# Precipitation polymerization in mixed monomer–solvent droplets

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**ABSTRACT:** This contribution reports the precipitation copolymerization of lauryl methacrylate–divinylbenzene (LMA–DVB) in stable isolated droplets dispersed in water. The droplets contain either $n$-hexadecane (HD) or HD–toluene (HD–T) or toluene as a nonsolvent for the resulting P(LMA–DVB) copolymer. The polymerization proceeds smoothly with an appreciably high content of DVB without the formation of coagulum and thus proves the quite high stability of the droplet reactors. The differences in the interaction between the nonsolvent–copolymer combinations allow the variation of the internal morphology of the particles between core and shell type, highly porous, and solid sphere. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41881.

## INTRODUCTION

Micrometer-sized polymer particles are useful as separation media, ion-exchangers, support materials, toners, coatings, calibration standards, and functional beads for medical diagnostics.[1,2] For many industrially important applications, a certain hydrophobicity of the polymers is required in order to reduce water penetration into substrates or specifically to remove hydrophobic contaminants. Prominent examples are the use of such polymer dispersions in water purification, as oil absorbers, viscosity modifiers, and oil-soluble drag reducers.[3,4] Lauryl methacrylate (LMA) is one such monomer frequently used to produce hydrophobic polymer particles. However, the very poor water solubility ($\ll 0.01$ g/100 g at 25°C) makes conventional emulsion polymerization of LMA anything but routine.[5] Even miniemulsion polymerization of LMA is quite challenging and requires special care to prevent specific instabilities of the monomer droplets.[6] Quite a few studies try to avoid the problems connected with the hydrophobicity of LMA and describe the homopolymerization and/or copolymerization of LMA under homogeneous conditions in organic solvents employing various polymerization mechanisms.[3,7–13] Recently, we reported the emulsion copolymerization of LMA with methyl methacrylate (MMA) in water/ethanol dispersion media using water-soluble initiator.[14] The addition of ethanol in the continuous phase improved the solvency for LMA and favored the formation of submicrometer-sized copolymer latex particles. Further experimental study was carried out to see how the emulsion terpolymerization behavior of LMA and MMA in water/ethanol

dispersion media using poly(vinyl pyrrolidone) as a steric stabilizer is influenced by the nature of the third monomer.[15] The rate of polymerization, the latex particle, and the polymer properties are strongly affected by the nature of the third monomer. Another study describes the preparation of hydrophobic PLMA latex particles via suspension polymerization using poly(vinyl alcohol) (PVA) as steric stabilizer.[16] However, this process leads to quite a high amount of coagulum and to PLMA latex particles that suffer from the low glass transition temperature of the polymer[17] and could not be used for further application studies. Nowadays, cross-linked structures have received wide industrial importance due to properties such as superior thermal and mechanical resistance, applicability of surface modification and adaptability in a wide pH range.[18]

In this study, we take advantage of the hydrophobic monomer mixture divinylbenzene (DVB)/LMA and restrict the polymerization mainly to the droplet phase by employing benzoyl peroxide as hydrophobic initiator. Particularly, the hydrophobic LMA contributes to droplet stability and hence, a kind of combined suspension–precipitation polymerization is studied where the monomer droplets contain additional organic liquids (toluene, T, hexadecane, HD, and a 1 : 4 mixture T : HD). The monomers (DVB and LMA) are soluble in the additional solvents, but the polymers not. Looking at the overall reaction volume, one might consider this kind of heterophase polymerization with oil-soluble initiators as combination of suspension–precipitation polymerization. However, focusing only on the droplet reactors, it is a precipitation polymerization in

isolated droplets. The quality of the interaction between the additional solvent/solvent mixture and the forming polymer/copolymer is quite different and determines crucially the particles morphology. Okubo *et al.* reported that the use of nonsolvents in suspension polymerization of DVB favors the phase separation within the droplets at the early stage of polymerization and leads to the formation of hollow particles.[19,20]

In this contribution, we focus on the investigation of the influence of the composition of the monomer mixture (increasing amount of DVB) and nature of the additional nonsolvents for the polymers on the average particle size, particle size distribution, and particle morphology by means of scanning electron microscopy (SEM), transmission electron microscopy (TEM) cross sections, light microscopy, and dynamic light scattering. In other words, the aim of this study is to prove the influence of compatibility or noncompatibility of components present in polymerizing droplets on the resulting morphology of the final polymer particles.

### EXPERIMENTAL

#### Chemicals and Instruments

LMA from Fluka, Chemika (Switzerland) was washed with 10% NaOH aqueous solution to remove any inhibitor and finally passed through activated basic alumina by column chromatography. Cross-linking agent DVB from Sigma-Aldrich, Chemie (80% grade) was used after purification with aqueous 10% NaOH solution and subsequent dehydration with anhydrous $CaCl_2$. Benzoyl peroxide (BPO) from BDH Chemicals Ltd., UK was recrystallized from methanol and preserved in the refrigerator before use. PVA from Thomas Baker (Chemicals) Limited, India of molecular weight $1.4 \times 10^4$ $gmol^{-1}$ was used as a polymeric stabilizer. Hexadecane (HD) and toluene (T) were used without any purification. Other chemicals used were of reagent grade. Deionized (DI) water was distilled using a glass (Pyrex) distillation apparatus.

SEM was performed with a JSM-6510 microscope (JEOL, Tokyo, Japan) at a voltage of 20 kV and TEM either with JEM 1230 (JEOL, Japan) or a Zeiss EM 912 Omega microscope (Zeiss, Germnay) both operating at 100 kV. Either light microscopy was carried out with a Nikon MICROPHOT-FXA or a Keyence VHX digital optical microscope (dried samples). The measure tool of the Keyence software was used to evaluate the

**Table I.** (Co)polymer–Solvent Interactions in the Polymerized Solution Droplets

| Monomer(s) | Solvent(s) | | |
| --- | --- | --- | --- |
| | HD | T | HD–T (4 – 1) |
| DVB | − | + | ± |
| DVB–LMA (1–1) | ± | ± | + |

HD: hexadecane, T: toluene, DVB: divinylbenzene, LMA: lauryl methacrylate, −: maximum incompatibility, +: maximum compatibility, ±: mixed compatibility situation.

size distribution of the particles. Fourier transform infrared (FTIR) spectra were recorded with a FTIR8044 (Shimadzu, Japan) and thermogravimetry with a TGA EXSTAR-6000 (Seiko Instrument Inc., Japan) was used for the characterization of the latex particles.

#### Preparation of Cross-Linked Latex Particles by Suspension Polymerization

For all polymerizations, the overall amount of monomer(s) was fixed to 2 g, the amount of additional solvent to 2 g, the amount of continuous phase to 120 g, the amount of PVA stabilizer to 0.4 g, and the amount of BPO initiator to 0.04 g. The influence of three different additional solvents was investigated: pure HD and toluene (T) and a mixture HD–T (1.6 g/0.4 g). The composition of the monomer(s) was varied regarding the LMA content from zero over 0.2, 0.6, and 1.0 g. Prior to the polymerization, monomer droplets were prepared by preemulsification with magnetic stirring (900 rpm) of all ingredients for 1 h followed by homogenization with an Ultra Turrax T 25 (IKA, Germany) at 9500 rpm for 3 min. During the homogenization, the container with the reaction mixture was placed in an ice water bath. Then, the suspension polymerization was carried out under nitrogen atmosphere in a three-necked round-bottom flask equipped with a mechanical stirrer placed in a thermostat water bath at 75°C for 24 h.

Conversion irrespective of nonsolvent composition was over 90% as measured gravimetrically.

#### Observation of the Ultrathin Cross Sections of Particles

For the preparation of thin cross sections, the samples were dried and then embedded in LR White acrylic resin medium
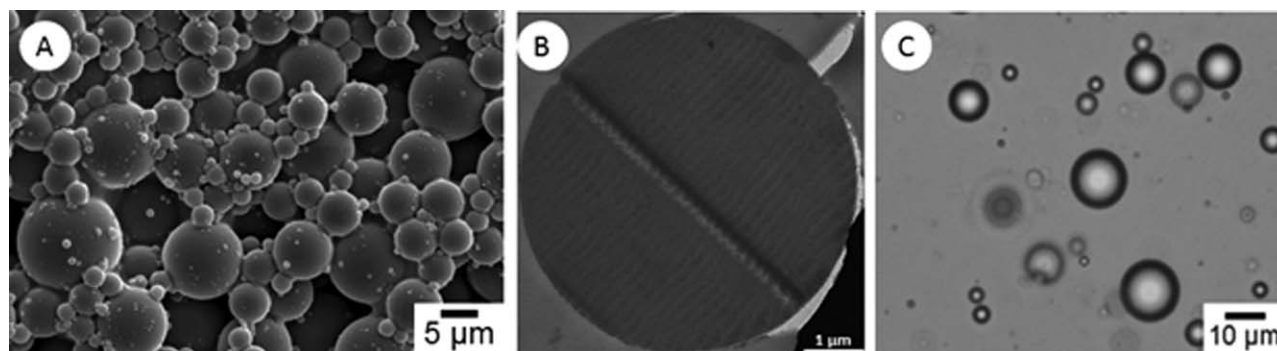


**Figure 1.** PDVB/T latex particles prepared by precipitation polymerization in DVB/T droplets: (A) SEM image, (B) TEM cross-sectional image, and (C) light microscopic image.
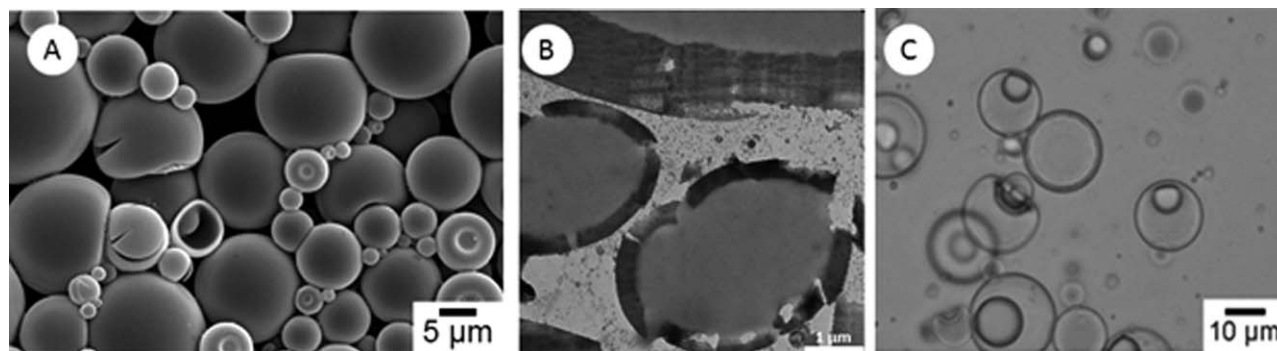
**Figure 2.** PDVB/HD latex particles prepared by precipitation polymerization in DVB/HD droplets: (A) SEM image, (B) TEM cross-sectional image, and (C) light microscopic image.

grade (R1281 London Resin Company, UK) and microtomed after hardening at 60°C. The 50–70 nm thick cross sections were investigated with TEM (Zeiss EM 912 Omega microscope).

### Thermogravimetric Analysis

Thermal properties of the dry powdered samples of latex particles were measured by heating samples under flowing nitrogen atmosphere from 40° to 600°C at a heating rate of 20°C min$^{-1}$ and the weight loss was recorded.

### Dynamic Light Scattering

The intensity-weighted average particle size ($D$) was measured by dynamic light scattering with NICOMP particle sizer (model 380 PSS, Santa Barbara, California).

### RESULTS AND DISCUSSION

Table I summarizes the limiting cases regarding the composition of the monomer(s)–solution droplets studied and classifies the corresponding (co)polymer–solvent interactions in the polymerized droplets. Despite the fact that the polymer is cross-linked, there are differences with respect to the polymer–solvent interactions that can be estimated according to the principle "*similia similibus solvuntur*," that is, "similar substance will dissolve similar substance." Accordingly, one might expect the most homogeneous particles after polymerization of DVB in toluene and after copolymerization of DVB–LMA in HD–T mixed solvent. In contrast, the lowest compatibility and hence the most structured particles are expected after polymerization of DVB

solution droplets with HD as additional solvent. For all copolymerizations, one can assume a somehow mixed compatibility for all additional solvent(s) because one comonomer is compatible with one component of the solvents mixture.

The influence of the compatibility/incompatibility of the solvent(s)–(co)polymer mixtures (cf. Table I) inside the polymerizing droplets on the morphology of the resulting particles is illustrated by the electron microscopy micrographs and light microscopy images displayed in Figures 1–6.

Since this contribution focuses on the morphology of the resulting particles, the homopolymerization of LMA was not studied because the investigation of the morphology of PLMA homopolymer particles requires very special preparation and investigation techniques (cryotechniques and/or flow cells for electron microscopy) due to the low glass transition temperature of this homopolymer which were not available at the moment.

Nevertheless, the microscopy images put together in Figures 1–6 allow to draw some usefull conclusions regarding the influence of the interaction between the (co)polymers and the additional solvent(s) on the particles morphology. All three microscopy techniques give complementary information regarding the morphological features. Electronmicroscopy gives information of the dry state and optical microscopy of the dispersions in the wet state. SEM micrographs (images A) allow conclusions regarding the surface structure, whereas TEM cross sections prove the inner structure of the particles. The images obtained with
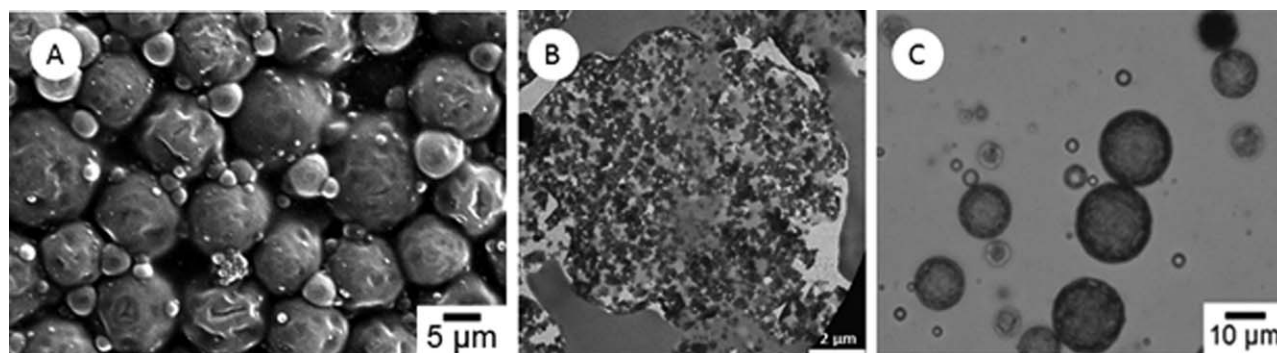


**Figure 3.** PDVB/HD/T latex particles prepared by precipitation polymerization in DVB/HD/T droplets: (A) SEM image, (B) TEM cross-sectional image, and (C) light microscopic image.
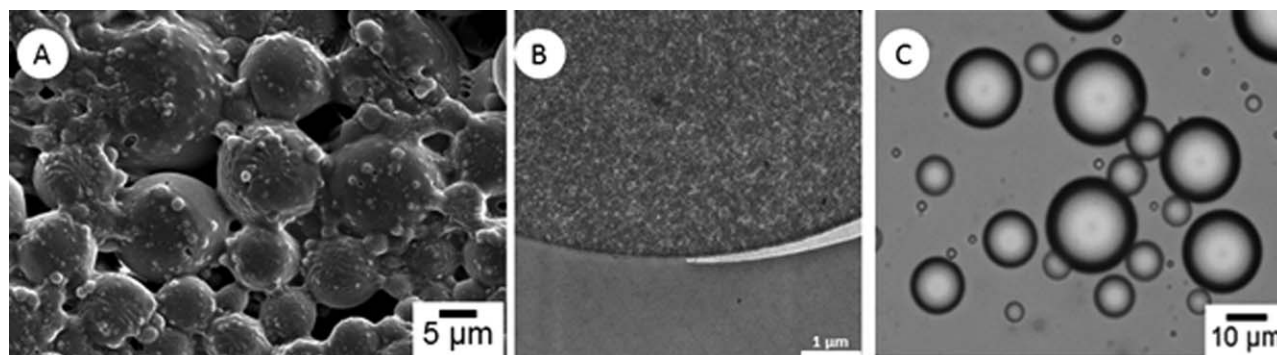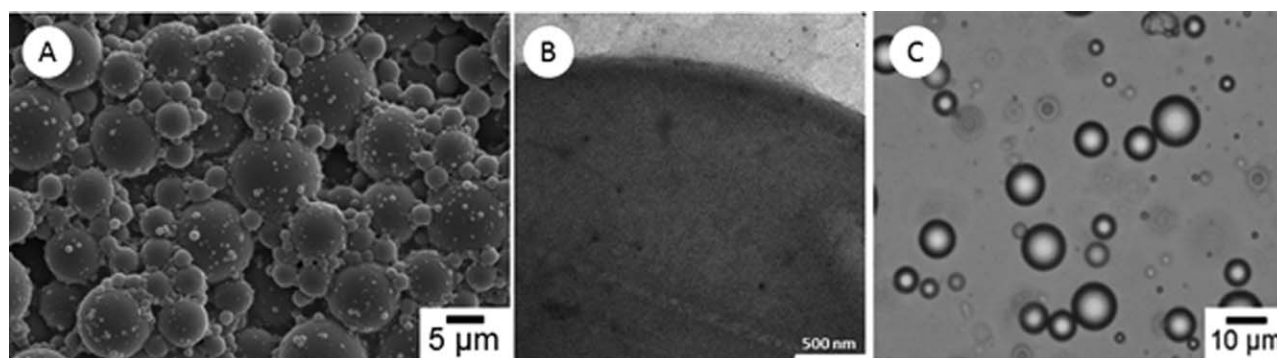
**Figure 4.** P(DVB/LMA)/HD latex particles prepared with LMA content 50% (w/w) by precipitation polymerization in DVB/LMA/HD droplets: (A) SEM image, (B) TEM cross-sectional image, and (C) light microscopic image.

optical microscopy contain information of both the particles interior and the shape (circumference).

The morphology of the PDVB homopolymer particles shows a clear dependence on the nature of the nonsolvent inside the droplets (polymerization loci). According to the above argumentation in context with Table I, toluene (Figure 1) and hexadecane (Figure 2) represent the extreme cases with respect to particles morphology. Obviously, the compatibility of the polymer with the additional liquid is to be observed most clearly on the TEM cross-sectional micrographs. The highest compatibility between PDVB and toluene finds expression in the most homogeneous internal structure (micrograph 1B), whereas the lowest compatibility between HD and PDVB leads to almost hollow particles with either broken, dimpled, or intended PDVB shells (micrograph 2B). Comparing electron and light microscopy images reveals that the destruction of the particles shell happens during drying of the dispersions. It should be noted that the PDVB dispersions obtained in the presence of toluene possess a much broader size distribution which is evident from the many small particles (diameter below 1 μm) recognizable on the SEM micrographs. The morphology of the PDVB particles obtained in the presence of the HD–T mixture in the polymerizing droplets can be considered as an overlay of both the compatibility and incompatibility of the PDVB with toluene and HD, respectively. In this case, phase separation does not lead to the formation of hollow particles but to internal phase separation into nm-sized domains (micrograph 3B).

Also, the appearance of the PDVB particles in the light microscope shows a distinct influence of the nature of the additional solvents. The larger particles obtained in the presence of the solvent mixture appear, due to the enhanced scattering at the domain interfaces, over the whole-volume turbid [Figure 3(C)]. In contrast, the interior of the particles polymerized in the presence of either HD or toluene is transparent indicating internal homogeneity [Figures 1(C) and 2(C)]. Only the edge of the particles obtained in the presence of HD [the hollow particles, Figure 2(C)] appears thinner than that of the solid particles [homogeneous interior for visible light, Figure 1(C)] made in the presence of toluene.

Compared with the homopolymer particles (PDVB), the morphology of the copolymer particles P(DVB–LMA) is much less influenced by the nature of the additional solvent (Figures 4–6). The morphology of the particles as displayed on the optical microscopy images is practically identical for all samples and virtually independent of the solvent [Figures 4(C), 5(C), and 6(C)]. Only the SEM and TEM cross-sectional micrographs reveal slight differences between the samples, the SEM micrographs more than the TEM cross sections. For the copolymer samples, the most striking difference is that the particles surface on the SEM micrographs looks smooth for the particles made in the solvent mixture and much more rugged for the particles obtained in the presence of the pure solvent (HD or toluene). The thin cross sections (cf. Figure 5) show at a glance rather something similar to a solid core morphology than the porous



**Figure 5.** P(DVB/LMA)/T latex particles prepared with LMA content 50% (w/w) by precipitation polymerization in DVB/LMA/T droplets: (A) SEM image, (B) TEM cross-sectional image, and (C) light microscopic image.
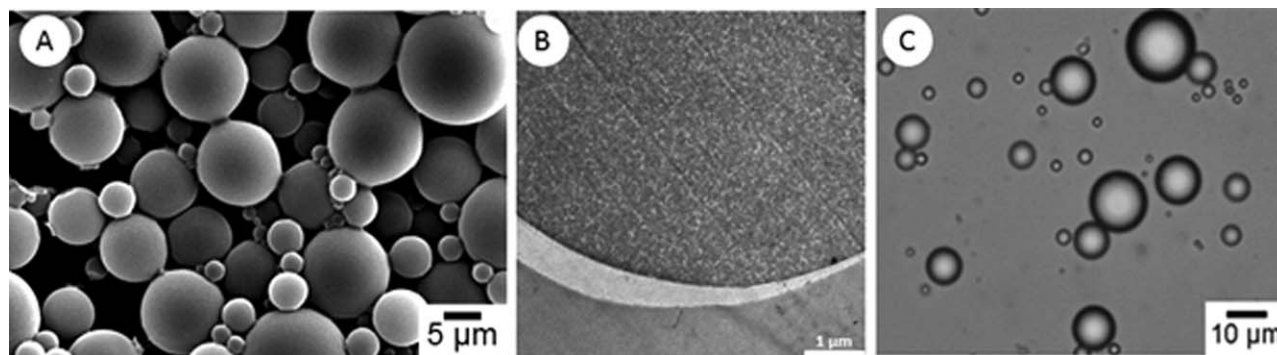
**Figure 6.** P(DVB/LMA)/HD/T latex particles prepared with LMA content 50% (w/w) by precipitation polymerization in DVB/LMA/HD/T droplets: (A) SEM image, (B) TEM cross-sectional image, and (C) light microscopic image.
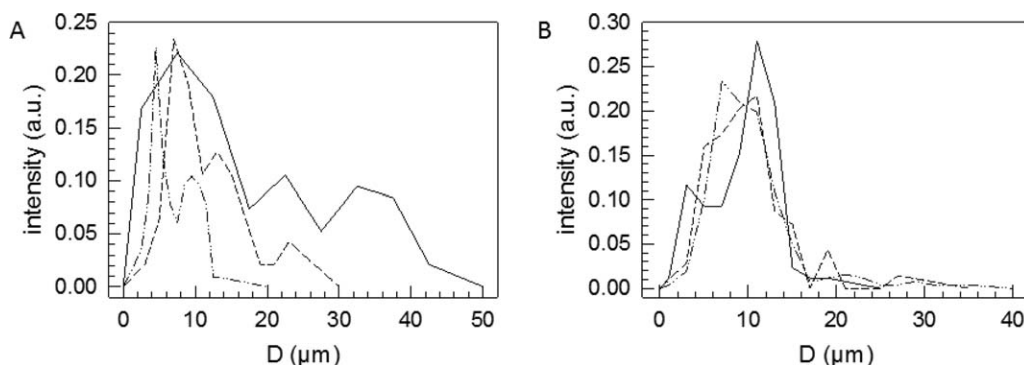


**Figure 7.** Particle size distribution as estimated from light microscopy images for PDVB homopolymer particle (A) and P(DVB/LMA) (1 : 1 comonomer weight ratio) copolymer particles (B) with the mixture HD/T (solid line), pure HD (dashed line), and toluene (dash-dot-dot line) as additional solvent during the polymerization.

morphology seen in Figures 3 and 4. A closer look reveals that brighter spots are unevenly distributed in the volume of the core and arranged in stripes and clouds. It is necessary to note that bright stripes have been observed in any thin section of this sample. The thin sections of the combination P(DVB–LMA) with the solvent mixture (cf. Figure 6) show also a kind of phase-separated structure similar to copolymer structure prepared in presence of HD (cf. Figure 4) with the darker and brighter spots are evenly distributed in the volume. Moreover,

the particle size distribution of the dispersions from either of the pure solvents extends over a broader range.

Light microscopy was also used to map the dried particles, and these images were used to estimate the particle size distribution (PSD) of the suspensions. The data put together in Figure 7 show that the influence of the solvent depends quite strongly on the monomer. For the PDVB homopolymer particles, the nature of the additional solvent has quite a strong influence on the width of the size distribution [Figure 7(A)]. In contrast, the
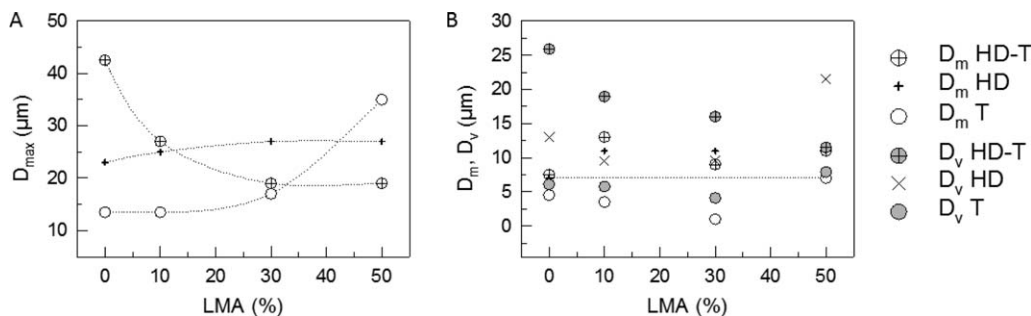


**Figure 8.** (A) Correlation between monomer composition expressed as weight content LMA in the monomer mixture with DVB and maximum particle size ($D_{max}$) as determined from light microscopy images of the PDVB homopolymer and PDVB/PLMA copolymer particles and (B) Correlation between monomer composition expressed as weight content LMA in the monomer mixture with DVB and the modal value of the PSD ($D_m$) and the volume weighted average particle size from DLS ($D_v$); the dotted line illustrates the limit as observed for the smallest particles obtained with pure toluene as additional solvent.
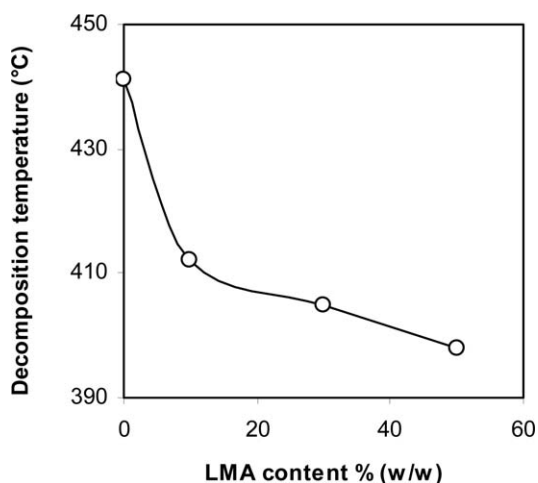
**Figure 9.** The onset decomposition temperature obtained from thermogravimetric analysis thermograms of P(DVB/LMA) latex particles prepared with variable LMA content by suspension polymerization of LMA/DVB/HD droplets.

particle size distribution is only little influenced by the nature of the solvent in the case of P(DVB–LMA) (1 : 1) copolymer particles [Figure 7(B)].

The data of Figure 8 illustrate the influence of the composition of the monomer mixture and the nature of the additional solvent on the particle by means of the maximum particle size in

the PSD ($D_{max}$) and the modal value of the PSD ($D_m$), Figure 8(A,B), respectively. The data of Figure 8(A) show that for HD as sole additional solvent, the composition of the monomer mixture has only minor influence on the maximum particle size. In contrast, for toluene as additional solvent, the composition of the monomer mixture has quite a strong influence as $D_{max}$ increases significantly with increasing content of LMA. Interestingly, for the HD–T mixture as additional solvent, the maximum particle size decreases with increasing LMA content.

The comparison of the modal value of the PSD with the volume-weighted average particle diameter from dynamic light scattering [Figure 8(B)] shows, in relation to the data of Figures 7 and 8(A), quite a nice agreement. For the pure additional solvents, $D_m$ and $D_v$ agree much better than for the solvent mixture which is reasonable taking into account the width of the particle size distributions. The data from both light microscopy and DLS show that toluene as sole additional solvent leads, regardless the composition of the monomer mixture, to the smallest particles.

The content of LMA in the copolymers not only influences their glass transition temperature and softness or hardness but also the thermal stability or the decomposition temperature.

The thermal decomposition temperature as depicted in Figure 9 shows expectedly decreasing thermal stability with increasing LMA content or decreasing cross-linking density. This behavior is caused by the action of DVB because increasing cross-linking
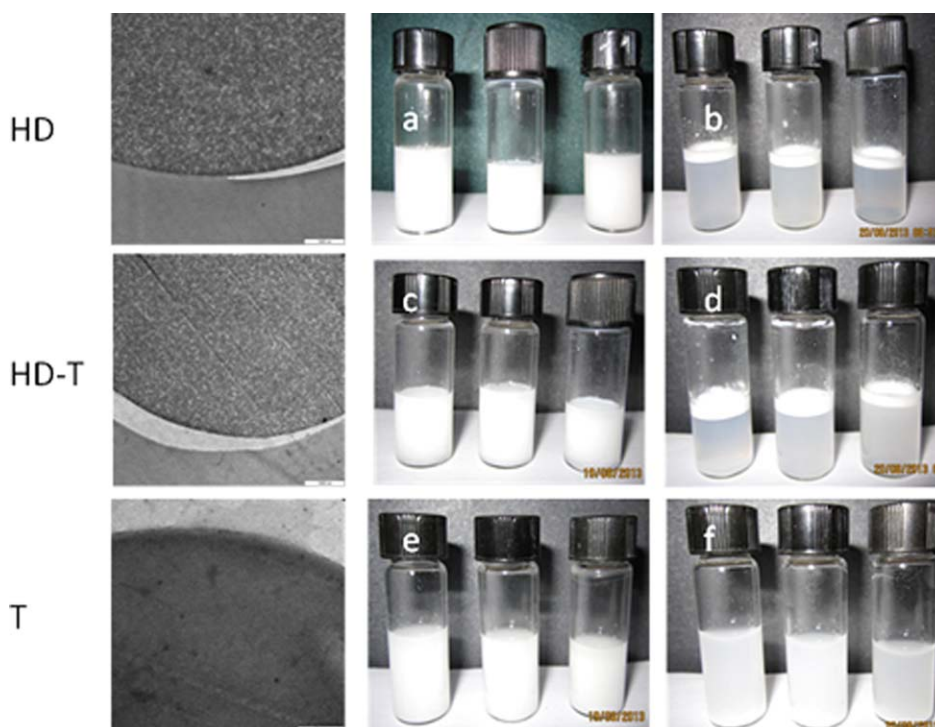


**Figure 10.** Photographic images of P(LMA/DVB) copolymer particles (a–f) illustrating the creaming (b, d) and sedimentation (f) during storage; images (a, c, e) homogeneously dispersed suspensions; the TEM micrographs of the thin cross-sections depicted left to the snapshots show the internal morphology of the particles with variable LMA fraction (50%, 30%, and 10% w/w) in the monomer mixture polymerized in the presence of HD (first row), HD/T mixture (second row), and T (third row) as additional solvent; the additional solvent is still present in the dispersions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

density contributes to higher thermal stability[21–23], and in general, styrenic polymers show higher thermal stability than (meth)acrylates.[24]

## CONCLUSIONS

The polymerization procedure described allows the synthesis of colloidally stable P(DVB–LMA) copolymer dispersions. The copolymer particles are properly stabilized by PVA despite the fact that during storage the particles undergo density-driven settling or creaming. However, in any case, the concentrated particle layers, either on top or at the bottom of the continuous phase, are easily re-dispersable (cf. Figure 10).

Whether sedimentation or creaming of the particles happens during storage depends on the degree of porosity in combination with the average particle size. Assuming that the bright regions in the micrographs of the thin cross sections correspond to the degree of porosity (cf. discussion above) the observation that the particles synthesized in the presence of HD and HD–T mixture show creaming and those made in the presence of toluene do sedimentation is very reasonable. The residual turbidity of the continuous phase is an expression of the quite broad PSD because the smaller particles are kept dispersed due to thermal energy which overrules the gravitational force.

The nature of the additional solvents and their interaction with the (co)polymers are the crucial parameters determining the phase separation during the solution suspension polymerization. The internal morphology of P(DVB–LMA) (co)polymer particles can be varied over a huge range with respect to the internal porosity.

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