variation of the precursor polymer concentration

It is to be mentioned that under optimized conditions, block copolymer yields of up to greater than 90% can be obtained ([22]).

The following results of styrene emulsion polymerizations with the MMA-*stat*-AA–DPE controlsurf (further on named as precursor or precursor polymer) underline the complexity of the reaction mechanism of heterophase polymerizations with double-functioning hydrophilic DPE precursor polymers. Each experimental data point is an average of at least four and at maximum 10 repeats. The block copolymer yield (BCY) relative to the amount of styrene strongly depends on the mass ratio precursor polymer to monomer ($\Phi_{pr/m}$) as shown in Fig. 7 for three different initiating systems.

The shape of the BCY–$\Phi_{pr/m}$ dependence as indicated by the enveloping lines of the data points in Fig. 8 reveals the strong influence of the precursor concentration on the block copolymer yield. Interestingly, both the initiator concentration and the kind of initiation are apparently only of minor influence. The conditions to get maximum BCY are summarized in Table 2. All three dependencies are characterized by a rather narrow range of $\Phi_{pr/m}$ values describing the maximum BCY. More specifically, the data hint that the steepness of the curves is obviously influenced by the primary radical stream. For the lower initiator concentration ($\Phi_{m/I}=455$, black dots) the curve is much steeper than for both the higher ACPA concentration ($\Phi_{m/I}=51$, grey triangles) and the thermally initiated polymerization. The latter two data sets are almost coinciding. This behavior might be explained with the different loci of primary radical formation, which are the droplets or monomer-swollen particles and the aqueous phase in the case of the thermal initiation and the chemical initiation with ACPA, respectively. A high primary radical flux is given in both cases, however, each from opposite sides of the droplet or particle interface, where the precursor is located.

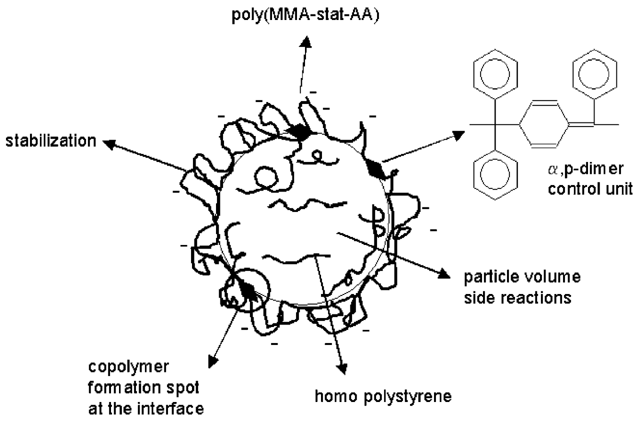


Fig. 6. Sketch of the conditions during DPE-controlled radical heterophase polymerization after particle nucleation.

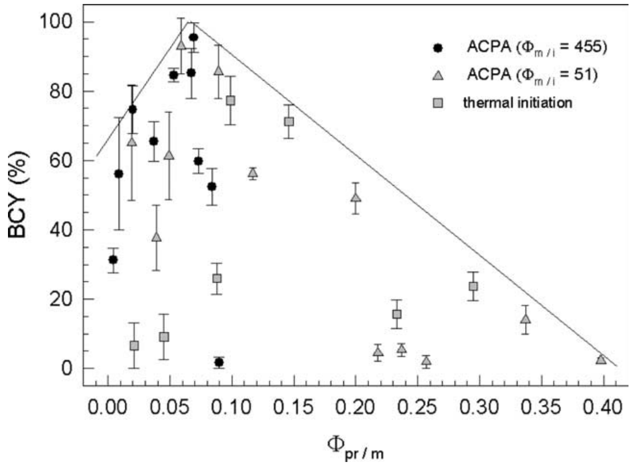


Fig. 7. Block copolymer yield as function of the mass ratio precursor to monomer in the final latexes for chemical initiation by means of ACPA at two mass ratios monomer to initiator ($\Phi_{m/i}$) and thermal initiation thus, realizing three different primary radical fluxes, recipe: 7 ml of water, 1 ml (~0.91 g) of styrene, 0.6 ml of aqueous ammonia solution (25 wt%), 18 or 2 mg of ACPA and variable amounts of precursor polymer (MMA-*stat*-AA–DPE controlsurf), 80 °C.

In general, the maximum in the BCY–$\Phi_{pr/m}$ curves might be explained in the way that an increasing amount of precursor leads to an increased probability of activating the

Table 2
Maximum block copolymer yield for the various initiating conditions as depicted in Fig. 8 and the mass ratios precursor to monomer ($\Phi_{pr/m}$) and precursor to initiator ($\Phi_{pr/i}$) at maximum BCY ($\Phi_{pr/I}$ is not applicable (n.a.) for thermal initiation)

Initiation	Maximum BCY (%)	At $\Phi_{pr/m}$	At $\Phi_{pr/I}$
ACPA $\Phi_{m/I}=51$	93.0	0.059	3
ACPA $\Phi_{m/I}=455$	95.4	0.069	26
Thermal	77.3	0.099	n.a.

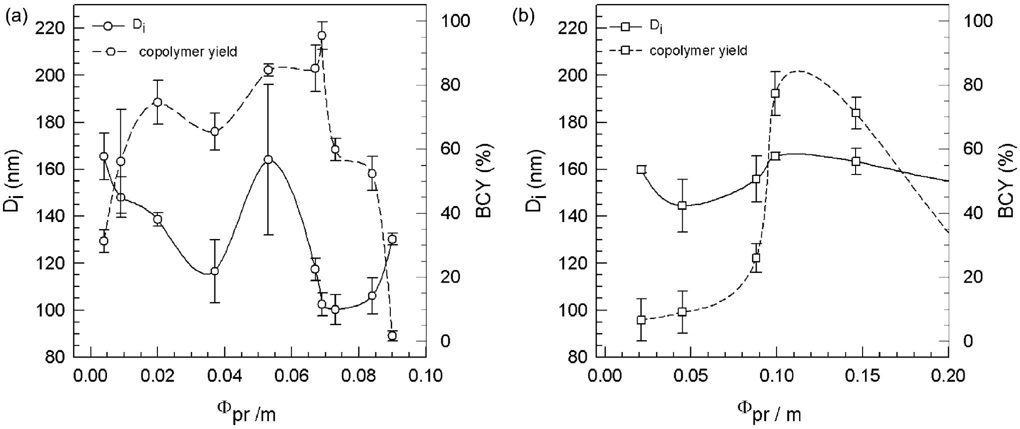


Fig. 8. (a) Average particle size and BCY in dependence on $\Phi_{pr/m}$ for initiation with ACPA at $\Phi_{pr/i}=455$ (polymerization condition cf. caption of Fig. 7). (b) Average particle size and BCY in dependence on $\Phi_{pr/m}$ for thermal initiation (polymerization condition, caption of Fig. 7).

α,p-dimer unit and hence, causes a higher BCY in the proper concentration ranges of the active components until the maximum is reached. It seems reasonable that both $\Phi_{pr/I}$ and $\Phi_{pr/m}$ are smaller for higher radical fluxes (lower $\Phi_{m/I}$-value). Contrary, the further increase in $\Phi_{pr/m}$ beyond the optimum values results in decreasing BCY as obviously the concentration of activated precursor polymers is so high that they are either wasted in mutual side reactions or in recombination reactions with primary or oligomeric radicals whose reaction products are not identified as block copolymers in the separation procedure because they are still soluble in acetone.

Due to the double function of the precursor polymer as controlsurf one might expect a relation between the average particle size and the BCY. The data put together in Fig. 9(a) and (b) for chemical and thermal initiation seemingly confirm this hypothesis as both the D_i–$\Phi_{pr/m}$ and the BCY–$\Phi_{pr/m}$ curves have a similar shape in either case.

However, also differences between the initiating systems are clear to see. The course of both dependencies appears for thermal initiation much smoother than for chemical initiation. The jumpy shape of the curves for chemical initiation (Fig. 8(a)) might be explained by the contribution of initiator derived cyano pentanoic acid end groups assisting or interfering with latex particle nucleation and stabilization. Evidently, the further path of the polymerization and also the final latex properties are strongly influenced by slight changes during the nucleation period and stabilization of the particles. As such interference is not possible in the case of thermal initiation the dependencies as depicted in Fig. 8(b) are much smoother.

The average molecular weight of the block copolymers as determined by SEC in DMF calibrated with polystyrene standards, which might be considered only as a hint regarding the real values, merely slightly changes with $\Phi_{pr/m}$ (data not shown here). Exemplary, in the range of $\Phi_{pr/m}$ between 0.004 and 0.084 the number average molecular weight and the polydispersity index (ratio

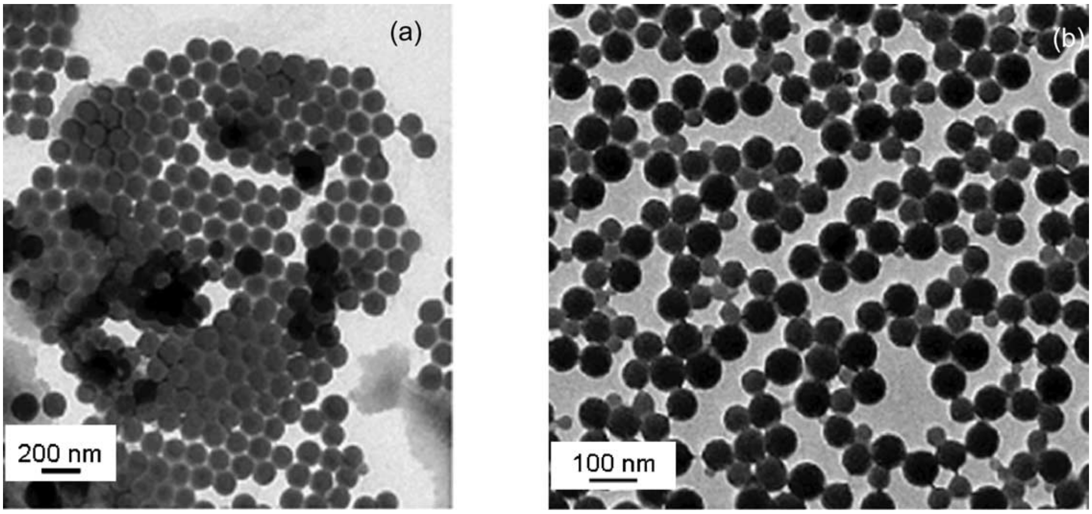


Fig. 9. (a) TEM picture of latex particles prepared at low amount controlsurf ($\Phi_{pr/m}=0.004$). (b) TEM picture of latex particles prepared at higher amount controlsurf ($\Phi_{pr/m}=0.069$).

between weight and number average molecular weight) vary between 1 and 2×10^5 g mol^{-1} and 4–8, respectively, for $\Phi_{pr/i}=455$ and ACPA as initiator. The values of the polydispersity index are in the lower range of values typical for heterophase polymerization, where the different reaction loci can cause even polydispersity indices larger than 10.

The surface tension of the final latexes of Fig. 8(a) is between 60 and 70 mN/m with the greater values measured for lower $\Phi_{pr/m}$. These data point to a not complete consumption of the precursor polymer especially if higher amounts are applied.

The influence of the concentration of the controlsurf on the particle size distribution (PSD) is illustrated by the TEM pictures in Fig. 9 at $\Phi_{pr/m}=0.004$ and $\Phi_{pr/m}=0.069$. The difference in the PSD proves the action of the controlsurf as surfactant, whereas the data in Figs. 7 and 8 demonstrate its action as control agent mediating block copolymer formation. For low stabilizer concentrations the particles are larger and PSD is quite monodisperse (Fig. 9(a) for $\Phi_{pr/m}=0.004$). The particles get smaller and its distribution broadens with increasing stabilizer concentration of $\Phi_{pr/m}=0.069$, which corresponds to the optimum value regarding BCY (Fig. 9(b)). This is exactly the same behavior as observed for classical emulsion polymerization with 'normal' low molecular weight surfactants.

The pretty large error bars associated with the data in Figs. 7 and 8 show that the polymerizations in dependence on $\Phi_{pr/m}$ or $\Phi_{pr/i}$ are afflicted with a larger error than 'normal' radical heterophase polymerizations. This might be attributed to the particular conditions by the use of the controlsurf causing a competition between its action as control agent and stabilizer.

3.5. Variation of the initiator concentration

The mechanism of block copolymer formation as discussed above and in Ref. [22] requires a dependence of the BCY on the initiator concentration as it is indeed observed (Fig. 10).

The BCY increases with increasing ACPA concentration as expected. If the initiator concentration is not too high an increasing radical concentration should lead to a higher number of attacks of free radicals upon the α,*p*-dimer unit (Fig. 5 and Section 3). Regarding the colloidal properties of the latexes the increasing initiator concentration causes an increase in the average particle size (or decrease in the particle concentration) as shown in Fig. 11. This result means that the overall stabilizing ability of the bound MMA-*stat*-AA copolymer is reduced compared with the free controlsurf.

3.6. Variation of the monomer concentration

The enormous influence of the styrene concentration at unchanged concentration ratios between monomer, initiator, and precursor polymer is exemplified by the data shown in Fig. 12. In that particular set of experiments the conditions for the maximum yield as depicted in data line 2 of Table 2 were applied that is $\Phi_{pr/i}=26$ and $\Phi_{m/i}=455$. The increase in the monomer concentration up to a factor of 5 allowed the preparation of stable latexes with solids contents as high as 37% with less than 2% of coagulum relative to the amount of monomer.

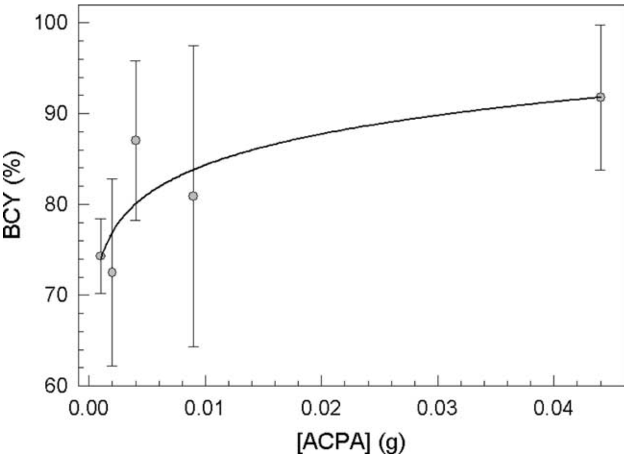


Fig. 10. Block copolymer yield in dependence on the amount of ACPA; filled circles are experimental points and the solid line is a fit of the data points, recipe: 7 ml of water, 1 ml (~0.91 g) of styrene, 0.6 ml of aqueous ammonia solution (25 wt%), 0.0537 g of precursor polymer (MMA-*stat*-AA–DPE controlsurf), variable amounts of ACPA, 80 °C, BCY values are averages of four repeats.

Expectedly, the average particle size in the final latexes changes with the amount of monomer. The nearly linear increase of D_i with v_{sty} implies a decreasing number of particles. Indeed, the particle number drops by almost an order of magnitude from 2.6×10^{14} to 3.2×10^{13} ml^{-1} of water at 1 and 5 ml of styrene, respectively. It is a somehow astonishing result as one might expect an unchanged number of particles due to the use of equal concentration ratios between monomer, precursor, and initiator. This behavior points to limited flocculation due to either the increasing solids content of the latexes (higher density of colloidal objects) or the increased ionic strength, however, without endangering the colloidal stability of the whole polymerizing system.

Furthermore, the results of Fig. 12 prove the importance of the interface as reaction locus for the activation of the α,*p*-dimer unit of the precursor polymer and hence also for controlling the block copolymer yield as discussed in context with Fig. 6. The BCY clearly depends on the volume to surface ratio (VSR) of the latex particles, which increases proportional to the average particle size.

3.7. Variation of the nature of the initiator

From the data in Figs. 7 and 8(a) and (b) and Table 2 one might already expect an influence of the nature of the initiator on the BCY at otherwise unchanged conditions. This expectation is verified by the data in Table 3 obtained

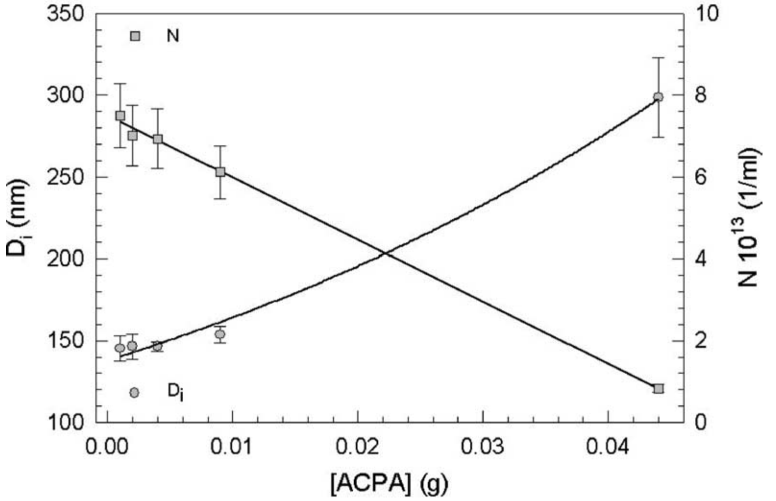


Fig. 11. Change of average particle size (D_i) and particle number (N per ml of water) in dependence on the amount of ACPA; recipe: 7 ml of water, 1 ml (~0.91 g) of styrene, 0.6 ml of aqueous ammonia solution (25 wt%), 0.0537 g of precursor polymer (MMA-*stat*-AA–DPE controlsurf), variable amounts of, 80 °C, values are averages of four repeats.

for various initiators at equimolar concentration. Note, these conditions are not the optimum conditions for each system even not for ACPA ($\Phi_{pr/i}=18.7$ and $\Phi_{m/i}=377$). Hence, these data only allow a comparison regarding the influence of the nature of the primary initiator radical and not an evaluation of the initiators regarding the optimum conditions.

The overall monomer conversion and the amount of coagulum strongly depend on the nature of the initiator. The higher amount of the coagulum for PEGA200 and AIBN is due to the solubility of these compounds in the styrene monomer phase. There is no clear explanation for the lower conversion in the case of PEGA200.

Surprisingly, the BCY is for all investigated initiators—except KPS—almost identical between 65 and 70% in average. Obviously, the particular conditions are for KPS closest to the optimum values.

The surface tensions of all the latexes mentioned in Table 3 except the one prepared with PEGA200 as obtained after the polymerizations are above 70 mN m^{-1}. This high value proves a vanishingly low concentration of free controlsurf in the continuous water phase.

Also, there is no distinct dependence of the average particle size on the kind of initiator may be except for PEGA200, where slightly larger average particles are measured by dynamic light scattering. Both the lower

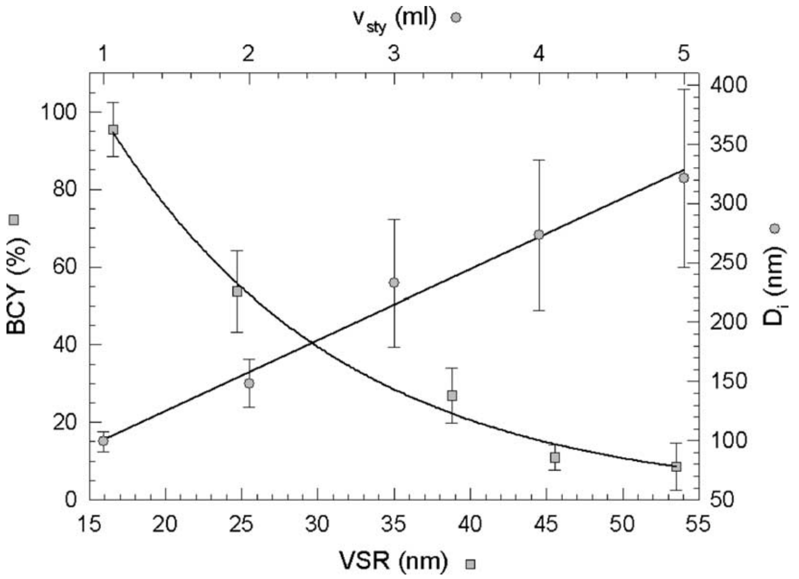


Fig. 12. Dependencies of the average particle size on the total volume of monomer (v_{sty}) (right y-axis and top x-axis) and of the block copolymer yield on the volume to surface ratio (VSR) of the latex particles (left y-axis and bottom x-axis); recipe: 7 ml of water, 1–5 ml of styrene, 0.6 ml of aqueous ammonia solution (25 wt%), variable amount ACPA, and variable amount of precursor polymer (MMA-*stat*-AA–DPE controlsurf), 80 °C.

Table 3
Influence of the nature of the initiator on the emulsion polymerization of styrene with MMA-*stat*-AA–DPE controlsurf, recipe: 7 ml of water, 1 ml of styrene, 0.6 ml of aqueous ammonia solution (25 wt%), amount of the initiators corresponding to 8.6×10^{-6} moles, and 0.045 g of precursor polymer (MMA-*stat*-AA–DPE controlsurf), 80 °C

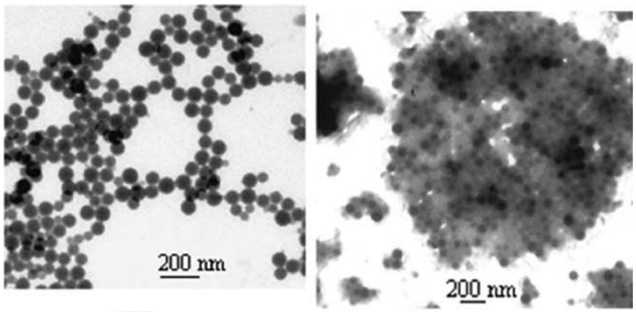
Parameter	KPS	ACPA	PEGA200	AIBN	APS
Conversion (%)	>98	>98	72±4	94±4	>98
Coagulum (%)	0.4	0.3	9.8	14.1	0.1
D_i (nm)	102.5±6.6	100.7±1.1	114.1±7.8	102.8±3.8	99.3±8.5
BCY (%)	90.7±10.3	69.6±16.3	64.8±12.0	64.6±12.0	673±7.8

overall conversion and the higher average particle size obtained for PEGA200 are unusual for this kind of initiator as with a variety of other anionic and cationic surfactants smaller particles and faster rates have been obtained compared with persulfate and other initiators [57]. A clue for an explanation can be obtained from TEM pictures as shown in Fig. 13.

For PEGA200 as initiator the TEM pictures reveal a stronger interaction between the latex particles compared with the other initiators. This stronger interaction is very likely the case also in the dispersed state and can cause the slightly higher average particle size determined by dynamic light scattering. Only when PEGA200 was used as initiator this kind of massive clustering of the particles was observed. The poly(ethylene glycol) chains introduced by PEGA200 as end groups can strongly interact with carboxylic acid groups arising from the controlsurf even at pH values above 8 [58]. This specific interaction might also be responsible for the lower conversion compared with the other initiators.

Table 3 reveals the interesting result that for this particular control strategy of radical heterophase polymerizations the nature of the primary radical is almost unimportant. This is underlined contrary for radical heterophase polymerization controlled with reversible addition fragmentation chain transfer agents, where a strong influence of the nature of the primary radical (carbon versus peroxo primary radicals) was observed [59].

Another astonishing result is the difference in the block copolymer yield between APS and KPS, which is clearly outside of the experimental error. Although differences between APS and KPS have been observed in both other heterophase polymerization systems [57] and during persulfate decomposition investigations [60] a satisfying explanation for this effect requires further investigations. Recently, differences in the distribution of sodium and ammonium ions in dried latex films made by emulsion polymerization of styrene, butyl acrylate, and acrylic acid in the presence of a poly(ethylene glycol) groups containing surfactant have been observed with element specific transmission electron microscopy [61]. These findings support the above results regarding the influence of the nature of the counterion on heterophase polymerization at least for active components containing acrylic acid and ethylene oxide units. In general, these considerations are obviously also in accordance with differences in the binding of counterions to polyelectrolytes [62].



APS PEGA200

Fig. 13. TEM picture of final latexes prepared according to the conditions in Table 3 with APS and PEGA200 as initiator.

In conclusion, the application of controlsurfs with α,*p*-dimer units of DPE in aqueous heterophase polymerization is a promising route to prepare block copolymer particles almost without any remaining free stabilizer in the continuous phase. Latexes made of block copolymer particles with high solids content are attainable without the addition of low molecular weight surfactants, which is an interesting feature for potential applications as coatings or adhesives. In order to get optimum results a well-balanced recipe is required as the reaction is sensitive regarding slight variations in the concentration ratios of the active components monomer, initiator, and controlsurf.

Acknowledgements

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