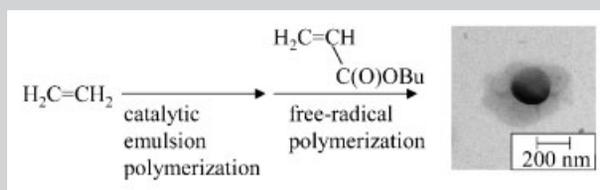


Summary: Free radical emulsion polymerization of styrene (S) or butyl acrylate (BA) in the presence of latices of linear polyethylene (PE) prepared by catalytic emulsion polymerization affords colloiddally stable multiphase latices. Coagulation of a PE/PS latex affords nanocomposites composed of small PE phases dispersed in a PS matrix, as evidenced by the large supercoolings of PE crystallization (by DSC). TEM of PE/PBA latices indicates a PBA phase around the PE particles under the emulsion polymerization conditions investigated. Films formed from these dispersions exhibit homogeneously dispersed PE particles.



Multiphase latices are obtained by free radical emulsion polymerization of butyl acrylate in the presence of latices of linear polyethylene (PE) prepared by catalytic emulsion polymerization.

Multiphase Polymer Dispersions and Nanocomposites by Catalytic/Free Radical Emulsion Polymerization^a

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Introduction

Emulsion polymerization is one of the most important and versatile polymerization processes.^[1] About 10 million tonnes of polymer latices are produced annually for a variety of applications, such as coatings and paints. A key step in most applications is film formation upon evaporation of the dispersing medium, rendering aqueous dispersions particularly environmentally benign.

Polymer dispersions containing not only one but two or more distinctly different types of polymer phases are frequently used in many applications. Multiphase latices can possess a multitude of morphologies, ranging from core-shell structures to hemispherical particles, “raspberry” structures (i.e. large particles with small particles on their surface) and separate particles of different polymers. Thermodynamic and kinetic techniques can determine the

morphology of an individual system under a given set of polymerization conditions.^[2] While it is evident that various factors such as the surface tension of the various polymer phases towards water and towards each other, optionally cross-linking, the polymerization temperature, and the type of polymerization process play a role, the synthesis of multiphase latices is still empirical to a large degree.

Polyolefin latices are attractive for a number of reasons. Amongst others, the raw materials are obtained directly from cracking of hydrocarbon feedstock, without the need for further energy- and raw-material-consuming conversion to other monomers (such as styrene, acrylates or vinyl acetate), making polyolefin latices both economically and environmentally attractive.^[3] The crystallinity of a given polyolefin, for example, polyethylene, can be varied over a wide range. As for the accessibility of polyolefin latices, free radical emulsion polymerization of ethylene suffers from the necessity of working at very high pressures (2000 bar) and a low variability regarding tailoring of the polymer microstructure.^[4] The preparation of secondary dispersions usually requires large amounts of solvents, and is also viable only for low-molecular-weight polymers.^[5] Moreover, the necessity of a second dispersing step is

^a Supporting information for this article is available at the bottom of the article's abstract page, which can be accessed from the journal's homepage at <http://www.mrc-journal.de>, or from the author. Supporting information shows the conversion over time diagram; AFM images of a PE/PS latex at different temperatures.

economically disadvantageous. In contrast, catalytic emulsion polymerization can yield latices of polyethylenes with a wide range of crystallinities and molecular weights,^[6–8] substantially increasing the attractiveness of polyolefin latices in general. We now report for the first time the synthesis of multiphase polymer dispersions by free radical emulsion polymerization in the presence of latices from catalytic polymerization.

Experimental Part

General Considerations

Demineralized water was distilled under argon. Styrene (Fluka), butyl acrylate (Lancaster) and potassium peroxydisulfate (Lancaster) were used without further purification.

Differential scanning calorimetry (DSC) was performed on a Perkin Elmer DSC 7 instrument or on a Pyris 1 DSC at a heating and cooling rate of 10 K·min⁻¹. Heating curves reported are second heats. Transmission electron microscopy (TEM) investigations were carried out on a LEO 912 Omega apparatus with an acceleration voltage of 120 kV. Samples were stained with RuO₄. Atomic force microscopy (AFM) experiments were performed with a Molecular Imaging Pico II scanning probe microscope. The height and phase images were obtained simultaneously while operating the instrument in the tapping mode under ambient conditions. Images were taken at the fundamental resonance frequency of the Si cantilevers, which was typically around 170 kHz. Typical scan speeds during recording were 0.3–1 line/s using scan heads with a maximum range of 120 × 120 μm. The phase images represent the variations of relative phase shifts (i.e. the phase angle of the interacting cantilever relative to the phase angle of the freely oscillating cantilever at the resonance frequency) and are thus able to distinguish materials by their material properties (e.g. amorphous and crystalline polymers).

Polymerization Procedure

Polyethylene latices were prepared according to ref.^[6f] In short, a miniemulsion of a solution of a catalyst prepared in situ from chloranil, triphenylphosphane and bis(1,5-cyclooctadiene)-nickel in a small amount of toluene (ca. 2 mL; 98 mL water, SDS as a surfactant) was exposed to 40 bar ethylene in a pressure reactor at 50 to 70 °C, affording the PE latex.

The second-stage emulsion polymerization was carried out in a 250-mL glass reactor equipped with a blade stirrer (260 rpm), an argon inlet and a reflux condenser. The reaction temperature (80 °C) was controlled by means of an oil bath. Polyethylene latex, water and the second-stage monomer were added into the reactor and heated to 80 °C under continuous argon flow. The reaction was started by the addition of an aqueous solution (1.5 mL) of the initiator. The polymer latex formed was filtered through a funnel packed with glass wool, to determine and separate any coagulate formed. For DSC measurements, the PE/PS latex was added to an excess of methanol, the precipitated polymer was isolated, washed with methanol, and dried in vacuo (for the PE/PBA latices the precipitation was

not applicable). Alternatively, the PE/PS or PE/PBA latex was dried at room temperature (1 atm), the residue was stirred with water to remove the surfactant, and then filtered, washed with water, and dried in a vacuum.

Results and Discussion

Dispersion Synthesis

Polyethylene latices were prepared by nickel(II)-catalyzed emulsion polymerization.^[6f] The latices are composed of linear polyethylene (PE) with \bar{M}_n in the range of 2×10^3 to 3×10^3 g mol⁻¹, and \bar{M}_w/\bar{M}_n in the range 2 to 5. Polymer crystallinities determined by DSC are in the range of 72 to 80%. The latex particles are nonspherical. Multilamellae ellipsoids as well as single-lamella particles exist.^[6g] Typical average particle sizes determined by dynamic light scattering (DLS) are about 150 nm. Dialysis provided to be a convenient method for the removal of excess surfactant, if desired. The removal of excess surfactant was monitored by measurements of the surface tension, which was >70 mN·m⁻¹ for the latices after dialysis (neat water: 73 mN·m⁻¹).

The second-stage free radical polymerization was carried out with batch addition of the monomer, styrene or butyl acrylate to the PE dispersions (Table 1). Polymerization was initiated by thermal decomposition of potassium peroxydisulfate (KPS). Conversion of the second-stage monomer was monitored by means of the solids content of periodically drawn samples. High conversions of ≥90% were achieved within two hours (see Supporting Information; Figure S1). The course of the reaction does not differ significantly from similar free radical polymerization experiments in the absence of PE particles under otherwise identical conditions. Colloidally stable dispersions were obtained. Under the reaction conditions investigated additional surfactant was required to prepare stable PE/PS latices. In the case of BA polymerization, dialysed latices of PE without any added surfactant already afforded a stable multiphase latex.

As the polyethylene particles are highly crystalline and contain only a relatively low portion of amorphous regions,

Table 1. Typical polymerization conditions.

Component	Amount
PE content ^{a)} (g)	0.8 to 1.6
Water (mL)	30 or 50
SDS ^{b)} (g)	<0.05 to 0.20
Styrene or acrylate (g)	1 to 3
KPS (mg)	40
Temperature	80 °C

^{a)} Amount of polyethylene contained in dispersion.

^{b)} Total amount introduced with PE dispersion + SDS added for second-stage free radical polymerization.

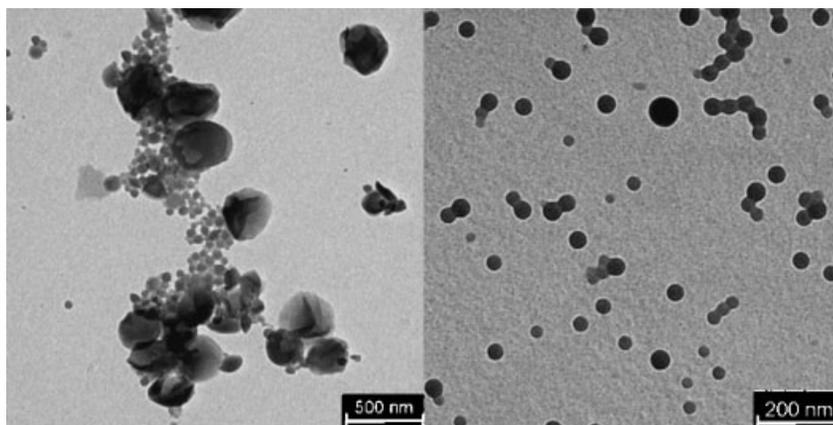


Figure 1. TEM images of a PE/PS latex (left; larger particles: PE, lamellar; smaller particles: PS, spherical) and of a PS latex prepared under identical conditions (right); note that scales are different.

swelling by the second-stage monomer can be expected to be very limited. Accordingly, upon “pre-swelling” of the PE latex by stirring with styrene or butyl acrylate for 17 h at room temperature prior to the free radical polymerization, no dramatic effect on the course of the polymerization or the latices formed was observed in comparison with the usual polymerization procedure.

Multiphase latices consisting of semicrystalline PE and an amorphous polymer with a glass-transition temperature above (polystyrene, PS) or below (poly(butyl acrylate), PBA) room temperature were obtained. To enable meaningful further analysis, dispersions containing about the same amount by weight of PE, PS or PBA, or an up to threefold excess of PS or PBA were prepared (Table 1).

Morphology and Thermal Behavior

Transmission electron microscopy revealed the PE/PS dispersions to consist of separate PE and PS particles (Figure 1).

DSC studies on the PE/PS dispersions showed high supercoolings around 50 °C due to an independent crystallization of individual PE droplets ($T_c \approx 78$ °C; Figure 2), as reported previously for neat PE latices.^[6g] Apparently, the presence of polystyrene latex particles does not affect the colloidal stability of the PE droplets. By comparison, in a macroscopic mixture of bulk PE and PS (both polymers originating from precipitation of a neat PE or PS latex), crystallization of the PE occurs at around 114 °C, as expected for typical heterogeneous crystallization in bulk PE phases. An unexpected behavior was found for samples obtained by precipitation of PE/PS latices (weight ratio PE/PS 1:3; precipitation was induced by pouring the latex into excess methanol). For the resulting material, high supercoolings are observed ($T_c \approx 74$ °C; Figure 2). This demonstrates that the PE phase must consist of very small individual domains, which also do not coagulate strongly at

high temperatures. A sample obtained by simple evaporation of the liquid phase from a PE/PS latex showed the same behavior.^[9] Thus, the latices provide facile access to nanocomposites consisting of an amorphous PS matrix containing individual, nonaggregated crystalline PE particles.

This was also confirmed by a series of AFM images taken at different, gradually increasing temperatures from 25 to 120 °C (Supporting Information, Figure S2). Heating a sample obtained by evaporation of a PE/PS dispersion reveals that the PE particles sink into the increasingly soft PS matrix formed with increasing temperature, resulting in a dispersion of PE particles within a continuous PS matrix.

For PE/PBA dispersions, PE particles surrounded by a PBA phase were observed by transmission electron microscopy (Figure 3). This is indicative of core-shell structured particles with a hard PE core and a soft PBA surrounding. It should be noted that the TEM images are not an unambiguous proof in this respect, as a concentration of PBA

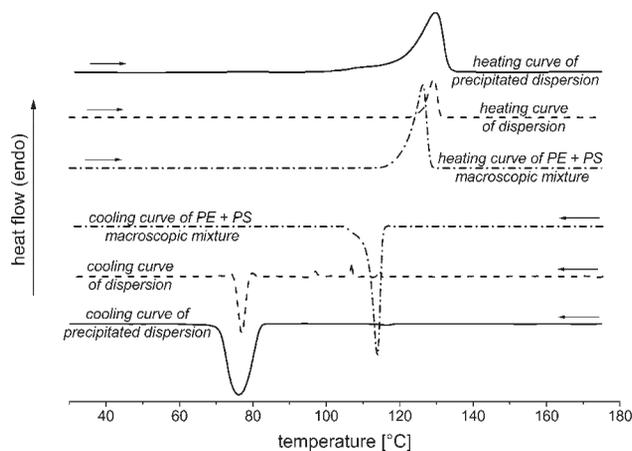


Figure 2. DSC traces of a PE/PS dispersion, a sample isolated from the dispersion by precipitation, and a macroscopic mixture of PE with PS (heating rate 10 K·min⁻¹). Note that the glass transition of PS is dominated by PE melting and crystallization.

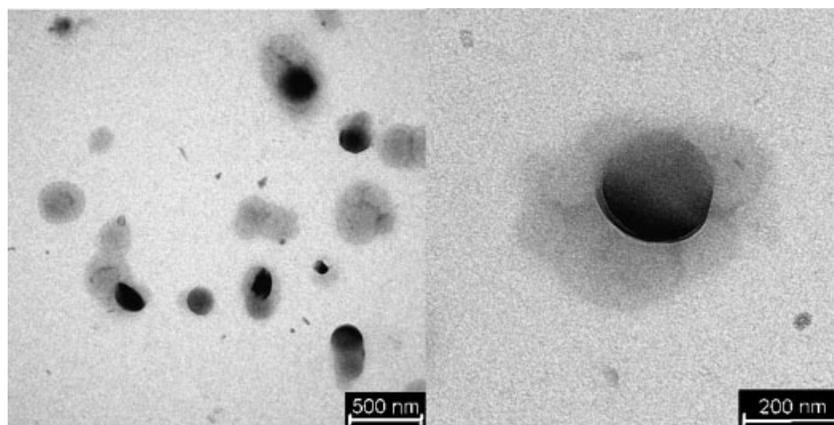


Figure 3. TEM images of a PE/PBA latex (weight ratio PE/PBA ca. 1:3).

around the PE particles by capillary forces during sample preparation cannot be excluded. To this end, in TEM images of a mixture of separately prepared PE and PBA latices, no PBA “shells” were observed, which supports the fact that in the synthesis of PE/PBA latices a PBA phase is indeed formed on the PE particles.

As pointed out in the introduction, the structure of two-phase latices depends on a variety of thermodynamic and kinetic factors.^[2] One should be cautious about generalizations, as for a given polymer system morphologies can depend, for instance, on surfactant concentrations, monomer swelling, which itself depends on temperature, or type of monomer addition (batch vs. continuous), to name but a few. Therefore, it should be noted that the different behavior observed in butyl acrylate polymerization versus the formation of separate particles in styrene polymerization cannot be generalized beyond the reaction conditions investigated, that is, batch polymerization at 60 to 80 °C in the range of polymer and monomer compositions and surfactant concentrations given in Table 1. A possible tentative explanation for the observed different behavior is

the formation of longer chain oligomeric radicals for the more water-soluble monomer butyl acrylate due to a higher rate of polymerization in the aqueous phase, which have a relatively high propensity for collision with an existing particle as their charge (one sulfate end group per chain, the latter being relatively long) is comparably low. By comparison, in styrene polymerization, nucleation of a new particle will be more likely (at a lower chain length of the oligomeric radical, which grows slower). Another reason for the different behavior found may be the higher surfactant concentration in styrene polymerizations (observed to be required for the formation of colloiddally stable latices), which may favor formation of new particles.

AFM images of a PE/PBA latex show characteristic lentil-like PE particles dispersed in a continuous PBA film (Figure 4). Remarkably, the PE particles do not aggregate but are distributed homogeneously in the PBA film.

In DSC measurements on samples isolated from PE/PBA latices by drying, the majority of the PE crystallizes at around 105 °C, although some of the PE crystallizes at about 70 °C (PE/PBA weight ratio 1:1 to 1:3). This demonstrates

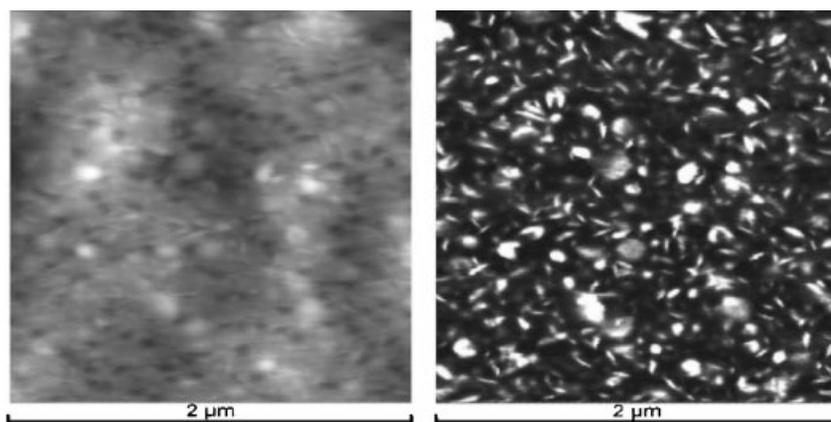


Figure 4. AFM images of a PE/PBA latex (left: height mode; right: phase mode with dark = soft PBA; weight ratio PE/PBA ca. 1:3).

that at least a portion of the PE exists in the form of small domains. It can be speculated that by comparison with the PE/PS samples the softer PBA matrix facilitates coagulation of PE domains.

Conclusion

Free radical emulsion polymerization of styrene or butyl acrylate in the presence of latices of linear, semicrystalline polyethylene prepared by catalytic emulsion polymerization affords colloidally stable multiphase latices. For PE/PS latices, under the polymerization conditions investigated, separate PS particles are formed. Coagulation of the latex, or evaporation of the dispersing medium (water) affords nanocomposites composed of small, noncoagulated PE phases dispersed in a PS matrix. For PE/PBA latices, TEM indicates that a PBA phase is formed around the PE particles under the emulsion polymerization conditions investigated. Films formed from these dispersions exhibit homogeneously dispersed PE particles.

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