POLY(2-BROMOANILINE) AND ITS COLLOIDAL DISPERSIONS

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Poly(2-bromoaniline) was prepared by oxidation of 2-bromoaniline with ammonium peroxydisulfate in the presence of hydrochloric acid. The conductivity of the poly(2-bromo-aniline) hydrochloride so produced was 10^{-6} S cm^{-1}, its density at 20 °C 1.78 g cm^{-3} and weight-average molar mass 18 500 g mol^{-1}. The degree of protonation was estimated as being a half of that of polyaniline. The structure of poly(2-bromoaniline) is discussed on the basis of FTIR spectra. Colloidal dispersions were produced when the polymerization had been carried out in the presence of a particulate or polymeric stabilizer, *viz.* colloidal silica, poly(vinyl alcohol), poly(*N*-vinylpyrrolidone) or (hydroxypropyl)cellulose. The UV-VIS spectra of colloidal dispersions are used to discuss the transition between the protonated and base forms.

Keywords: Colloidal dispersions; Colloids; Conducting polymers; Dispersion polymerization; Poly(2-bromoaniline); Polyaniline; Protonations; Oxidations.

Polyaniline is used in diverse applications requiring semiconducting or coloured polymers responding to various external stimuli[1]. Methods for improving its processibility and tuning of properties are based on the modification of the polymer structure. On the molecular level, the polymer structure is tailored either by copolymerization of aniline with a suitable monomer or by introducing functional groups into polyaniline (PANI) by chemical reactions. The bromination of polyaniline may serve as an example of the latter approach[2]. Preparation of PANI colloids by dispersion polymerization represents the route to processable supramolecular forms. In the present study, both modification approaches are combined by using an aniline derivative, 2-bromoaniline, as a monomer and by preparing colloidal poly(2-bromoaniline) (PBANI) dispersions.

Poly(2-bromoaniline) is a relatively new polymer whose electric proper-
ties have been reported in only a single case. Prasad *et al.*[3] oxidized
2-bromoaniline with potassium peroxydisulfate in aqueous solutions of var-
ious acids. The products had conductivities of 10^{-7}–10^{-5} S cm^{-1}, depending
on the acid used in experiment. Pringsheim *et al.*[4] prepared PBANI films on
polystyrene support by *in-situ* polymerization of 2-bromoaniline. The films
were tested in connection with optical sensing of pH. The oxidation
products of 2,5-dibromoaniline and 3,5-dibromoaniline had conductivities[5]
$< 2 \cdot 10^{-12}$ S cm^{-1}. The low conductivity of bromine-containing polyanilines
thus makes 2-bromoaniline a good candidate for the modification of the elec-
trical properties of PANI by copolymerization of this monomer with aniline.

Colloidal dispersions of substituted polyanilines have been studied only
rarely. When investigating PANI colloids prepared by the oxidation of ani-
line complexed with poly(acrylic acid), colloidal suspensions of poly-
(2-chloroaniline) in the presence of poly(styrenesulfonic acid) were also
prepared[6]. Gospodinova[7] and Janča[8] produced poly(*o*-toluidine) and poly-
(*m*-toluidine) dispersions stabilized with poly(vinyl alcohol-*co*-vinyl
acetate). The typical particle size of a poly(*m*-toluidine) dispersion was
400–3 000 nm, while PANI dispersion prepared under the same conditions
was composed of particles 200–600 nm in diameter. Ghosh and Siddhanta
have also reported the preparation of poly(*o*-toluidine) dispersions[9,10].
Okubo *et al.*[11,12] oxidized 3,5-dimethylaniline with ammonium peroxy-
disulfate using poly(vinyl alcohol) as a stabilizer. The oxidation of 1,3-
phenylenediamine in an aqueous solution of water-soluble polymers
yielded poly(1,3-phenylenediamine) dispersions[13]. The preparation of
PBANI colloids have not yet been reported. Because of the high density of
2-bromoaniline, the introduction of this comonomer into PANI macro-
molecules may be used for the control of colloidal-particle density. This
may be important for the preparation of coloured marker particles used to
study various separation processes.

EXPERIMENTAL

Polymerization of 2-Bromoaniline

Poly(2-bromoaniline) hydrochloride was obtained by the oxidation of 2-bromoaniline
(0.2 M) with ammonium peroxydisulfate (0.25 M) in 1 M hydrochloric acid at room tempera-
ture. Sonication was used to speed up the monomer dissolution before introducing an oxi-
dant. The colourless monomer mixture became dark violet within one minute. The
colouration becomes more pronounced as the polymerization proceeds. After two weeks, a
green-to-grey PBANI precipitate was collected on a filter, washed repeatedly with 1 M HCl,

followed by acetone, and dried at 60 °C *in vacuo*. A part of the product was treated with an excess of 1 M ammonium hydroxide to obtain a PBANI base. The polymerization in the presence of HBr, instead of HCl, was not successful, possibly due to the insufficient acidity of the reaction medium or because of HBr oxidation. PANI hydrochloride was prepared by following an analogous procedure[14].

Colloidal PBANI dispersions were prepared in the same manner in the presence of the stabilizer: colloidal silica (5 wt.%; Aldrich, Ludox AS-40), poly(vinyl alcohol) (2 wt.%; Fluka, type 72,000), poly(*N*-vinylpyrrolidone) (2 wt.%; Fluka, type K90) or (hydroxypropyl)cellulose (2 wt.%; Aqualon, Klucel GF).

Properties of Poly(2-bromoaniline)

Conductivity was measured at room temperature by a four-probe method on compressed pellets, 13 mm in diameter and 1 mm thick, using a Keithley 237 high-voltage current source and Keithley 2010 low-noise multimeter. Conductivities below 10^{-3} S cm^{-1} were evaluated using a two-probe technique with a Keithley 6517 electrometer. The Archimedes method was used to determine the polymer density by weighing the same pellets in air and in decane at 20 °C with a Sartorius Research R160P balance. Infrared absorption spectra were recorded in the range of 400–4 000 cm^{-1} with a Nicolet IMPACT 400 FTIR spectrometer (200 scans per spectrum at 2 cm^{-1} resolution) on polymers dispersed in potassium bromide and compressed into pellets. The spectra were corrected for the moisture and carbon dioxide in the optical path. Molar-mass distribution of PBANI (dissolved in *N*-methylpyrrolidone containing 0.025 g cm^{-3} of triethanolamine for the deprotonation, 0.005 g cm^{-3} lithium bromide to prevent aggregation, and 0.4 vol.% benzene as an internal standard) was assessed with a gel-permeation chromatograph using a 8 × 500 mm Labio GM 1000 column calibrated with polystyrene standards[14].

Characterization of Colloidal Dispersions

The sizes of colloidal particles and their polydispersity index (a relative variance of the particle-size distribution) were determined after dilution of dispersions with 1 M HCl by dynamic light scattering using an Autosizer Lo-C apparatus (Malvern, U.K.). UV-VIS spectra were recorded with a Lambda 20 UV/Vis spectrometer (Perkin–Elmer, U.K.) using the same diluted dispersions.

RESULTS AND DISCUSSION

The conductivity of polymers, like PANI, is due to the presence of unpaired electrons, cation radicals, in the polymer backbone that act as charge carriers. The polaron structure is generated by the protonation of imine nitrogens in the polymer chain of the emeraldine base (Fig. 1). This event is followed by the injection of two electrons into a quinoid ring that converts to a benzenoid one, leaving an unpaired electrons at nitrogens, which are eventually redistributed along the polymer chain[15,16]. After protonation with an acid, the conductivity of the PANI (emeraldine) base, 10^{-11}–10^{-8} S cm^{-1}, thus increases to 10^{-1}–10^1 S cm^{-1}.

Polyaniline exists in a variety of forms that differ in the degrees of oxidation and protonation[17] and, consequently, also in electrical, optical and chemical properties. The oxidation of 2-bromoaniline may produce polymeric structures that resemble, *e.g.*, an emeraldine (Fig. 2a) or its reduced form, the leucoemeraldine type of polymer chain (Fig. 2b). While the former would most probably be conducting, as in the case of PANI, the latter would be not.

Elemental analysis of PBANI hydrochloride reveals that the total halogen content is lower than that calculated according to the formula shown in Fig. 2a (Table I). This means that the extent of protonation is lower than that assumed for the emeraldine-like structure. The presence of sulfur reflects the benzene-ring sulfonation that occurs during the oxidation of aromatic amines with peroxydisulfate[18].
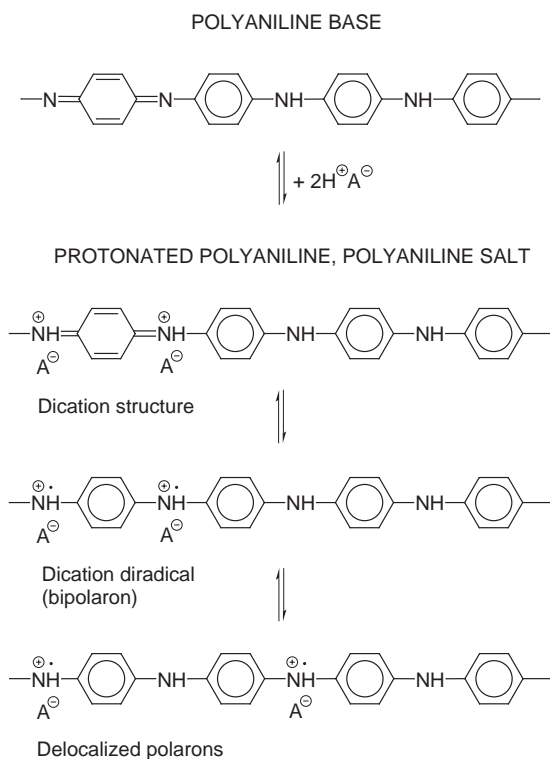

FIG. 1
The reaction of the non-conducting polyaniline (emeraldine) base with an acid yields a conducting polyaniline (emeraldine) "salt". A⁻ denotes an arbitrary anion

Elemental analysis of poly(2-bromoaniline) (wt.%)

Poly(2-bromoaniline)	C	H	N	Br	Cl	S
	Poly(2-bromoaniline) hydrochloride					
Found	39.7	2.4	7.2	47.4[a]		0.6
Calculated ($C_{24}H_{16}Br_4Cl_2$)	38.4	2.1	7.5	42.6	9.4	–
	Poly(2-bromoaniline) base					
Found	41.6	2.4	8.2	45.6[a]		0.6
Calculated ($C_{24}H_{14}Br_4$)	42.5	2.1	8.3	47.1	–	–

[a] Total halogen content.
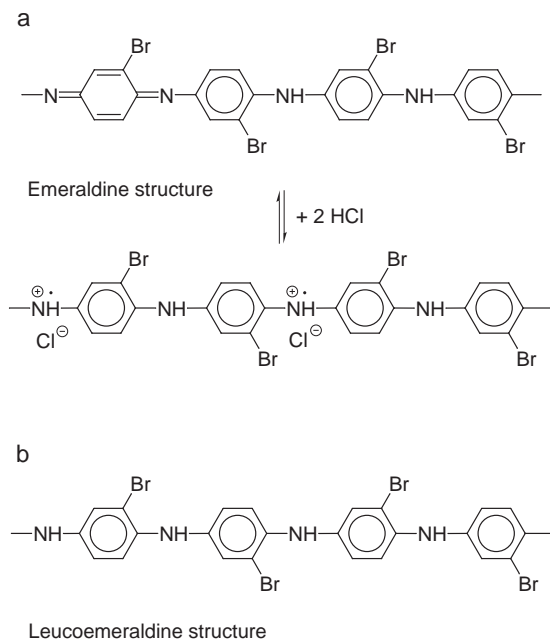
FIG. 2
Poly(2-bromoaniline) may have, in principle, a structure resembling emeraldine (a) or leuco-emeraldine (b). The former can be protonated, *e.g.*, with hydrochloric acid as shown here, while the latter cannot

Electrical Conductivity

The conductivity of PBANI hydrochloride obtained directly after polymerization is low, $1 \cdot 10^{-6}$ S cm^{-1} (Table II), but still higher than that of common non-conducting polymers, 10^{-13}–10^{-10} S cm^{-1}. The oxidation of 2-bromo-aniline yields a polymer, as demonstrated below by the determination of molar mass. This suggests that the polymer structure has features of both the emeraldine and leucoemeraldine type. After treatment with ammonium hydroxide, the conductivity of PBANI base falls to $8.7 \cdot 10^{-10}$ S cm^{-1}, comparable to a value for PANI base[15].

Degree of Protonation

The extent of protonation can be found experimentally from the loss of mass after deprotonation with ammonium hydroxide. If the PBANI structure were a hydrochloride, the hydrochloric acid would amount to 9.7 wt.% of the mass. The weight loss observed after deprotonation is 5.6 wt.%, which means that the degree of protonation is 58%, approximately one half of the amount of acid found in PANI (emeraldine hydrochloride). The structure of PBANI proposed on the basis of this result would correspond to about equal proportions of the structures shown in Fig. 2. While every other nitrogen in PANI is of the imine type and can be protonated (Fig. 1), it seems that about every fourth such nitrogen is present in PBANI. The reduced degrees of oxidation and protonation in ring-substituted poly-(chloroaniline), compared with an emeraldine, have also been reported on the basis of X-ray photoelectron spectroscopy[19].

TABLE II
Properties of poly(2-bromoaniline) and polyaniline hydrochlorides at 20 °C

Property	PBANI	PANI
Solid hydrochlorides		
Conductivity, S cm^{-1}	$1.0 \cdot 10^{-6}$	11.9
Density, g cm^{-3}	1.78	1.33
Colloidal dispersions stabilized with poly(*N*-vinylpyrrolidone)		
Particle diameter, nm	391	490
Polydispersity	0.11	0.23

FTIR Spectra

The spectra of protonated PBANI and of PBANI base resemble the spectra of PANI (emeraldine) base (Fig. 3). The broad absorption in the region above 2 000 cm^{-1}, which is typical of protonated emeraldine and reflects the presence of charge carriers[20,21], has not been observed in PBANI spectra. The peaks corresponding to quinone and benzene ring-stretching deformations at 1 592 and 1 499 cm^{-1} in the bases are red-shifted after protonation only to 1 589 and 1 496 cm^{-1} in PBANI hydrochloride but much more, to 1 570 and 1 480 cm^{-1}, in protonated PANI (ref.[22]). This means that the protonation of PBANI base with hydrochloric acid is limited or the production of cation radicals that are responsible for the conduction is less efficient. Consequently, the conductivity of protonated PBANI is expected, and indeed observed, to be much lower compared with protonated PANI (Table II).

The band at 1 374 cm^{-1}, present in PANI base spectrum and attributed to C–N stretching in the vicinity of a quinoid ring, is absent in the spectra of both the protonated and base forms of PBANI. The absorption band at 1 308 cm^{-1} (C–N stretching in secondary aromatic amine) in the spectrum of PANI, is situated at 1 296 cm^{-1} for both forms of PBANI. Because of various conformations of polymer chains, the C–N bonds have different chemical environment[23] and, consequently, different frequencies of the C–N stretching vibration band. The band characteristic of the conducting
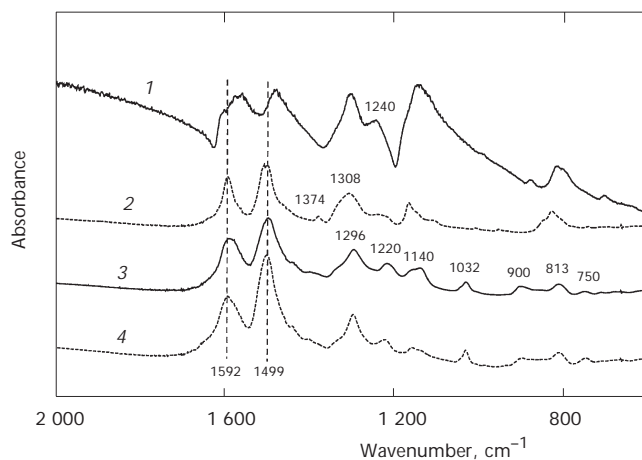

FIG. 3
FTIR absorption spectra of poly(2-bromoaniline) hydrochloride (PBANI·HCl, *3*) and of poly-(2-bromoaniline) base (PBANI base, *4*). Corresponding spectra for polyaniline (PANI·HCl, *1* and PANI base, *2*) are included for comparison

protonated form, which is observed at about 1 240 cm^{-1} in protonated PANI and is interpreted as a C–N$^{•+}$ stretching vibration in the polaron structure[22], has not been observed in the spectra of either form of PBANI. Their spectra are close to the spectrum of PANI base in this region, with a band at about 1 220 cm^{-1}.

The profile of the aromatic C–H in-plane bending modes observed in the 1 010–1 170 cm^{-1} region has been changed, the maximum at 1 158 cm^{-1} shifts to 1 140 cm^{-1}, when going from the spectrum of PBANI base to the PBANI hydrochloride. The 1 140 cm^{-1} band is assigned to a vibration mode of the –NH$^+$= structure in the spectrum of PANI hydrochloride, which is formed by protonation[24]. The new band at 1 032 cm^{-1}, present also in the spectra of brominated PANI (ref.[2]), corresponds most probably to the C–H in-plane bending mode of PBANI. The region 900–700 cm^{-1} corresponds to aromatic out-of-plane C–H deformation vibrations. Their frequencies are mainly determined by the number of hydrogen atoms in the ring but are not very much affected by the nature of substituents[25]. Two bands at about 813 and 900 cm^{-1} and a band at about 750 cm^{-1} in the spectra of PBANI base and PBANI hydrochloride correspond to the 1,2,4-trisubstituted benzene ring, as observed with the brominated PANI (ref.[2]).

Molar Mass

Gel-permeation chromatography proves the polymer nature of PBANI (Fig. 4). Its weight-average molar mass, M_w = 18 500 g mol^{-1}, is lower than molecular weight of PANI prepared under the same reaction conditions, M_w = 50 900 g mol^{-1}. The polydispersity characterized by the weight-to-number average molar-mass ratio, M_w/M_n = 2.9 and 3.8, for PBANI and PANI, respectively, is comparable in both cases.

Poly(2-bromoaniline) Dispersions

When aniline is oxidized in the presence of a suitable stabilizer, colloidal PANI dispersions are produced[26] instead of a precipitate. Both particulate stabilizers, like nano-colloidal silica[27,28], and water-soluble polymers have been used for the stabilization. Poly(vinyl alcohol)[11,29–32], poly(*N*-vinylpyrrolidone)[33,34] and (hydroxypropyl)cellulose[35,36] are examples of the latter group. Many other polymers have been successfully used for the stabilization of PANI dispersions[26].

When 2-bromoaniline was similarly oxidized in the aqueous media containing such stabilizers, well-defined colloidal dispersions have also been

obtained (Table III, Fig. 5). The particle size is in the submicrometre range and the polydispersity of particles is similar to that of PANI colloids[26]. The shape of particles is spherical except in dispersions stabilized with poly-(vinyl alcohol) where they are formed by aggregation of smaller particles (Fig. 5b).

TABLE III
The average diameter, D, of dispersion particles and the polydispersity index, P, of colloidal poly(2-bromoaniline) dispersions stabilized with various stabilizers (determined by dynamic light scattering[a])

Stabilizer	D, nm	P
Colloidal silica	933 ± 91	0.12 ± 0.05
Poly(vinyl alcohol)	643 ± 30	0.19 ± 0.02
Poly(N-vinylpyrrolidone)	391 ± 8	0.11 ± 0.02
(2-Hydroxypropyl)cellulose	549 ± 6	0.17 ± 0.02

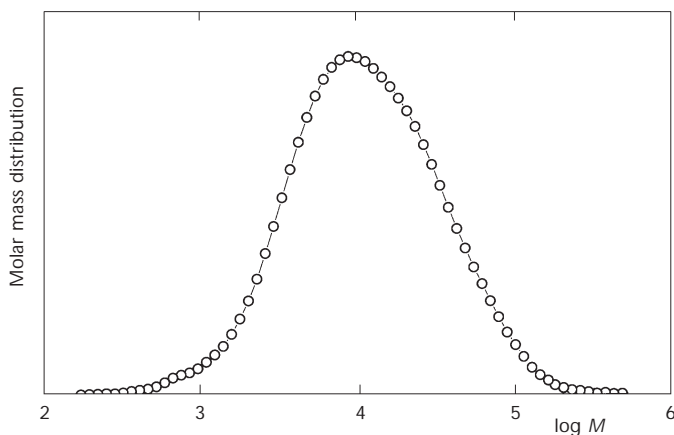[a] In 1 M HCl. Dispersions were sonicated for several minutes before measurement. Particles are shown in Fig. 5.

FIG. 4
Molar mass distribution determined by gel permeation chromatography of PBANI in N-methylpyrrolidone. M_w = 18 500 g mol^{-1}, M_w/M_n = 2.9

UV-VIS Spectra of Dispersions

Colloidal dispersions can conveniently be used for studies of optical absorption. For this purpose, they can be used instead of true solutions which, for conducting polymers, are difficult to obtain. In emeraldine, quinone diimine and 1,4-phenylenediamine units, assisted by electron pairs on ni-
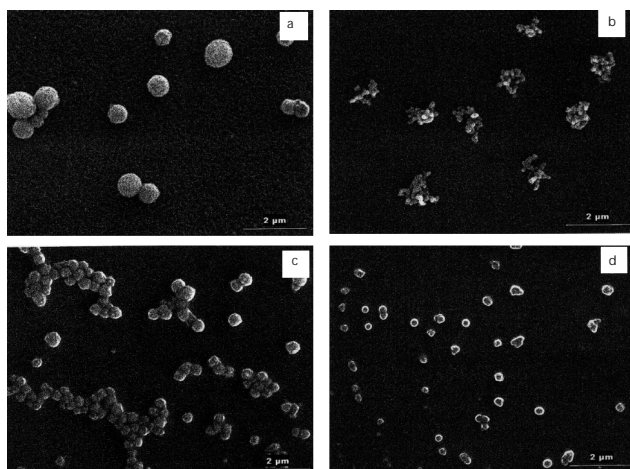

FIG. 5

Colloidal poly(2-bromoaniline) dispersions stabilized with colloidal silica (a), poly(vinyl alcohol) (b), poly(*N*-vinylpyrrolidone) (c) and (hydroxypropyl)cellulose (d)
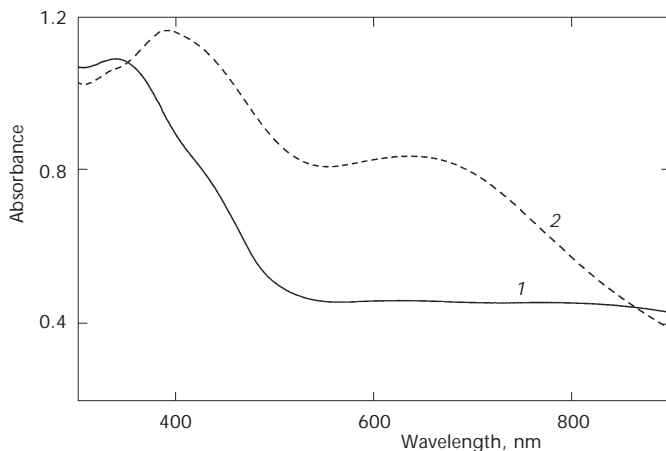

FIG. 6

Visible spectra of PVP-stabilized poly(2-bromoaniline) dispersion 60 × diluted with 1 M HCl and with 1 M ammonium hydroxide. PBANI·HCl (*1*), PBANI base (*2*)

trogens, produce a system of conjugated bonds. The length of conjugation in the PBANI base is also sufficient to produce an absorption band at 634 nm (Fig. 6), positioned similarly to a band observed at 610–630 nm for blue emeraldine base[17,37]. The protonation of emeraldine base leads to the shift of the latter absorption band to 810 nm, because the formation of cation radicals still supports the conjugation. Protonation of PBANI, however, results only in the band decrease, accompanied by an absorption broadening to the region around 800 nm. This suggests that protonation of imine nitrogens took place but, due to their infrequent occurrence, a low number of cation radicals has been generated. The absence of charge carriers is manifested by the low conductivity of PBANI, in both protonated and base forms (Table II). The UV-VIS spectra thus prove the presence of units capable of protonation in PBANI and the inability of such a process to generate cation radicals.

CONCLUSIONS

Compared with polyaniline, poly(2-bromoaniline) has less quinoid rings and, consequently, a lower number of imine nitrogens capable of protonation. This fact is supported by a low weight loss after deprotonation, reduced optical absorption in UV-VIS spectra, and by the reduced shifts of peaks reflecting the protonation in FTIR spectra. The limited protonation of poly(2-bromoaniline) results in low conductivity of the bulk polymer.

As with PANI, poly(2-bromoaniline) can be prepared in a colloidal form using various water-soluble polymers or nanocolloidal silica for stabilization. The dispersion particles have a submicrometre size and a moderate polydispersity, regardless of the stabilizer type, but their shape and morphology depend on the stabilizer used.

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