Nanoparticles of Conjugated Polymers

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Contents

1. Introduction

Since the broader awareness of the conductivity of conjugated polymers,[1−5] this class of materials has received ever-increasing attention. Conjugated polymers are widely propagated for applications relying on their conductivity, photo- or electroluminescence,[6] or light-induced charge generation, such as light-emitting devices and displays,[7−11] photovoltaics,[12−20] or chemical sensors[21] of variable complexity concerning their structure and function. Among others, such devices can be advantageous toward inorganic materials in terms of cost and flexibility. The most prominent types of conjugated polymers are polyaniline, polypyrrole, and polyacetylene and derivatives thereof, which have been studied intensely primarily due to their intrinsic conductivity, while polythiophenes, polyphenylenes, polyfluorenes, poly-(arylenevinylene)s, and poly(phenyleneethynylene)s have also been studied extensively due to their electrooptical and photoluminescence properties. In contrast to these intense studies of the preparation of conjugated polymers and their properties in the bulk or in thin films, which have also been reviewed extensively,[3−5,7−9,13−17,21] nanoparticles of conjugated polymers have been relatively little addressed. To render the term more precisely, a particle is considered to

Johannes Pecher (right), born in 1980 in Koetzting, Germany, studied chemistry at the University of Regensburg. He concluded these studies in 2006 with a diploma thesis on biomineralization at the CEA (Commissariat à l'Energie Atomique) in Saclay, France, in the framework of the international course "Complex Condensed Materials and Soft Matter", working with Corinne Chevallard and Werner Kunz. Currently, he is in the final stages of his Ph.D. studies at the University of Konstanz under the guidance of Stefan Mecking on fluorescent conjugated polymer nanoparticles from catalytic polymerization in emulsions and their imaging in cells. Stefan Mecking (left), born in 1966, received his Ph.D. degree from RWTH Aachen under the guidance of W. Keim in 1994. After an 18 month postdoctoral stay in the group of M. Brookhart (University of North Carolina at Chapel Hill) as a Feodor-Lynen-Fellow of the Alexander von Humboldt-Foundation, he went into corporate research at Hoechst AG in Frankfurt. In 1998 he joined Freiburg University, where he habilitated in macromolecular chemistry, before moving to his present position as Full Professor at the University of Konstanz in 2004. He has received several national and international awards, including the DECHEMA Young Lecturer Award, the BASF Catalysis Award, a Hermann-Schnell-Stipend, the Otto-Roelen-Medal, a Chemiedozenten-Stipend of the Fonds der Chemischen Industrie, and the Karl Ziegler-Giulio Natta-Lectureship of the Società Chimica Italiana. His research is focused on functional group tolerant polymerization catalysis regarding polymerization and deactivation mechanisms, the generation of crystalline and luminescent nanoparticles, and conversion of renewable resources.

be a submicrometer entity which represents a separate discontinuous phase, surrounded by a continuous free-flowing medium (usually a low-molecular-weight liquid, most often water) or placed on a surface. In terms of the classical systematization of colloid chemistry, this refers to particulate colloids and excludes true solutions of macromolecules in a low-molecular-weight solvent. Particulate colloids most commonly consist of particles with a lyophobic polymer interior, but also include cross-linked microgels, and two oppositely charged polyelectrolytes can also form particles. The above definition of particles also differentiates them from nanophase-separated solid bulk materials.

Submicrometer polymer particles are broadly applied in the form of aqueous dispersions for the preparation of

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coatings and in paints.[22−25] A key step in these applications is film formation upon evaporation of the dispersing medium, usually water. In comparison to solutions of high-molecular-weight polymers in organic solvents, which possess a very high viscosity even at low polymer concentrations, the particle dispersions retain a low viscosity also at high polymer solids contents. This can be beneficial for handling and processing. Particle dispersions are also useful for the generation of highly disperse heterophase materials.[26] A recent example is polyacrylate films rendered resistant to soiling by silica nanoparticles, which are prepared from dispersions of organic polymer/inorganic composite nanoparticles.[27−29] Concerning photoluminescence as a specific property of conjugated polymers, it is notable that nanoparticles of inorganic semiconductors have also been studied intensely more recently for this reason.[30−32]

The first reports of colloidal dispersions of nanoparticles of conjugated polymers appeared in the 1980s. Polyacetylene, polypyrrole, and polyaniline dispersions were generated by dispersion or emulsion polymerization. A motivation of these studies was the desire to overcome the notoriously difficult processing of conjugated polymers, most of which are insoluble unless substituted with appropriate side chains. Nanoparticles composed of the conjugated polymer poly[3,4-(ethylenedioxy)thiophene] (PEDOT) and the polyelectrolyte poly(styrenesulfonate) (PSS) are commercially available as aqueous dispersions under the trade name Baytron P/Clevios P. Aqueous and nonaqueous dispersions of doped polyaniline are marketed by Ormecon. Films prepared from such dispersions exhibit conductivities of up to $>10^3$ S cm^{-1}. Correspondingly, the dispersions are used, for example, for the preparation of hole injection layers in organic light-emitting diodes (OLEDs) or even as replacements for the common indium tin oxide (ITO) electrodes.

Nanoparticles of luminescent conjugated polymers have found attention only more recently, the first reports dating essentially to the past decade. They are studied, e.g., in the preparation of nanoscale multiphase films for photovoltaics or in biological imaging and cell labeling. In this review we give a comprehensive account of the preparation, properties, and utilization of such nanoparticles.[33] Concerning the aforementioned nanoparticles of polymers primarily associated with conductivity as such, issues specific to conjugated polymer nanoparticles in general are summarized, as well as the more recent advances beyond existing reviews. Particles are considered according to the above definition; that is, nanoparticles grown directly on a substrate or dispersed in a polymeric matrix, as well as other highly disperse composite materials containing conjugated polymers,[34] are strictly not in the scope of this overview, but are considered where appropriate.

2. Preparation of Nanoparticles

In principle, nanoparticles of conjugated polymers are accessible either by postpolymerization dispersion of separately prepared polymers or directly by polymerization in disperse heterophase systems. Both approaches have their merits and limitations. Postpolymerization nanoparticle generation can rely on commercially available polymers with given specifications and does not require equipment and expertise in organic and polymer synthesis. If required, polymers can be purified extensively after polymerization. Direct polymerization, on the other hand, is not restricted to polymers soluble in organic solvents and in principle can

afford a broader scope of nanoparticles in terms of size control and particle structure.

## 2.1. Postpolymerization Dispersion

Postpolymerization generation of polymer particle dispersions is also referred to as secondary dispersion. Note that such processes are also applied for the preparation of aqueous dispersions of polyurethanes on a larger scale[35] or more recently polyolefins[36] by various techniques. Of the different techniques possible for postpolymerization dispersion, dispersion of conjugated polymers has employed polymer solutions in an organic solvent as a starting point. Particle formation most commonly occurs either by solvent removal from emulsified solution droplets, which requires a solvent immiscible with the continuous phase of the final particle dispersion, or by precipitation of the polymer upon rapidly adding the polymer solution to an excess of the continuous phase, which requires a solvent miscible with the continuous phase.

2.1.1. Emulsion Technique

The preparation of nanoparticle dispersions by emulsification of a polymer solution, and subsequent removal of solvent from the droplets, requires the initial generation of sufficiently small droplets, which are also colloidally stable enough over time to allow for solvent removal without detrimental droplet coalescence. Submicrometer droplets are obtained by applying high shear, typically by means of a sonotrode. The emulsions generated commonly represent miniemulsions,[37−39] in which coalescence is prevented by surfactant adsorbed at the droplet/water interface and, more specifically, Ostwald ripening[40] by solvent diffusion through the aqueous phase is suppressed by a hydrophobe. The latter can be an additional additive, but in many cases this function is presumably fulfilled by the polymer itself. Subsequent evaporation of the organic solvent from the emulsion affords an aqueous dispersion of the conjugated polymer particles, which are stabilized toward coagulation by the surfactant.

In a typical procedure,[41] a mixture of a solution of the polymer in chloroform (1−5 wt % polymer) with a 5-fold excess of an aqueous solution of sodium dodecyl sulfate (SDS) surfactant (0.3−0.5 wt % SDS) was ultrasonicated for several minutes. Subsequently, the organic solvent was removed by keeping the emulsion at elevated temperature (60 °C) for several hours to afford stable polymer particle dispersions with a polymer solids content of up to 9 wt %. Average particle sizes amounted to 75−250 nm, depending on the amount of surfactant and the polymer concentration. Landfester et al. reported the preparation of secondary dispersions of methyl-substituted ladder-type poly(p-phenylene) **5** (Figure 1), of the polyfluorene derivatives **6c** and **6d**, of poly[[2-methoxy-5-[(2-ethylhexyl)oxy]-1,4-phenylene]vinylene] (MEH-PPV) (**7a**),[42] and of the poly(cyclopentadithiophene) **10** (see Scheme 1 for polymer molecular structures).

This approach has also been utilized for the preparation of multiphase particles.[44−46] From a miniemulsion containing poly(9,9-dioctylfluorene-2,7-diyl-co-benzothiadiazole) (**13**) and poly(9,9-dioctylfluorene-2,7-diyl-co-N,N′-bis(4-butylphenyl)-N,N′-diphenyl-1,4-phenylenediamine) (**21**), nanoscale-phase-separated particles of 40−150 nm size were prepared, the morphology of which was probed by fluorescence microscopy on films spin-cast from the particle dispersion.[45]
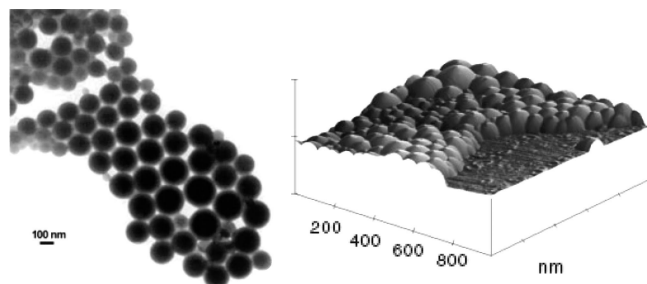
Figure 1. TEM image of nanoparticles of the poly(*p*-phenylene) **5** (left). Reprinted with permission from ref 41. Copyright 2002 John Wiley & Sons. 3D AFM image of a monolayer of nanoparticles of **5** on a glass substrate (right). Reprinted with permission from ref 43. Copyright 2003 John Wiley & Sons.

Figure 2. AFM image of MEH-PPV (**7a**) nanoparticles on a silicon substrate (left) and corresponding nanoparticle height histogram (right). Reprinted from ref 53. Copyright 2006 American Chemical Society.

Particles of only 13 nm size have been accessed by the postpolymerization emulsion technique using highly diluted solutions of polymer **7e** in dichloromethane, in combination with a large excess of poly(ethylene glycol) (PEG; PEG: polymer (mol/mol) >10^2) as a nonionic steric stabilizer. The resulting dispersions contain a low portion of ca. 0.002 wt % conjugated polymer.[47] In a related fashion, nanoparticles of **7a**, **7e**, **8b**, and **13** have been prepared using PEGylated phospholipids as steric stabilizers, which enable a subsequent covalent attachment of proteins at the particle surface with regard to biofunctionalization. Particles of typically 100 nm average size were found.[48] A study of the partioning of the tetradecyltrimethylammonium bromide (TTAB) cationic surfactant in the preparation of poly(9,9-di-*n*-tetradecylfluorene-*co*-fluorene) nanoparticles (50 nm) suggested that, due to the preference of this surfactant for the chloroform phase of the miniemulsion, a significant portion of TTAB segregated into the final polymer particle.[49] Not an emulsion technique, but notable in this context, is the preparation of suspensions of poly(3,3‴-didodecylquarterthiophene) (**15**) nanoparticles in an organic solvent reported by Ong et al. Sonication of a relatively concentrated (0.3 wt %), hot solution of **15** in dichlorobenzene afforded, after cooling, a suspension of nanoparticles with a size range of about 6–40 nm. This was attributed to a breaking of larger lamellar stacked networks by ultrasonication.[50]

2.1.2. Precipitation Technique

The generation of nanoparticles by precipitation, also termed reprecipitation or nanoprecipitation, involves the rapid addition of a very dilute (e.g., several tens of parts per million) polymer solution to an excess volume of nonsolvent, usually water. Mixing of the solvent with the nonsolvent results in a sudden decrease of solvent quality, which induces precipitation of the polymer. Under appropriate conditions, polymer nanoparticles result. Rapid mixing has been sought to be aided by ultrasonication, which may also otherwise impact the particle formation processes. In the preparation of poly(arylenevinylene) and polyfluorene nanoparticles, subsequent stirring at elevated temperatures evaporated the THF solvent and resulted in a surfactant-free dispersion of conjugated polymer nanoparticles in water with an average size in the range of 5–50 nm (Figure 2).[51,52] The nanoparticle size is adjustable primarily via the concentration of the organic polymer solution. The mechanism of colloidal stabilization of the nanoparticles remains unclear in this particular case; in contrast to the aforementioned emulsion techniques, no surfactant was added and also the polymer contains no significantly hydrophilic moieties. While charge
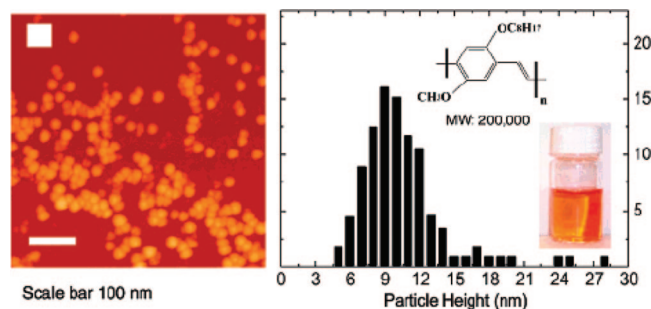
accumulated at the particle-dispersing medium interface may contribute to stabilization toward particle aggregation and coalescence, it must also be considered that impurities, present at low levels but sufficient with respect to the low concentration of polymer nanoparticles, can adsorb to their surface to provide steric or electrostatic stabilization.

The polymer chains are suggested to possess a collapsed conformation in these particles, which accounts for the spherical particle shape—representing the thermodynamically favorable lowest surface per volume—despite the rigidity of the polymer chain.[53]

The precipitation of a poly(aryleneethynylene), substituted with hydrophilic amine and PEG groups, from dilute DMSO solution afforded an aqueous dispersion of ca. 500 nm particles.[54] Note that amino groups on the particle surface can be useful for binding functional entities, e.g., proteins. Nanoparticles of 40–400 nm size of a substituted polythiophene, **2b**, were obtained by addition of THF solutions to water.[55] In comparison to the aforementioned studies, in these two examples, mixing was accomplished by stirring rather than ultrasonication, which may contribute to the larger particle sizes. By a related method, the exact nature of which remains somewhat unclear from the data reported, Moon et al. generated nanoparticles of polymer **16b** by solvent exchange via sequential ultrafiltration in the presence of acetic or ethylenediaminetetraacetic acid, which was suggested to facilitate removal of copper and palladium residues from the polymer that had been freshly prepared in a nonaqueous system.[56]

Reports of the generation of nanoparticles of conjugated polymers are not restricted to aqueous systems. Lai et al. prepared poly[1,3-bis(3-alkylthien-2-yl)azulene] and poly[1,3-bis(3-alkoxythien-2-yl)azulene] **12a**–**f** nanoparticles in a purely organic system by mixing equal amounts of a chloroform solution of the polymer and methanol.[57] Nanoparticles with an adjustable size from a few tens to five hundred nanometers grew over time via hydrophobic interactions and π-stacking (Figure 3). Nanoparticles of **13** were obtained by mixing THF solutions and cyclohexane.[58]

In an alternative approach, a solution of a substituted polythiophene, **2c**, in supercritical carbon dioxide has been expanded into an aqueous surfactant solution, which resulted in the formation of nanoparticles 45 nm in size.[59]

Fluorescent amphiphilic polymers with a hydrophobic polyfluorene backbone and hydrophilic PEG side chains formed nanoparticles in aqueous solutions. Other than the aforementioned precipitation methods, water was slowly added to a solution of the polymer in THF, which is a solvent for both the backbone and the PEG moieties. "Micellization"

Scheme 1. Conjugated Polymers Studied in the Form of Nanoparticles
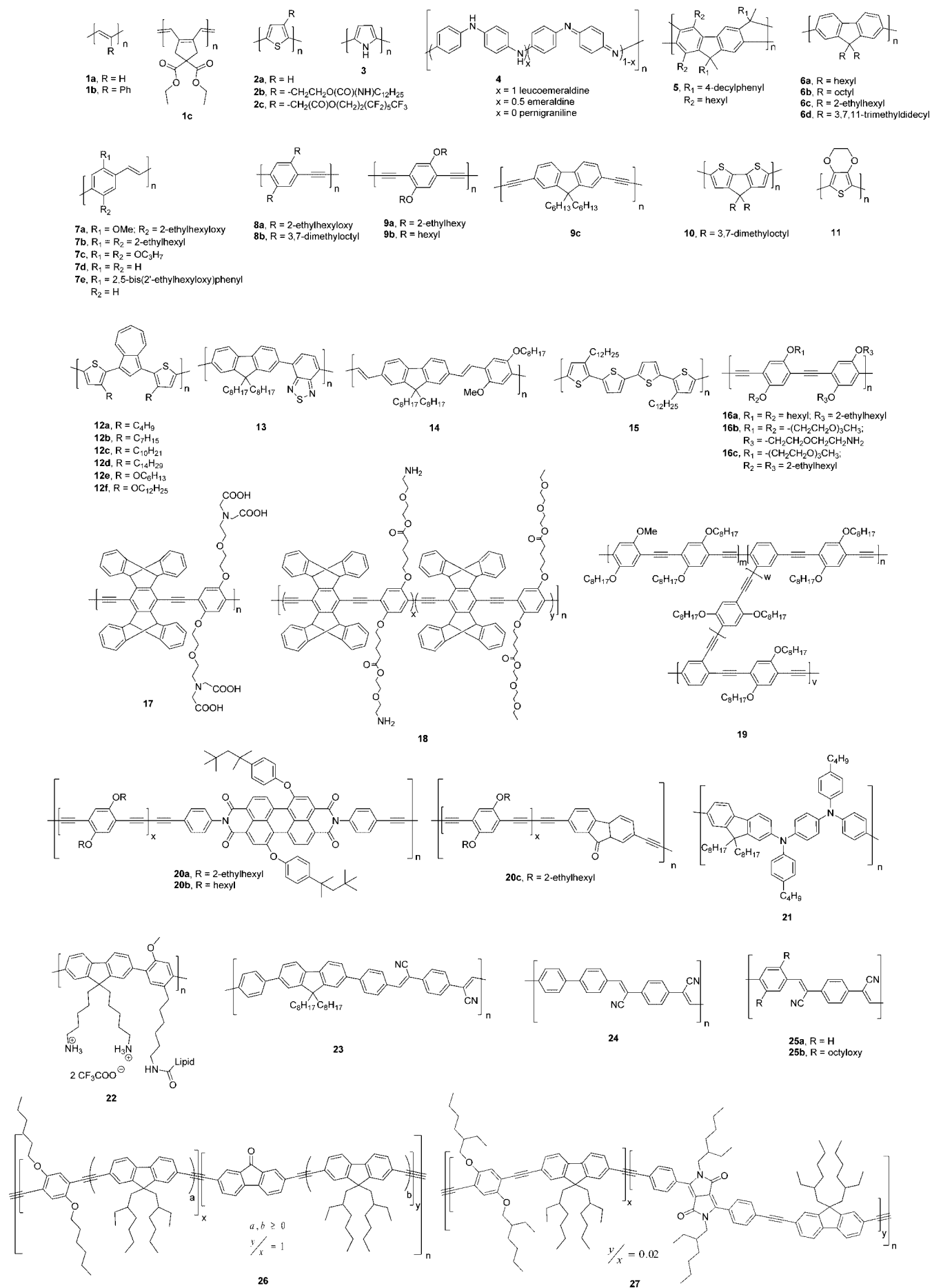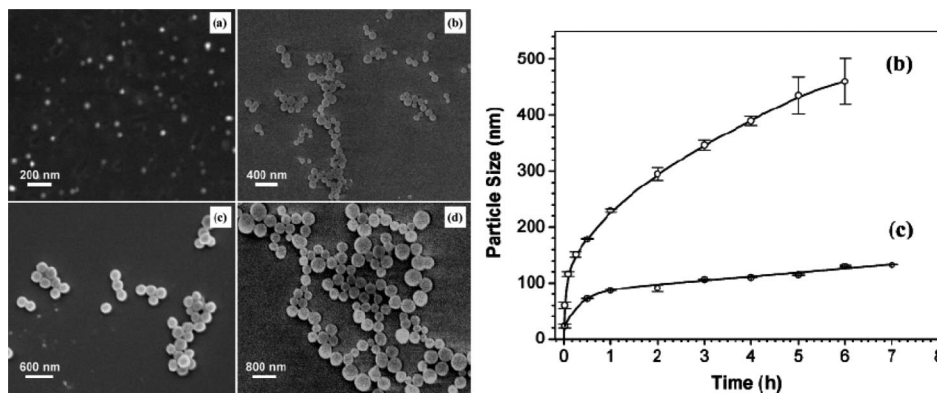
Figure 3. SEM images of nanoparticles of **12c** formed in 1:1 chloroform/methanol mixtures over the course of (a) 1 min, (b) 10 min, (c) 60 min, and (d) 240 min (left). Evolution of nanoparticle size over time employing a 10^{-5} M solution of (b) **12c** and (c) **12f** (right). Reprinted from ref 57 Copyright 2005 American Chemical Society.

Table 1. Particle Size and Composition of Conjugated Polymer Nanoparticle Dispersions Prepared via the Precipitation Technique

polymer	particle size (nm)	polymer solids content[a] (10^{-4} wt % $\equiv$ ppm)	M_w (10^3 g mol^{-1})	ref
2b	40−420[b,c]	20−200[b]	27	55
6a	3−7[d]	3.6	55	53
6b	50[d]	8	147	63
7a	5−14[d]	3.6	200	53
	5−30[d]	10	200	51
	10−100[e]	47	186	64
7d	340[c]	90[f]	nd	62
12c	60−400[c]	110	26	57
12d	30−100[c]	130	30	57
13	5−30[e]	50	(70)	65
14	8−12[d]	3.6	270	53
16b	97[c]	600	nd	66
17	28[c]	5	nd	67
18	400−500[c]	1	47	54

[a] Under the assumption that the volume of the aqueous phase is not reduced during evaporation of the organic solvent. [b] Adjustable by varying the preparation conditions. [c] Determined by DLS. [d] Determined by AFM of isolated particles on solid substrates. [e] Determined by comparing the single-nanoparticle fluorescence intensity distribution to that of a reference nanoparticle sample with a known size distribution. [f] Units of milligrams per liter.

resulted in nanoparticles between 85 and 178 nm in diameter.[60] Amphiphilic lipid- and alkylammonium-substituted poly(phenylenefluorene) **22** was reported to form nanoparticles of ca. 50 nm size in water, albeit the preparation procedure was not given.[61]

Like emulsion methods (section 2.1.1), precipitation methods are restricted to solution-processable polymers. However, the rigid backbone of conjugated polymers results in low solubilities in organic solvents, and the unsubstituted parent polymers are virtually insoluble in any solvent. Solubility requires the introduction of substituents as side chains, which also alters the electronic properties and often requires additional synthetic effort. Only most recently, the preparation of a dispersion of nanoparticles of an unsubstituted conjugated polymer by the precipitation method was reported, employing a precursor route. Shimomura et al. generated nanoparticles of a water-soluble PPV precursor polymer by adding an ionic liquid, which by itself is a poor solvent, to an aqueous polymer solution and evaporating the water.[62] The high boiling point of the ionic liquid allowed for the subsequent thermal conversion of the precursor polymer to poly(p-phenylenevinylene) (**7d**) in the form of nanoparticles. The molecular weights of the polymers and the issue of colloidal stability remain to be addressed.

In comparison to the emulsion technique, generation of nanoparticles by the precipitation technique generally yielded

smaller particles (Table 1), and the polymer solids contents of the resulting dispersions or suspensions are much lower. In some cases, particle sizes are so low that they correspond to single-polymer-chain particles.[51,58] Note that this probably does not reflect a limitation of emulsion methods regarding the accessibility of particularly small particles, but rather emulsion techniques have been employed when substantial polymer contents of the resulting dispersions were aimed for.

2.2. Polymerization in Heterophase Systems

The direct generation in the form of nanoparticles of a polymer during its synthesis from low-molecular-weight monomers, by polymerization in a dispersing medium which is a nonsolvent for the polymer, provides access to a broad scope of nanoparticles in terms of size control and particle structure. Also, polymers entirely insoluble in any solvent are accessible as nanoparticles, which is of particular interest regarding the lack of solubility of many conjugated polymers. This low solubility (and infusibility) in general, and the corresponding lack of processability, was indeed a motivation for the first studies of conjugated polymer nanoparticles. In 1983 Vincent et al. reported on the preparation of submicrometer polyacetylene (**1a**) particles by acetylene polymerization in the presence of block copolymers as steric stabilizers.[68] Bjorklund and Liedberg obtained colloidal

polypyrrole (**3**) dispersions,[69] and Armes and Aldissi reported on colloidal dispersions of polyaniline (**4**).[70] During the following decade, sterically stabilized nanoparticle dispersions of polyacetylene, polypyrrole, and polyaniline were studied intensely, a major aim being the processability to conducting polymeric materials. This work has been reviewed by several authors.[71−77] The polymerization of 3,4-(ethylenedioxy)thiophene (EDOT) in the presence of polyelectrolyte is employed commercially for the preparation of PEDOT/PSS dispersions.[78] More recently, the scope of direct polymerization to nanoparticles has been extended to other classes of conjugated polymers, which among others are of interest for their luminescence, such as poly(phenylenevinylene) **7**,[79] poly(phenyleneethynylene) **16**,[80] and polyfluorene **6**. Other than polypyrrole, polyaniline, or polythiophene, these polymers cannot be prepared by aqueous oxidative polymerization. Rather, their preparation frequently involves transition-metal-catalyzed coupling reactions, which must be compatible with the specific heterophase polymerization for nanoparticle synthesis.

Prior to a discussion by polymer types, the relevant types of heterophase polymerizations are briefly defined and differentiated. *Dispersion polymerization* refers to a polymerization in a reaction medium completely miscible with the monomer, but in which the polymer is insoluble. In this respect it is akin to precipitation polymerization. However, the particles formed are prevented from extensive agglomeration and macroscopic precipitation by steric stabilizers adsorbed or covalently bound to the particle surface, keeping their size small and number density high and rendering the particles colloidally stable. In *emulsion polymerization* the monomer possesses a limited, low solubility in the dispersing medium and forms a separate droplet phase. Polymerization starts in the dispersing medium (commonly water), which requires initiators or catalysts to be dissolved in the latter. Chain growth results in the nucleation of hydrophobic particles, which are stabilized by adsorption of added surfactant or by lyophilic moieties covalently incorporated into the polymer. Further polymerization occurs in the particles, to which the monomer diffuses from the monomer droplets through the aqueous phase, the latter serving only as a reservoir but ideally not being the site of polymerization. This requires a low, but sufficient, water solubility of the monomer. A variant is *miniemulsion polymerization*. Other than the aforementioned (macro)emulsions, in which monomer droplets constantly coalesce and are broken up by shear (typically provided by a stirrer), miniemulsions once formed can be sufficiently stable over the time scale of the polymerization experiment. This requires suppression of Ostwald ripening by a hydrophobe present in small amounts (vide supra). Polymerization occurs in the droplets (50−500 nm in size), and ideally a given droplet is polymerized to a nanoparticle, such that the final particle dispersion is a replica of the initial miniemulsion. Initiators or catalysts can be soluble either in the monomer phase or in the dispersing medium. In the latter case, undesirable nucleation outside the droplets is suppressed by the large capture cross section provided by a high droplet number density and by the absence of free surfactant. *Microemulsion polymerization* starts from a monomer microemulsion as the initial state. Microemulsions[81,82] are thermodynamically stable mixtures which can exist in a certain composition regime for a given system of monomer, surfactant, dispersing medium, initiator, etc. Practically, the existence of a micro-

emulsion is indicated by the gradual formation of a single transparent phase without application of shear. The dynamic nature of microemulsions renders particle formation processes more complex in comparison to miniemulsion polymerization.[83] Essentially, due to their extremely high degree of dispersion, with a typical length scale around 10 nm, microemulsions are suited for the synthesis of particularly small particles (<20 nm).

In heterophase polymerizations, the miscibility of monomer and polymer decisively impacts the course and outcome of the reaction. For example, in dispersion polymerization a high solubility of the monomer in the polymer particles, that is, swelling of the particles by monomer, favors polymerization to occur in the particles once they are formed, rather than in the dispersing medium. In miniemulsion polymerization, a low solubility of the polymer in the monomer will promote phase separation in the droplets. In general, the formation of spherical particles with a thermodynamically favorable minimum surface to volume ratio is favored by miscibility of monomer and polymer, as exemplified by the textbook polystyrene spheres prepared by emulsion polymerization. A typical feature of the parent unsubstituted representatives of the various classes of conjugated polymers is a low miscibility with their monomers, which indeed frequently results in particle shapes other than perfect spheres (note that a nonspherical shape can also result from ordering phenomena such as crystallization). Another, sometimes underrated, feature of many heterophase polymerizations is that the final particles and their number density are determined just as essentially by coagulation of existing particles during polymerization as by nucleation and growth. If the original particles do not completely coalesce in the final particles, this will influence not only their size but also their morphology. This is particularly relevant for polymers not in a rubbery, viscoelastic state during polymerization, which applies to many conjugated polymers. Therefore, final particles may consist of more or less strongly bound smaller primary particles, which is not always evident from the analytical data provided.

2.2.1. Polypyrrole

Polypyrrole (**3**) is usually prepared by oxidative polymerization. Polymerization can be performed in an aqueous medium, in which pyrrole is essentially soluble (saturation concentration 0.9 M in water), using $FeCl_3$ or ammonium persulfate (APS) as oxidants. Theoretically, 2.33 mol of ferric chloride is required to convert 1 mol of pyrrole to the polymer.[84]

A first approach toward polypyrrole nanoparticles was reported by Bjorklund and Liedberg, who polymerized pyrrole in water in the presence of methyl cellulose. Particles of 100−200 nm size were observed in films spread from the reaction mixture.[69] Contemporaneously, Armes and Vincent prepared colloidally stable dispersions of polypyrrole nanoparticles by aqueous dispersion polymerization in the presence of poly(vinylpyrrolidone) (PVP) or poly(vinyl alcohol-*co*-vinyl acetate) (PVA) as a stabilizer.[85] Such steric stabilization by "protective colloids" or amphiphilic polymers, which prevent macroscopic precipitation of the growing polymer, was studied comprehensively with the aim of generating conductive polypyrrole in processable form. Besides PVP[85] and PVA,[86,87] a wide range of polymers act efficiently as stabilizers including poly(ethylene oxide) (PEO),[88,89] various vinylpyridine homo- and copolymers,[90−92]

poly(vinyl acetate),[93] poly(vinyl methyl ether) (PVME),[94] a multiblock copolymer consisting of PEG and poly(tetramethylene ether glycol) blocks,[95] and PSS.[96,97] Beyond these examples, Stejskal provides a comprehensive summary of steric stabilization in polypyrrole colloid syntheses.[73] It is believed that the polymeric stabilizers are adsorbed onto the surface of the polypyrrole particle, basically by H-bonding of the N−H moieties of the pyrrole units in the particles and suitable counterparts of the stabilizer, resulting in a core−shell morphology.[86,90,91] The layer thickness of this shell has been determined to be approximately 25 nm in the case of poly(4-vinylpyridine-co-n-butyl methacrylate) (P4VP-BMA).[92] Covalent incorporation of a reactive steric stabilizer on the surface of polypyrrole particles has been reported.[98] Depending on the nature of the stabilizing polymer, the amount of steric stabilizer required to prepare stable polypyrrole nanoparticle dispersions varies strongly (Table 2).

A minimum quantity of the stabilizer is necessary,[86] which decreases with increasing molecular weight of the polymeric stabilizer,[99] which again needs to be essentially high to exert stabilizing properties, as found for PEO,[88] PVP, and P4VP.[90] Increasing the initial stabilizer concentration under otherwise identical conditions results in a reduced particle size and also a decrease of conductivity in the case of, e.g., PVA[86] and EHEC,[102] whereas no influence was observed for P4VP-BMA.[90] In general, unimodal spherical polypyrrole particles are obtained ranging from 50 to 400 nm in size, depending on the nature of the stabilizer and its concentration and molecular weight. Additionally, the oxidant appears to play a significant role. A size reduction of roughly one order of magnitude was observed when using potassium persulfate instead of FeCl$_3$.[88] The particle size could be controlled via the concentration of the oxidant in the range of 40 nm to 1 μm, in combination with the polyelectrolyte PSS as a stabilizer.[96] Recently, the dispersion polymerization of pyrrole under ultrasonication, with the aim of reducing the particle size, was reported to yield an average particle size of 67 nm.[97]

Dispersions of sterically stabilized polypyrrole nanoparticles in nonaqueous solvents are accessible by several different approaches. Appropriately sterically stabilized particles can be redispersed after isolation by centrifugation or freeze-drying. Thus, they may be transferred into other media, which are good solvents for the stabilizing polymer. This concept has been demonstrated for methanol and dioxane[88] as well as for chloroform, acetone, and dimethylformamide (DMF).[103] Polypyrrole nanoparticles were also prepared by nonaqueous dispersion polymerization in protic and aprotic organic solvents (methyl acetate, methyl formate, propyl formate,[104] 2-methoxyethanol,[93] or ethanol[105]). Another approach to dispersions in organic solvents is based on an aqueous dispersion polymerization in the presence of a polyelectrolyte with bromide counterions as a stabilizer. The resulting polypyrrole nanoparticles precipitate upon addition of organic salts, which render the polyelectrolyte hydrophobic by counterion exchange, and can be redispersed in various organic solvents such as DMF, acetone, THF, butanone, or toluene, depending on the nature of the counterions.[106]

To enhance the conductivity of materials prepared from dispersions, it can be beneficial to remove the steric stabilizer, which was shown to lower the conductivity of pressed pellets.[86] Vincent et al. found that, with PEO, a steric stabilizer thought not to adsorb as strongly to the polypyrrole surface as PVA or PVP, exhaustive dialysis and several centrifugation/redispersion cycles in water may strip off the stabilizer, resulting in "bare" charge-stabilized particles.[88,100]

In addition to polymeric stabilizers, electrostatic stabilization by low-molecular-weight ionic surfactants is also feasible. While these studies have been termed emulsion polymerization, microemulsion polymerization, and the like, the actual initial state and structure of the reaction mixture have rarely been clarified explicitly. Basically, pyrrole is polymerized in a stirred aqueous surfactant solution containing APS or FeCl$_3$ as an oxidant, with varying surfactant concentrations, including high surfactant concentrations in the general range of microemulsions. At these high concentrations, very small particles of <10 nm size can be formed. The observation of very different final structures, from spherical particles to nonspherical and extended structures, can be taken as an indication that the structure of the initial reaction mixture significantly influences the morphology of the polymer formed.[107−109]

Concerning the colloidal stability of the individual nanoparticles toward aggregation, the polypyrrole nanoparticles typically were precipitated directly after the appropriate reaction time by addition of methanol, or they precipitated already during polymerization. A direct preparation of explicitly colloidally stable surfactant-stabilized polypyrrole nanoparticles is rare.[110] A study of pyrrole polymerization in the presence of a range of different surfactants stated that polymer precipitated in all cases, and no colloids formed.[111,112] Thus, it is worth noting when considering the shapes and sizes of the surfactant-stabilized polypyrrole nanoparticles that they are usually based on TEM observation of the isolated dried bulk materials, rather than nonaggregated[107,108,113,114] individual nanoparticles. In some cases nanoparticles can be redispersed, but the colloidal stability of the resulting dispersions remains unreported.[107,115,116]

Cationic,[108,113,115,116] anionic,[117,118] and nonionic[109,114] surfactants, as well as mixed surfactant systems,[107] and the addition of alcohols as "cosurfactant"[119] were employed in polypyrrole nanoparticle synthesis. Anionic surfactants can be incorporated into the particles, as counterions to cationic protonated, that is, "doped", repeat units of the polymer.[111,112] The observed particle sizes and shapes appear to depend subtly on the experimental conditions of preparation and further analysis. For particles prepared under identical conditions except for a minor modification of the surfactant (octyltrimethylammonium bromide (OTAB) vs dodecyltrimethylammonium bromide (DTAB), different authors re-

Table 2. Composition and Particle Sizes of Polypyrrole Dispersions[a]

	m(stabilizer)/ m(pyrrole)				
stabilizer	polymerization mixture	final particles[e]	solids content (%)	particle size (nm)	ref
PVA	0.2−0.5	0.12	1	100−150	86
methyl cellulose	0.032−1.6	nd	0.25−1.8	100−200	69
P4VP-BMA	0.4−0.6	0.23−0.35	1	85−112	90
P2VP-BMA	0.5−1	0.11−0.2	1	130−200	91
EHEC[b]	0.25	0.13−0.16	2	54−125	99
PEO	0.1	nd	2	300−450	100
P2AEM-VT[c]	1	0.25	1	100	98
P2AEM-BMA[d]	2	1	1	50−70	101

[a] FeCl$_3$ as oxidant. [b] Ethyl hydroxyethyl cellulose. [c] Poly[2-(dimethylamino)ethyl methacrylate-co-3-vinylthiophene]. [d] Poly[(N,N-dimethylamino)ethyl methacrylate-block-n-butyl methacrylate]. [e] Composition of particles obtained by removal of excess stabilizer by centrifugation.
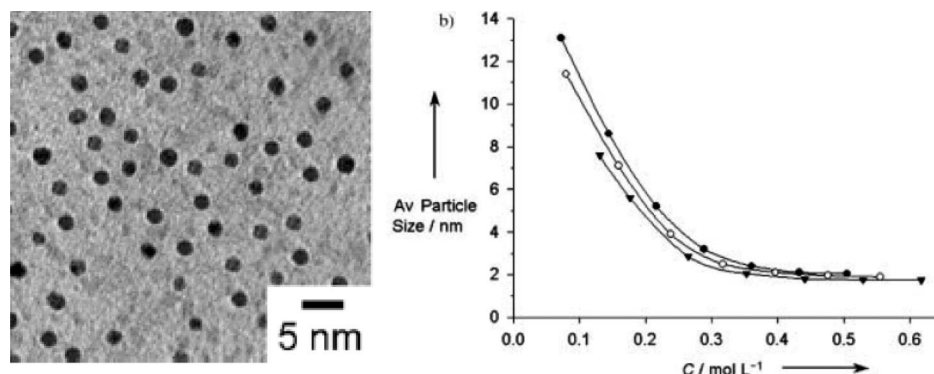
Figure 4. TEM image of **3** nanoparticles prepared in the presence of 0.44 M octyltrimethylammonium bromide (left). Reprinted with permission from ref 113. Copyright 2002 Royal Society of Chemistry. Dependence of the average nanoparticle size on the surfactant concentration (right): ●, dodecyltrimethylammonium bromide; ○, decyltrimethylammonium bromide; ▼, octyltrimethylammonium bromide. Reprinted with permission from ref 108. Copyright 2002 John Wiley & Sons.

ported particle diameters of 2−8 nm[113] and 100−200 nm,[115] respectively.

Remarkably, polypyrrole particles with sizes as small as 2 nm could be obtained (Figure 4).[108,113] Beyond the concentration of surfactant (Figure 4), further factors decisively influence the particle size and shape. An increase of the particle size by an order of magnitude with increasing ratio of oxidant to pyrrole was observed.[118] The combination of surfactant and oxidant also can have a strong impact. With decyltrimethylammonium bromide, sheetlike or layerlike structures formed, which is attributed to lamellar phases formed by the cationic surfactant and the bivalent counterion originating from the oxidant ammonium persulfate, whereas the anionic surfactant sodium bis(2-ethylhexyl) sulfosuccinate afforded spherical nanoparticles under otherwise identical conditions.[118] With the same cationic surfactant at much higher concentrations, Jang et al. obtained spherical nanoparticles, which might be rationalized by the nature of the oxidizing agent used, $FeCl_3$ instead of APS.[108] The effects of the monomer concentration, surfactant concentration, nature of the surfactant, and various oxidizing agents on the morphology of polypyrrole have been investigated in more detail by Tauer and co-workers[246] and Zhang et al.[109]

In addition to low-molecular-weight ionic surfactants and polymeric stabilizers, nanoparticles of inorganic solids have also been employed for colloidal stabilization of polypyrrole as well as polyaniline dispersions. The resulting submicrometer-sized particles exhibit a distinctive raspberry-like morphology ascribed to an agglomeration of silica nanoparticles coated individually with a very thin layer of the conjugated polymer.[73,120−123]

Plasma polymerization was reported to yield uniformly distributed spherical polypyrrole nanoparticles of 100−200 nm size, grown on a glass substrate.[124,125]

2.2.2. Polyaniline

Polyaniline (**4**) has been studied extensively due to its environmental stability and ease of preparation.[126] As for **3**, processing to conductive films, coatings, and the like is a major motivation for the study of polyaniline nanoparticles. The comprehensive studies on polyaniline nanoparticle preparation and morphology have been reviewed.[72−76,127−130]

Traditionally, polyaniline is obtained via chemical-oxidation polymerization in acidic aqueous media with oxidants such as APS. Seminal studies of PANI nanoparticles were carried out by Armes and Vincent.[70,131] Employing a block

copolymer with polymerizable aniline moieties as a steric stabilizer in combination with a suitable oxidant, particles of ca. 100 nm length with a "rice grain" shape were obtained. With another stabilizer, spherical (polydisperse) particles formed. Vincent argued that, to overcome the aggregation of nanoparticles, which occurs in a chainlike fashion, resulting in fibrils associated with gel networks, a rapid efficient stabilization of nanoparticles during the polymerization process is required. Dispersion polymerization with polymeric stabilizers has become a well-established process for the generation of PANI nanoparticles, which is subject to ongoing studies concerning variations of stabilizers and oxidants and their impact on the particle size and morphology. Dilute or semidilute sodium PSS solutions allow for the synthesis of PANI nanoparticles as small as 2−3 nm, which is on the scale of molecular dimensions for such conjugated polymers.[132,133] PANI−PSS nanoparticles (with an average diameter of 28 nm) were reported to be sufficiently colloidally stable for processing via inkjet printing to chemical sensors.[134] Carboxymethyl chitin as a steric stabilizer afforded ca. 500 nm sized globular aggregates of small primary particles, from which the carboxymethyl chitin could be removed after polymerization.[135] Electrically conductive hydrogels containing PANI nanoparticles were prepared by a conventional aniline dispersion polymerization with PVP as the steric stabilizer, followed by γ-irradiation-induced cross-linking of the PVP components.[136] Horseradish peroxidase-catalyzed enzymatic polymerization, which unlike oxidation with traditional chemical oxidants is not autocatalytic and allows for control of the oxidation rate, in dispersion with PVA, chitosan, and poly(N-isopropylamide) as steric stabilizers in combination with a variety of "doping" agents afforded mainly spherical particles with sizes ranging from 50 to 350 nm.[137−139] Interfacial polymerization of aniline in a biphasic system was reported to yield PSS-stabilized PANI nanoparticles of 5−15 nm size. Polymerization was suggested to occur at the interface of two immiscible solvents, containing the aniline and PSS, respectively (e.g., chloroform and water), by reaction of protonated aniline monomer and APS oxidant to yield PSS-stabilized nanoparticles which diffuse into the aqueous phase.[140]

In addition to polymeric stabilizers, colloidal stabilization of PANI nanoparticles by low-molecular-weight surfactants has also been further studied.[141] Aniline polymerization has been investigated in systems termed emulsion polymerization or microemulsion polymerization and the respective reversed systems[142,143] with organic solvents as the continuous phase.

In a study by Im et al. at low surfactant concentrations stable (spherical) PANI nanoparticles were only obtained using anionic surfactants, which can be incorporated into the particles as counterions to cationic protonated, that is, doped, repeat units of the polymer.[144−147] Wallace et al. found an optimum ratio of aniline to oxidant (APS) and "dopant" (DBSA) of 1:1:1 for obtaining PANI dispersions with spherical particles around 10 nm in diameter[148] suitable as inkjet printable formulations.[149,150]

For substantially higher amounts of surfactant in the general range of microemulsions, extremely small monodisperse spherical particles with a diameter of 4 nm were obtained in the presence of the cationic surfactant octyltrimethylammonium bromide. The particle size could be controlled as functions of the surfactant concentration, surfactant alkyl chain length, and polymerization temperature (Figure 5).[151] Similar trends have been observed in the preparation of polypyrrole nanoparticles.[108]

Corresponding inverse systems have been reported for cationic, anionic, and nonionic surfactants in various organic solvents, resulting typically in spherical 10−50 nm sized PANI nanoparticles.[152−154] Such polymerization systems were found to yield PANI nanoparticles with high crystallinity.[155,156]

Miniemulsion polymerization has been examined in both the direct and inverse states in PANI nanoparticle preparation.[157] Stable PANI latices could be obtained with H_2O_2 as the oxidizing agent, providing highly crystalline PANI in the emeraldine form in a new crystal morphology. In direct miniemulsion polymerization, the addition of steric stabilizers after miniemulsification with ionic surfactants was necessary to obtain colloidally stable particles.

Recently, surfactant-free, stable aqueous PANI nanoparticle dispersions have been prepared by oxidative polymerization of a boronic acid-substituted aniline in the presence of fluoride in 0.1 M phosphoric acid. The colloidal stability of the 25−50 nm sized particles is attributed to the formation of a boron−phosphate complex. The coordinating fluoride affords doping of the polymer, such that it is in the emeraldine salt form up to pH 9.[158]

PANI nanoparticles have also been prepared by alternative procedures, briefly outlined here. Electrochemical PANI nanoparticle synthesis[159] combined with a sonochemical pulse generated 20−40 nm sized particles, grown at the electrode during the on time of the potential and removed from the electrode surface during the off time by the sonochemical pulse.[160] Aniline was polymerized inside a polymeric matrix, generated by solvent casting of a PVA/aniline hydrochloride

Figure 5. TEM images of PANI nanoparticles prepared in a microemulsion at 3 °C using (a) OTAB and (b) DTAB. Reprinted with permission from ref 151. Copyright 2007 Korea Institute of Science and Technology Information.

solution, by γ irradiation. Randomly distributed PANI particles of 50−100 nm size formed inside the film, which changed color and increased its conductivity substantially during irradiation.[161]
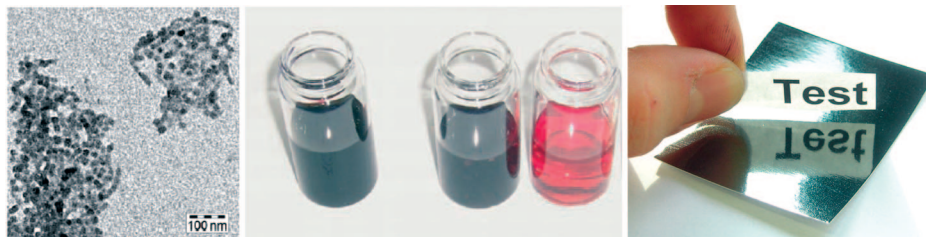
2.2.3. Polyacetylenes

Albeit the conductivity of polyaniline was known at the time,[162,163] it was the discovery of the conductive properties of doped **1a** which triggered widespread interest in conjugated polymers. Polyacetylene is the simplest conjugated polymer in terms of molecular structure and thus can be considered the prototype of conducting polymers. Studies of nanoparticles of polyacetylene are, however, scarce in number. In contrast to the oxidative polymerization of pyrrole and aniline, the insertion polymerization of acetylene employs transition-metal catalysts, which are commonly extremely sensitive to moisture and oxygen. In 1983, Vincent et al. reported the preparation of polyacetylene nanoparticles by polymerizing acetylene gas in a THF/cyclohexane solution in the presence of poly(*tert*-butylstyrene-*block*-ethylene oxide) as a steric stabilizer, employing the cobalt-based Luttinger catalyst. Roughly spherical latex particles in a rather polydisperse distribution with sizes ranging from 40 to 200 nm were obtained.[68] Essentially comparable results were achieved in a closely related polymerization system with the titanium-based Shirakawa catalyst. The nonaqueous sterically stabilized nanoparticles exhibited diameters between 60 and 420 nm.[164] More recently, a nonaqueous emulsion consisting of cyclohexane as the continuous phase and acetonitrile as the dispersed phase, containing poly(isoprene-*block*-methyl methacrylate) as an emulsifier, was used as a medium for acetylene polymerization with the Luttinger catalyst. Bubbling acetylene gas through the emulsion resulted in nanoparticles with 40 nm size.[165] As far as has been addressed, the conductivities of these polyacetylenes after doping were unsatisfactory, likely due to the steric stabilizers.[164]

A polymerization of acetylene in an aqueous system was reported only recently.[166] A palladium(II) catalyst modified by 1,3-bis(di-*tert*-butylphosphino)propane proved to be stable and very active in acetylene polymerization in an aqueous emulsion. In comparison to the aforementioned nonaqueous polymerizations, in which catalyst productivities were rather low (35 mol of acetylene/mol of metal),[165] productivities in this aqueous polymerization amount to >10³ mol of acetylene polymerized/mol of Pd. The catalyst system dissolved in hexane/ethanol was miniemulsified in an aqueous SDS solution by sonication. Bubbling of acetylene gas through the miniemulsion resulted in stable dispersions of polyacetylene nanoparticles ca. 20 nm in size, with solids contents up to 7 wt % (Figure 6).

The aforementioned Pd(II)/diphosphine catalyst system also polymerizes phenylacetylene with very high activities of >10⁵ mol of acetylene/mol of Pd in an aqueous emulsion. An SDS-stabilized miniemulsion of the monomer, containing the dissolved lipophilic catalyst, was generated by sonication. Polymerization was subsequently triggered by addition of a small amount of strong acid, which activates the catalyst. Stable poly(phenylacetylene) (**1b**) dispersions with solids contents of up to 36 wt % were obtained, composed of spherical particles with sizes in the range from 50 to 150 nm.[167] Polymerization in a microemulsion afforded poly(phenylacetylene) dispersions with only 25 nm particle size, at polymer solids contents of 6 wt %.[167] Polymerization of
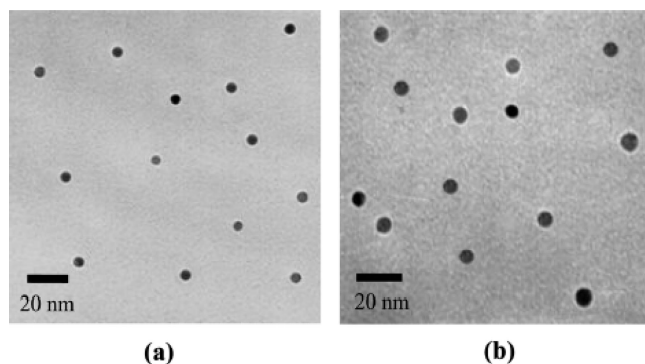
Figure 6. TEM images of **1a** nanoparticles (left). Macroscopic appearance of the polyacetylene dispersion (center) (polymer solids content 6.4 wt %; left to right, undiluted, 10^3- and 10^4-fold dilution). Film prepared by spreading and drying the dispersion on white paper (right). Reprinted with permission from ref 166. Copyright 2006 John Wiley & Sons.

acetylenes substituted with chiral substituents in aqueous microemulsions containing DMF and SDS surfactant by a hydrophobic rhodium catalyst yielded dispersions of helical, optically active polymers. Average particle sizes observed by TEM of 70−100 nm are relatively large given the large amount of surfactant employed, which exceeds the amount of monomer. The polymers formed have molecular weights around $M_n = 2 \times 10^4$ g mol^{-1}, with narrow distributions, as determined by GPC in THF vs polystyrene standards.[168] Free radical polymerizations in the presence of such polyacetylene particles yielded core−shell particles with a polyacrylate shell.[169]

An approach to polyacetylene that is an alternative to insertion polymerization is ring-opening metathesis polymerization (ROMP) of cyclooctatetraene (COT).[170−172] In employing a liquid monomer rather than gaseous acetylene, this is to some degree complementary in terms of the initial state of the reaction mixture and avoids the handling of thermodynamically unstable acetylene. Ruthenium-catalyzed ROMP in general has been demonstrated to be well suited for aqueous systems.[173,174] However, the ROMP of COT is associated with a very low release of ring strain as a driving force. Nonetheless, ROMP of COT in an aqueous miniemulsion by lipophilic N-heterocyclic carbene-substituted ruthenium alkylidene (Hoyveda−Grubbs catalyst precursor) proceeded to colloidally stable dispersions. Polymerization in a miniemulsion at 50 °C with a monomer:catalyst ratio of 200 resulted in virtually complete conversion. Polyacetylene nanoparticles of ca. 100 nm average size resulted. Employing a COT/cyclooctadiene mixture resulted in copolymers with a shorter conjugation length. Hydrogenation in the dispersion afforded polymer amenable to GPC analysis, revealing a molecular weight around $M_n = 10^4$ g mol^{-1} and a distribution M_w/M_n of 2.5. Analogous polymerization of COT in microemulsions afforded very small particles of only 8 nm size according to DLS.[175]

Metathesis was also employed by Buchmeiser et al. in the cyclopolymerization of 1,6-heptadiynes with a polymer-bound ruthenium-based metathesis catalyst. The amphiphilic block copolymer to which the catalyst is bound also stabilizes the polymer particles formed. Aqueous dispersions of substituted polyacetylenes **1c**, stable for several weeks, with particle sizes between 100 and 200 nm were obtained.[176]

2.2.4. Polythiophenes

Regarding nanoparticles of polythiophenes, PEDOT (**11**) is the most studied representative. PEDOT has gained considerable scientific and commercial interest in recent years due to a number of advantageous properties such as high transparency in the visible range and excellent thermal stability.[78] Aqueous dispersions of PEDOT containing substantial amounts of the anionic polyelectrolyte PSS, which

serves also as a charge balance for the cationic oxidized PEDOT, have been developed by Bayer AG and commercialized under the trade name Baytron P. Today, various PEDOT/PSS aqueous dispersions are available from H. C. Starck GmbH sold as Clevios P. These dispersions contain the stabilizer in at least the same weight fraction as PEDOT with solids contents ranging from 1.2 to 3.2 wt %. The particle sizes are 35−100 nm, and thin films thereof exhibit conductivities up to 900 S cm^{-1}.[177]

PEDOT nanoparticle dispersions are usually prepared by aqueous oxidative polymerization of 3,4-(ethylenedioxy)-thiophene with iron(III) salts or peroxodisulfate in the presence of polyelectrolytes, steric stabilizers, or low-molecular-weight surfactants. As exemplified by the aforementioned example of PEDOT/PSS, anionic additives will function as counterions to the cationically charged doped PEDOT.

Nanoparticles of unsubstituted polythiophene (**2a**) were generated by oxidative polymerization of thiophene in aqueous surfactant solutions.[178] Oxidation with H_2O_2 and catalytic amounts of Fe^{3+} ions was found to be advantageous over iron(III) salts as the sole oxidant, as iron can deteriorate the photoluminescence properties. Of a range of surfactants studied, SDS was found to be most convenient in terms of monomer conversion (99%). This was related to electrostatic interactions between SDS and Fe^{3+}, which ensure proximity of the latter to the swollen micelles or droplets during polymerization. Polythiophene dispersions of irregularly shaped ca. 30 nm particles with solids contents of 9 wt % (polymer and surfactant) were obtained. TEM analysis of the particle sizes agrees with the sizes and distributions from capillary hydrodynamic fractionation. On samples of nitrated polymer, obtained by treating the isolated polythiophene with H_2SO_4/HNO$_3$, degrees of polymerization of ca. 10−50 were estimated by GPC. The polythiopene could be redispersed in organic solvents after removal of water in vacuo.

Cramail et al. studied the preparation of PEDOT nanoparticles by dispersion polymerization in water/methanol mixtures in the presence of reactive stabilizers.[179−181] PVA- or PEO-based reactive stabilizers with a polymerizable N-methylpyrrole, thiophene, or fluorene moiety at the chain end were utilized. Incorporation during EDOT polymerization yields particles with a covalently attached steric stabilizer. Spherical particles with diameters of several hundred nanometers and in some cases rather narrow size distributions (Figure 7) are formed generally, but the formation of regularly shaped nonspherical "doughnut" particles was also observed. These particles are suggested to be composed of 20−30 nm primary particles formed in the dispersion polymerization, in analogy to pyrrole polymerization in a dispersion. The particle size was found to decrease with increasing molecular weight of the stabilizer
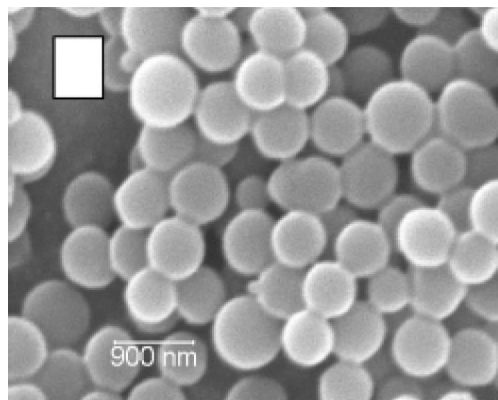
Figure 7. SEM image of PEDOT (**11**) particles prepared in the presence of copolymerizable *N*-methylpyrrole-substituted PEO. Reprinted from ref 180. Copyright 2008 American Chemical Society.

and with increasing concentration of the latter, which was related to an increase in the surface coverage with stabilizer.

Nonaqueous dispersions of PEDOT were generated by ion exchange of the counterions of the stabilizing polyelectrolyte. Aqueous PEDOT dispersions generated by oxidative polymerization in the presence of the polycation poly(1-vinyl-3-ethylimidazolium bromide) were precipitated by addition of the lithium salt of the less hydrophilic anion bis[(pentafluoroethyl)sulfonyl]imide. The precipitate could be redispersed in protic or aprotic organic solvents (methanol, DMF, or acetone). DLS demonstrated particle sizes of several hundred nanometers, albeit the nature and structure of the particles remains open.[182] Optimization of the reaction conditions yielded smaller particles around 50 nm in diameter.[183] Direct oxidative polymerization of EDOT by $FeCl_3$ in acetonitrile droplets dispersed in cyclohexane as the continuous phase by means of poly(isoprene-*block*-methyl methacrylate) block copolymer yielded cyclohexane dispersions of nonaggregated PEDOT nanoparticles with sizes of ca. 30 nm.[165] Polymerization occurs in the polar droplets, by a miniemulsion or emulsion mechanism. The block copolymer employed as a steric stabilizer is soluble in THF; this is suggested to be advantageous to prepare particles free of stabilizer which can reduce the conductivity of polymer films.

Polymerization of EDOT in aqueous microemulsions with the cationic surfactant decyltrimethylammonium bromide by iron salts afforded nonaggregated particles of ca. 30 nm size. To remove the substantial amount of surfactant required for the initial reaction mixture to be in the microemulsion regime, the dispersions were centrifuged and redispersed in methanol or water to afford colloidally stable dispersions with solids contents up to 10 wt %.[184]

Polymerization of EDOT in aqueous solutions of the water-soluble oligo- or polyelectrolyte poly[[2-(3-thienyl)ethoxy]-4-butanesulfonate], which itself features a substituted polythiophene backbone, afforded PEDOT particle dispersions. At the appropriate molecular weight of the polyelectrolyte, separated spherical particles of approximately 100 nm size, with a broader size distribution, formed.[185]

Polymerization of EDOT in the presence of the anionic surfactant DBSA resulted in rather irregularly shaped particles,[186,187] as previously reported for anionic surfactants. This was also found in PEDOT polymerization in water in oil emulsions.[188]

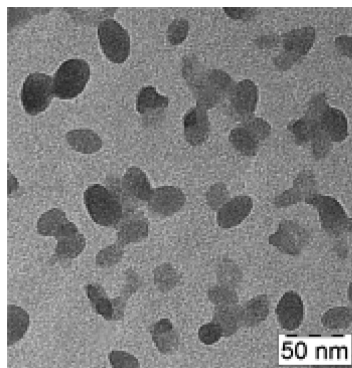### 2.2.5. Poly(p-phenyleneethynylene)s and Poly(p-phenylenediethynylene)s

The synthesis of poly(*p*-phenyleneethynylene) (PPE) and its derivatives is accomplished by metal-catalyzed cross-coupling reactions of appropriate monomers, typically via an $A_2 + B_2$ step growth polymerization. In such polymerizations, a high conversion of functional groups is mandatory to obtain higher molecular weight polymers. This requires that an exact monomer stoichiometry is ensured also in the highly disperse multiphase systems of emulsion polymerization, in which the various components may have different distribution coefficients for the phases.

Weder et al. prepared cross-linked substituted PPE **19** nanoparticles via Sonogashira coupling of 2,5-diiodo-4-[(2′-ethylhexyl)oxy]-1-methoxybenzene and 1,4-diethynyl-2,5-bis(octyloxy)benzene with 1,2,4-tribromobenzene as a cross-linker in an aqueous SDS emulsion. Mixing of the immiscible components was aided by polymeriztion in an ultrasonic bath. The nanoparticles precipitated during polymerization, but could be redispersed in toluene to a certain extent. SEM reveals particles with sizes from 50 to 400 nm. The cross-linked material is insoluble, prohibiting the determination of the molecular weight and consequently insight into monomer conversion and catalyst activity, which seemed to be very limited in this case, as concluded from a yield of only 4.4%.[80]

Stable aqueous dispersions of linear substituted PPE **8a** are accessible by Sonogashira coupling of 1,4-bis[(2′-ethylhexyl)oxy]-2,5-diethynylbenzene and 1,4-dibromo-2,5-bis[(2′-ethylhexyl)oxy]benzene in a miniemulsion process. A solution of monomers and catalyst in a small amount of toluene was miniemulsified in an aqueous SDS solution by means of high shear generated by ultrasound. Polymerization occurred inside the droplets to afford a dispersion of nonaggregated PPE nanoparticles with an average size around 80 nm in the absence of any coagulates. Dialysis and concentration of the dispersion yielded a stable dispersion with a solids content of 15 wt %. GPC of the isolated polymer revealed a high molecular weight of 1.7×10^5 g mol^{-1}.[189] Further extension of this methodology yielded poly(aryleneethynylene) nanoparticles with dialkoxybenzene and fluorene repeat units and optionally covalently incorporated pyrrolopyrrole and fluorenone dyes **26** and **27**.[190]

Poly(*p*-arylenediethynylene) can be prepared by Glaser coupling polymerization, a coupling reaction also compatible with aqueous systems. The reaction involves an oxidative coupling between two alkyne groups to the corresponding diethynyls, with air as an oxidant.[192] Copper-catalyzed polymerization of 1,4-diethynyl-2,5-bis[(2′-ethylhexyl)oxy]-benzene in an aqueous miniemulsion afforded nanoparticles of **9a** with a size of ca. 30 nm (Figure 8). A key to conducting such reactions in an aqueous emulsion was found to be the utilization of an appropriate lipophilic bidentate ligand, dinonylbipyridine, in the copper(I/II) catalyst system, which solubilizes the catalyst in the organic monomer phase, rather than in the aqueous phase. Unlike $A_2 + B_2$ polycondensation, due to the utilization of only a single organic monomer, the exact adjustment of the stoichiometry is not an issue. The resulting intensely yellow colored dispersions of high-molecular-weight poly(arylenediethynylene) nanoparticles were stable for at least several months to years. Copolymerization of difunctional dyes, e.g., diethynyl-substituted perylene, yielded nanoparticles of poly(arylenediethynylene)s with 0.5−10 mol % covalently incorporated dyes **20a**−**c**.[191]

Figure 8. TEM image of nanoparticles of substituted poly(*p*-phenylenediethynylene) **9c**. Reprinted from ref 191. Copyright 2009 American Chemical Society.

2.2.6. Poly(p-phenylenevinylene)s

The viability of the generation of nanoparticles by acyclic diene metathesis (ADMET) polycondensation[193] of *p*-divinylbenzenes in an aqueous miniemulsion has been demonstrated.[79,194] Note that, in contrast to the aforementioned ROMP, ADMET is a step-growth reaction, the growing polymer chain leaves the active site after each addition of a repeat unit, and the intermediately formed unsubstituted alkylidenes L$_n$Ru=CH$_2$ are particularly sensitive to decomposition. Nonetheless, N-heterocyclic carbene-substituted ruthenium alkylidene catalyst precursors were found to be applicable to ADMET in the aqueous system. At 50 °C and slightly reduced pressure, to facilitate removal of ethylene, polycondensation occurred to afford colloidally stable bright colored dispersions of nanoparticles with an average particle size of 100–200 nm. The alkoxy-substituted (**7c**; red) and alkyl-substituted (**7b**; green) materials are oligomers with degrees of polymerization of up to DP$_n$ = ca. 10; this is slightly lower than molecular weights obtained in comparative ADMET polymerizations under nonaqueous but otherwise similar conditions.

The preparation of cyano-substituted poly(phenylenevinylene)s **23**–**25** by base-catalyzed Knoevenagel polymerization[195,196] in an aqueous emulsion has been studied.[197] Due to the insolubility of the products in organic solvents, the molecular weights and functional group conversions were not accessible. The fluorescent particles, stabilized by nonionic surfactant (Tween 80), possess sizes around ca. 50 nm according to DLS and TEM. They were found to be colloidally stable also in serum.

Cadmium selenide nanoparticles with oligo(phenylenevinylene)s on their surface have been generated by Heck coupling of a divinylbenzene and dibromobenzene (both substituted with octyl groups) in the presence of cadmium selenide particles substituted with aryl bromide-functionalized phosphine oxide. This approach results primarily in phenylvinylene trimers and tetramers on the particle surface. These particles were found to be dispersed in a poly[(2,5-dioctyl-*p*-phenylene)vinylene] matrix in an essentially nonaggregated fashion. By contrast, pyridine-covered quantum dots aggregated in this matrix.[198] Cadmium selenide particles substituted with oligo(phenylenevinylene)s were prepared also employing a single AB monomer, 1-bromo-2,5-di-*n*-octyl-4-vinylbenzene, rather than using the aforementioned A$_2$ + B$_2$ approach.[199] Composite particles with an organic shell of molecules of defined molecular weight were generated by exchange of pyridine ligands from quantum dots for

oligo(phenylenevinylene) tetramers with phosphine oxide end groups, which bind to the cadmium selenide surface.[200]

3. Properties

Studies of conjugated polymer nanoparticles are motivated primarily by the conductivity and luminescence of conjugated polymers. The nature of the samples employed for investigation of these physical properties is related to envisioned applications and available methods. While conductivity is commonly studied on bulk samples, such as films generated from nanoparticle dispersions, luminescence is also often determined on ensembles of dispersed, nonaggregated particles, or even single nanoparticles.

3.1. Electrical Conductivity

The conductivity of films and other bulk samples generated from nanoparticles of intrinsically conductive polymers, namely, polypyrroles, polyaniline, polyacetylene, and polythiophene and respective substituted derivatives, since the 1980s has been, and continuous to be, an issue of interest. The results and insights gained have been reviewed extensively.[72,201] Typically, the electrical conductivity of the nanoparticles is measured on macroscopic bulk samples by the standard Van Der Pauw direct current (dc) method[202] or the four-point probe method[203] after isolation of the nanoparticles from the dispersions by precipitation, centrifugation, freeze-drying, or casting on substrates. Samples for conductivity measurements are usually prepared by compressing the dried and often thoroughly cleaned powder to a pellet or by spin-casting films from the as-prepared nanoparticle dispersions, i.e., containing impurities such as surfactants, stabilizers, unreacted monomer or oxidant, and catalyst residues to various extents.[149] The latter is also used to prepare composite conductive films of conjugated polymer nanoparticles in a polymeric matrix by adding soluble host polymers to the dispersion prior to spin-casting.[108,133,147] Conductivities cover the range from 10^{-5} to 10^2 S cm^{-1}, depending on the type of polymer and overall preparation conditions. Due to the multitude of parameters which can have a significant impact, there is no straightforward or generic approach to adjust the material's conductivity, which depends among other things on the degree of doping, the oxidation state, the particle morphology and size, the crystallinity, the inter- and intrachain interactions, the molecular weight and effective conjugation length, or the content of surfactants and other stabilizers. Several studies report a decrease in conductivity with increasing amount of insulating steric stabilizers or surfactant.[69,86,95,105,154] In contrast, it was found that the incorporation of anionic surfactants in polypyrrole and PANI nanoparticles enhances their conductivity relative to those of similar materials prepared in the absence of surfactants or the presence of cationic surfactants, which is likely due to the surfactant functioning as a counterion for cationic sites in the conjugated polymer, in this sense representing a dopant.[111,112,144,146] Polymerization in a microemulsion and miniemulsion was found to yield conducting polymer nanoparticles with high crystallinity,[153–157] which is believed to be beneficial for conductivity.[204,205] For example, PANI nanoparticles obtained via polymerization in a microemulsion with cationic surfactants at low temperature yielded bulk samples with a conductivity of 85 S cm^{-1}. This was attributed to a highly compact and ordered structure of PANI chains
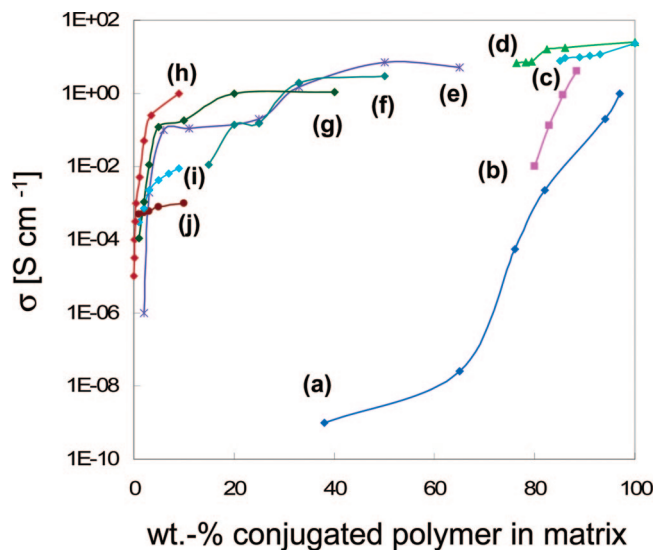
Figure 9. Electrical conductivity vs the concentration of conjugated polymer nanoparticles in polymeric composite films or pressed pellets (solid lines are fitted through the data points as a guide to the eye): (a) PPy (100−200 nm), methyl cellulose, ref 69; (b) PPy (100−150 nm), PVA, ref 86; (c) PPy (100−130 nm), PVME, ref 99; (d) PPy (50−120 nm), EHEC, ref 105; (e) PPy, PEMA, ref 207; (f) PPy (120−140 nm), multiblock copolymer consisting of poly(ethylene glycol) and poly(tetramethylene ether glycol) blocks, ref 95; (g) PANI (5−30 nm), PVA, ref 208; (h) PANI (<20 nm), PVA, ref 209; (i) PANI (4 nm), PC, ref 151; (j) PPy (2 nm), PC, ref 108.

originating from the reduced polymerization temperature and the very small particle size of only 4 nm.[151]

Films generated from aqueous polyacetylene nanoparticle dispersions could be processed by dip-coating or inkjet printing to continuous films or circuit paths, which displayed conductivities of up to 50 S cm^{-1} after doping with iodine.[166,175] For comparison, conductivities of bulk polyacetylene in the range from 10^2 to 10^5 S cm^{-1} have been reported, which are influenced among other things by the orientation induced by stretching and the doping procedure.[2,5,206] As expected due to the known air sensitivity of bulk polyacetylene, the stability of the films in air is limited. However, conductivity was still detected after 48 h in air, amounting to one-fifth the initial value of the freshly prepared film.

A related issue of long-standing interest have been blends of insulating polymers with conjugated polymer nanoparticles. Even at very low volume portions of conjugated polymers, substantial conductivity is observed for composites prepared by spin-casting mixtures of surfactant-stabilized nanoparticle dispersions and polymer solutions. This has been demonstrated for a range of matrixes (Figure 9e−k). By comparison, albeit they have usually been studied only at a higher conjugated polymer content, pellets obtained from sterically stabilized particles (Figure 9a−d) appear to display a pronounced loss of conductivity with decreasing conjugated polymer content (Figure 9a,b). Possibly, this indicates a lower propensity of the conjugated polymer core to aggregate, in comparison to electrostatically surfactant-stabilized particles in polymer matrixes. It has been shown that the latter self-assemble into networks in polymer blends, enabling the low thresholds of conducting polymer content for the onset of electrical conductivity.[210] Note that the role of primary particle domains for the conductivity of bulk polymer films, generated by secondary dispersion of doped conjugated

polymer powders in water or organic solvents, has also been discussed extensively.[211−215]

For layer-by-layer assemblies[216] of PEDOT nanoparticles stabilized by cationic surfactants with PSS, swelling and shrinking upon oxidation or reduction were studied by electrochemical surface plasmon resonance. In comparison to assemblies of commercial PEDOT/PSS with poly(ethyleneimine), shorter switching times were observed, which was attributed to a better diffusion of charge balancing counterions into the electroactive PEDOT layer.[184]

3.2. Photoluminescence and Electrooptical Properties

The photophysical properties of conjugated polymers, most prominently polythiophenes, polyphenylenes, polyfluorenes, poly(arylenevinylene)s, and poly(phenyleneethynylene)s, have been investigated extensively, motivated to a large extent by their practical utilization in light-emitting or photovoltaic devices. Studies of polymer solutions and of bulk polymer films revealed that luminescence, whether induced by photoexcitation or by charge injection, is strongly dependent on the chain conformations and the occurrence of aggregates of various types and sizes. This is due to the conjugation lengths and their distribution, and thus the nature of the chromophores, and inter- and intrachain interactions being influenced by these factors. Chain conformations and morphologies, in turn, are dependent on the presence of additional compounds optionally present and interacting with the polymer chain, such as solvents, and the preparation and history of the sample. Very generally, for a given polymer, the absorption spectrum shifts red with increasing inter- and intrachain interactions, which are usually dominant in thin films prepared from organic solutions and in aggregates consisting of highly ordered or crystalline domains, with respect to the polymer dissolved in a good solvent, i.e., a rather unfolded chain.[217] The corresponding emission spectra also commonly are red-shifted, as the inter- and intrachain interactions favor energy transfer to low-energy-emitting sites present typically in bulk materials such as thin films or aggregates. A review of the relation of chain conformation and film morphology to energy transfer and chain interactions has been provided by Schwartz.[218]

For nanoparticles, the absorption spectrum can exhibit an overall blue or red shift relative to that of a solution of the polymer in a good solvent, depending on the preparation conditions. Nanoparticles prepared by miniemulsion polymerization or reprecipitation typically exhibit a blue-shifted absorption maximum. This is attributed to a reduction of the conjugation length caused by kinks and bends of the polymer backbone as the polymer is constrained into a small volume and is believed to adopt a collapsed conformation.[51,79] In reprecipitation, particle formation occurs very rapidly, which can impede the formation of relaxed and ordered confirmations. In contrast, nanoparticles prepared by self-assembly over a more extended period of time from a mixed good and poor solvent system featured a red-shifted absorption maximum due to the formation of highly ordered structures, possibly consisting of aligned, stretched polymer chains.[50,57] This red shift increases linearly with the nanoparticle size. Moreover, annealing of dispersed nanoparticles prepared by the rapid reprecipitation method resulted in a red shift of the absorption peak, indicating that a certain level of distortion of the more or less collapsed chains in the as-formed nanoparticles is relaxed into ordered rearranged
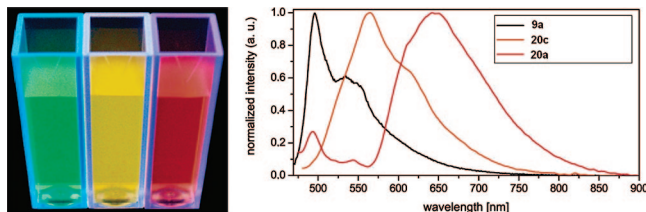
Figure 10. Dilute aqueous dispersions of nanoparticles of **9a** (green) with copolymerized diethynylfluorenone **20c** (yellow) and copolymerized diethynyl perylene diimide **20a** (red) under UV light (left). Corresponding fluorescence spectra (right, excited at 366 nm). Reprinted from ref 191. Copyright 2009 American Chemical Society.

structures.[55] A given conjugated polymer nanoparticle usually will contain a multitude of chain conformations and locally variable degrees of order, which accounts for the commonly observed long red tail of an overall blue-shifted absorption spectrum.[51]

The emission spectra of conjugated polymer nanoparticles are typically red-shifted with respect to that of a polymer solution in a good solvent, particularly due to energy transfer to low-energy chromophores, which increases with increasing chain−chain interactions. The red shift increases with particle size, approaching the spectrum of the bulk material.[64] Essentially, bulk spectral properties are already found for particle sizes ≥10 nm, which includes particles consisting of only a single polymer chain.[51] For poly(9,9-dialkylfluorene) **6** nanoparticles generated by rapid reprecipitation, a conversion of a disordered glassy phase to a crystalline β-phase occurred upon swelling of the as-prepared nanoparticles with solvent. Accordingly, the particle emission was red-shifted, toward the spectrum of the crystalline phase.[63] Concurrent data resulted from studies of the luminescence of thin films of poly(9,9-dihexylfluorene) (**6a**) prepared from a THF solution and from nanoparticle dispersion.[219] For films prepared from conjugated polymer nanoparticles generated by postpolymerization emulsification of polymer, no effect of the surfactant present in the nanoparticles on the absorption and emission spectra in comparison to solution-cast films was evident.[220]

From studies of energy transfer in nanoparticles composed of a blend of different conjugated polymers with different band gaps, McNeill et al. conclude that, in addition to Förster resonance energy transfer (FRET), exciton diffusion processes are involved as well.[221] Considering that exciton diffusion lengths of conjugated polymers typically range from 5 to 20 nm,[51,222,223] which is on the order of the size of the particles studied, such processes can be expected to occur very efficiently. Low amounts (e.g., 1 mol %) of lower energy chromophores, introduced in the form of other conjugated polymers or of low-molecular-weight dyes, are sufficient to ensure effective energy transfer from the main component conjugated polymer, such that emission is only observed from the former.[222] This allows for bathochromic tuning of the emission color of the nanoparticles by blending or covalent incorporation of dye (Figure 10).[44−46,190,191,221,222,224−228] For a given conjugated polymer, nanoparticles exhibiting different emission colors can be excited simultaneously with a single laser as a light source (Figure 13),[190] which is of particular interest for simultaneous identification of different analytes and biomedical imaging.

For oligo(phenylenevinylene)-functionalized cadmium selenide quantum dots dispersed in a poly(2,5-dioctyl-*p*-phenylenevinylene) matrix in a nonaggregated fashion,

energy transfer from the organic portion to the quantum dots was confirmed by fluorescence spectroscopy.[198] Single-particle fluorescence studies indicate an enhanced energy transfer for oligo(phenylenevinylene)-substituted quantum dots, in comparison to blends of simply aryl-substituted quantum dots with a poly(phenylenevinylene) matrix.[199]

For very small conjugated polymer nanoparticles (<10 nm), blinking phenomena have been observed. This was ascribed to a single photooxidation event, sufficient to induce a large change in emission intensity, which is not the case for larger particles.[64,229] Spectroscopic monitoring of electrochemical charging and discharging of individual conjugated polymer nanoparticles by Barbara et al. revealed that an observed loss of fluorescence intensity upon oxidation is dependent on the particle size and is particularly pronounced for smaller particles. This was ascribed to an irreversible chemical reaction at the particle surface. Photon correlation measurements suggest that conjugated polymer nanoparticles can behave as single-photon sources depending on their preparation and consequently chain conformations.[230]

Comparison of the spectroscopic data of different conjugated polymer nanoparticles (Table 3) reveals correlations with the particle size. For a given polymer, the quantum yield appears to decrease with increasing particle size (entry 3 vs 4 and entry 8 vs 9; also see ref 219, though the data refer to films from nanoparticles). The size dependence of the quantum yield has been attributed to the effect of the particle size on the efficiency of energy transfer to various fluorescence quenching sites present in the nanoparticle.[229] This qualitatively agrees with the observed lower quantum yield of the polymer nanoparticle—similar to bulk material—as compared to polymer solutions in organic solvents, which can be up to 25-fold lower.[53] Nonetheless, typical quantum yields for neat conjugated polymer nanoparticles range from ca. 10% to 40% for poly(9,9-dioctylfluorene) (**6b**). They can be increased by physical[221] or covalent[190,191] incorporation of dye, to which energy transfer occurs (also see Table 3). However, the amount of added dye is a critical issue as severe fluorescence quenching was observed upon dye aggregation at an elevated concentration of (noncovalently incorporated) dye.[222] Typical dye concentrations are 0.5−2 mol % with respect to the repeat units.[191]

The absorption cross section (σ) has also been correlated to the particle size and is assumed to increase linearly with the particle volume.[51] Typical values of absorption cross sections of molecularly dissolved conjugated polymers range from 0.01 to 1 nm^2,[48,53] which correlates reasonably with the reported cross sections of nanoparticles consisting of a single or very few polymer molecules (entries 1 and 3). Even rather small conjugated polymer nanoparticles exhibit relatively high absorption cross sections, and their fluorescence brightness, also when taking the particle volume into account, compares favorably to that of CdSe quantum dots in the visible and near-UV range.[229,232,233] Conjugated polymers are known to possess high multiphoton absorption coefficients.[234,235] Two-photon absorption cross sections (σ_2) of several conjugated polymer nanoparticles, usually reported as two-photon action cross sections (σ_2^*), have been found to range from 10^3 to 10^5 GM (Figure 11, left).[52,190,236] This is roughly 3 to 4 orders of magnitude higher than σ_2^* of organic dyes, and competes with σ_2^* of quantum dots of comparable size.[237]

Fluorescence decay traces of nanoparticles of different conjugated polymers of 15 nm size could be fit adequately

Table 3. Spectroscopic Data of Conjugated Polymer Nanoparticles

entry	compd	$M_w \times 10^3$ (g mol^{-1})	size (nm)	number of polymer chains/NP[a]	σ^b/NP[a] (nm^2)	σ^b/polymer chain (nm^2)	ε^c (M^{-1} cm^{-1})	φ^d (%)	ref
1	**7a**	200	10	1	4	4	2.4×10^7	nd	51
2	**7a**	200	15	21[f]	44	2	2.6×10^8	1	229
3	**14**	270	10	1	8.3	8.3	5.0×10^7	10	53
4	**14**	270	15	7[f]	55	7.9	3.3×10^8	8	229
5	**6a** (+ **14**)	55 (270)[e]	20	200	249	1.2	1.5×10^9	14	221
6	**6a** (+dye)	55	30	200	249	1.2	1.5×10^9	40	222
7	**6a** (+dye)	55	25	90	190	2.1	1.1×10^9	n.d.	231
8	**6b**	147	50	280	830	3.0	5.0×10^9	35	63
9	**6b**	147	15	22[f]	54	2.5	3.3×10^8	40	229
10	**6b** (+dye)	147	50	270	1200	4.4	7.2×10^9	n.d.	231
11	**8b**	nd	15	nd	46	nd	2.7×10^8	12	229
12	**13**	10	15	100[f]	28	0.3	1.7×10^8	7	229
13	**9a**	76	22	150[f]	nd	nd	nd	5	191
14	**9c**	64	29	350[f]	nd	nd	nd	11	191
15	**20a**	95	40	600[f]	nd	nd	nd	5	191
16	**20c**	88	22	130[f]	nd	nd	nd	6	191
17	**26**	380	124	3300[f]	nd	nd	nd	38	190
18	**27**	460	61	900[f]	nd	nd	nd	46	190

[a] NP = nanoparticle. [b] Absorption cross section. [c] Molar absorption coefficient. [d] Fluorescence quantum yield. [e] Molecular weight of **14**. [f] Estimated from the molecular weight (M_n) and particle size, assuming a spherical particle shape and a particle density of 1 g mL^{-1}.
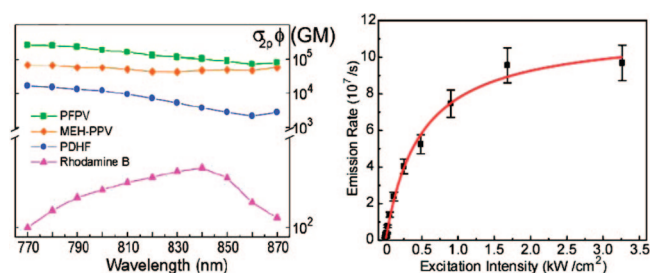
Figure 11. Semilog plot of the two-photon action cross section vs the excitation wavelength for nanoparticles of **6a**, **7a**, and **14** (left). Reprinted from ref 52. Copyright 2007 American Chemical Society. Fluorescence saturation of single nanoparticles of **13** with increasing excitation intensity (right). Reprinted from ref 229. Copyright 2008 American Chemical Society.

Table 4. Time Dependence of Fluorescence and Photostability Data of Nanoparticles of Different Conjugated Polymers (Ca. 15 nm Size)[229]

compd	fluorescence lifetime, τ (ps)	radiative rate, k (s^{-1})	photobleaching quantum yield	photon number
6b	270	1.5×10^9	$\sim 10^{-8}$	$\sim 10^7$
7b	127	7.9×10^7	$\sim 10^{-8}$	$\sim 10^6$
8b	242	5.0×10^8	$\sim 10^{-9}$	$\sim 10^8$
13	595	1.2×10^8	$\sim 10^{-10}$	$\sim 10^9$
14	133	6.0×10^8	$\sim 10^{-8}$	$\sim 10^7$

with a single-exponential function (except for **8b**). Fluorescence lifetimes are in the 0.1−1 ns range (Table 4).[229] The radiative rates were found to be similar to or slightly higher than those of typical organic dyes. These data are considered useful for applications such as flow cytometry and high-speed imaging or tracking. Photobleaching kinetics allowed for a rough estimation of photobleaching quantum yields and the number of photons emitted prior to complete bleaching (Table 4). While due to the interactions of multiple chromophores, the bleaching mechanisms of nanoparticles are more complex and not directly comparable to single dye molecules; for practical considerations it can be noted that the number of photons emitted per nanoparticle prior to bleaching is 3−4 orders of magnitude higher than the photon number of typical fluorescent dye molecules. These results, together with further photobleaching studies, indicate a reasonable photostability of conjugated polymer nanoparticles

for practical purposes, such as imaging.[61,236] Studies of the photoexcitation kinetics of films of **5** prepared from aqueous nanoparticle dispersions and from organic solution indicate similar lifetimes of single excitons for both films, an increased polaron density and triplet lifetime, and a significantly higher triplet yield for the nanoparticle-based film. The longer triplet lifetime was attributed to a hindered migration across the conjugated polymer nanoparticle boundaries.[238] The excitation-power dependence of the photoluminescent count rate was studied on single-molecule nanoparticles of polymers **7b** and **13** and was found to saturate quickly for excitation intensities up to 2 kW cm^{-2} (Figure 11, right),[229] indicating a mean saturation emission rate much higher than that of typical molecular dyes[239] or semiconductor quantum dots.[240]

Their brightness and reasonable photostability renders conjugated polymer nanoparticles interesting as probes for cell labeling and bioimaging under both one-photon and especially two-photon excitation. The latter allows for milder deep tissue imaging in the near-infrared spectral range. Obviously, the brightness of a nanoparticle when compared to a single low-molecular-weight dye molecule stems in the first place from its larger volume. Utilization of nanoparticles rather than dye molecules does require that the given system under investigation is not disturbed by the probe in an undesirable fashion. As has been demonstrated for nanoparticles of various types of conjugated polymers, and different types of cells, the nanoparticles are taken up and accumulated by living cells.[47,48,56,60,190,229,231,236,241] No evidence for cell toxicity of the nanoparticles was observed in these studies (also see ref 242). This also applies to nanoparticles generated directly by polymerization in an emulsion without intermediate purification of the isolated polymer (also see Figure 13). Typically, the conjugated polymer nanoparticles accumulate in the cytosol of the cell without penetrating the cell nucleus after being incubated with the living cells for several hours to days (Figures 12 and 13). Multicolor imaging with different particles varying in emission color allows for ready differentiation of particles located inside and outside cells.[190] The particles can be imaged by traditional fluorescence microscopy or via multiphoton excitation in the near-infrared.[190,236] The photostability of the particles is particularly important considering fluorescence-based imaging techniques, especially for
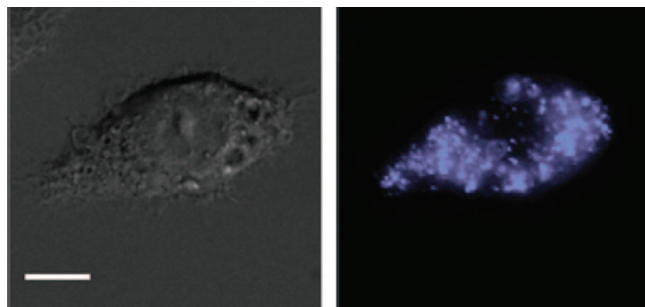
Figure 12. Differential interference contrast and fluorescence image of a macrophage cell labeled with PPE (**8b**) nanoparticles from reprecipitation. Reprinted from ref 229. Copyright 2008 American Chemical Society.

long-term imaging or tracking experiments. Several authors demonstrated that conjugated polymer nanoparticles show no severe photobleaching upon continuous excitation over minutes to hours in a cuvette[47,229] and when imaged in biological systems.[56] Longer term tracking of conjugated polymer nanoparticle labeled cells over several days under two-photon excitation has been illustrated in a tissue model. The growth of cells through the collagen gel-based microfluidic device was not stunted by the nanoparticles, proving that they do not affect the cell behavior nor show any toxicity.[236]

Sensing of specific analytes employing conjugated polymer nanoparticles has been demonstrated. The absorption of a rhodamine-labeled phosphorylated peptide (kemptide) to the surface of nanoparticles of **17**, mediated by trivalent metal ions, resulted in strong FRET. This effect is specific to the phosphorylated peptide, and enzymatic phosphorylation of the nonphosphorylated peptide by protein kinase A could be monitored with the nanoparticles.[67]

In poly(9,9-dialkylfluorene) **6a,b** nanoparticles containing platinum(II) octaethylporphine, upon excitation with UV/vis light, energy transfer to the metal-containing dye occurs, which results in phosphorescence. The latter is very sensitive to the concentration of molecular oxygen present, as observed also by imaging of single particles.[231]

From a comparison of 2D trajectories observed by confocal microscopy of stationary particles of **13**, and particles undergoing Brownian motion, it was concluded that these brightly fluorescing particles can be detected with <5 nm lateral resolution. By defocused imaging, in the third dimension a resolution of ca. 20 nm appeared viable.[61,243] Most recently, a first in vivo study demonstrated the real-time mapping of sentinel lymph nodes in a mouse model.[197]

An approach to control the phase separation generating the heterojunction in organic solar cells on the nanoscale is based on conjugated polymer nanoparticles. Neher et al. prepared solar cells by spin-casting dispersions of either a mixture of single-component nanoparticles of **13** and **21** or of nanoparticles consisting of a mixture of **13** and **21**. Significantly different device properties for the two types are reported with an optimum external quantum efficiency of ca. 4% for a device made of blended particles containing **13**:**21** at a weight fraction of 2:1.[44,45]

For an OLED device fabricated from aqueous dispersions of nanoparticles of **5**, typical characteristics are a much lower electroluminescence onset at the nanoparticle energy gap of 2.7 V and a slightly increased efficiency of ca. 0.5 cd A^{-1} compared to OLEDs fabricated from an organic solution of the same polymer and a maximum brightness of ca. 145 cd m^{-2}. The significant onset reduction is attributed to an enhanced electrical field resulting from the "stalactite"-type aluminum cathode deposited on the nanostructures' rough particle layer surface.[43] OLEDs have also been prepared by inkjet printing of aqueous dispersions of MEH-PPV (**7a**). However, the device performance was poor with extremely high current and light emission onset voltages. By addition of PEG to the aqueous dispersions, and doping with an alkali-metal salt prior to device layer fabrication, the performance was significantly improved to onset voltages for the current as well as for luminescence just slightly above 3 V and a remarkably enhanced light output.[244] Inkjet printing aqueous nanoparticle dispersions of **5** on a nonemitting polystyrene matrix layer and embedding the former by thermal annealing afforded well-ordered spots with a minimum feature size of 20 μm, which function as an OLED device.[245] Functioning OLED devices of poly(phenyleneethynylene) were also generated from nanoparticles prepared directly by polymerization in an aqueous emulsion, without intermediate purification. Defect-free devices in the square centimeter size range were readily obtained.[189]

4. Conclusion and Outlook

Widespread interest in conjugated polymer nanoparticles arose soon after the discovery of the high conductivity of doped polyacetylene. A prime motivation was to improve the processability of conjugated polymers, which is notoriously difficult due to intractability and insolubility in organic solvents. Academic and industrial efforts continue to further develop this area, aiming particularly at semiconducting layers and films. Notably, aqueous "solutions" of polycharged conjugated polymers, namely, polyaniline, also likely possess a particulate character.[73] Luminescent nanoparticles of conjugated polymers have attracted interest more recently, related to the unique electrooptical and photoluminescence properties of this class of materials. Polymer OLED devices have been prepared from nanoparticles, as an alternative to processing from solution in organic solvents. Also, proof of concept of preparation of photovoltaic devices from aqueous conjugated polymer nanoparticle dispersions has been provided. In this case, utilization of nanoparticles offers the possibility of generating blends with controlled domain sizes. In these approaches, utilization of water as a dispersing medium appears not to be detrimental for further steps, such as application of electrodes of reactive metals. Standard vacuum removal procedures were apparently sufficient. As far as can be judged from these laboratory-scale studies on
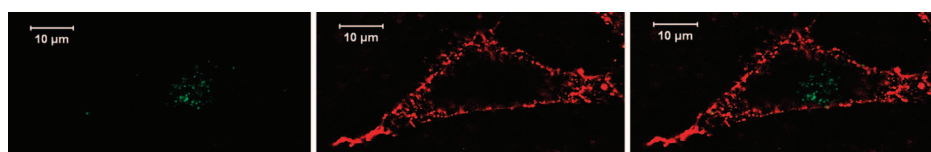
Figure 13. Spectrally resolved confocal fluorescence micrographs of HeLa cells labeled with nanoparticles of **27** (red), on the cell surface, and **16c** (green), inside cells, taken up prior to fixation, excited at 458 nm (from ref 190).

single-active-layer devices, their performance overall is similar to that of devices processed from organic solutions to first approximation. An issue that has been addressed to a limited extent is the fate of surfactant stabilizing the original nanoparticles upon film formation. A different line of potential applications is utilization of the intact nanoparticles as such, namely, as bright fluorescence probes. Due to the high multiphoton absorption cross sections of conjugated polymers, these nanoparticles can also be excited with lower energy, less damaging, and deeper penetrating near-infrared light. Uptake in cells, and nontoxicity toward cells, has been demonstrated for a number of nanoparticle and cell types. In comparison to single dye molecules, a given conjugated polymer nanoparticle not surprisingly is much brighter and less amenable to bleaching. Photon absorption cross sections, brightness, and photostability apparently can compete with inorganic quantum dots. As for inorganic quantum dots,[32] applications obviously require that the nanoparticles do not unfavorably disturb the system under investigation. Thus, it is debatable whether nanoparticles are indeed generically suited as replacements of small molecule fluorophores, as sometimes implied.

In the size range studied to this end, ≥10 nm, thus far limited size-dependent effects of optical properties have been observed. Already at the lower end of this size scale, a conjugated polymer particle will contain a multitude of different chromophores interacting with each other. Likewise, the physical properties studied of single-chain particles do not differ substantially from multichain particles.

The possible versatility of their surface chemistry is an advantage of conjugated polymer nanoparticles with their entirely organic nature, which to date is only rudimentarily exploited. This applies to particles from polymerization in disperse systems, as well as postpolymerization-generated particles. For the latter, namely, particles from postpolymerization precipitation, the nature of stabilization is even unclear. The physisorbed surfactants commonly introduced with emulsion methods can be problematic, as they may desorb in an undesirable fashion during applications. Improved preparation methods, employing monomers and polymers tailored to the synthesis of luminescent nanoparticles, are an issue. For applications relevant to living systems, conjugation with functional entities with specific binding properties, e.g., peptides and proteins, is desirable. At the same time, the generation of sub-10 nm conjugated polymer particles is a prospective target. An issue of particular relevance to such very small particles, which is not satisfactorily understood, is the internal particle structure and polymer chain conformation and its dependence on the particle preparation method as well as impact on the particle shape. While the stability of conjugated polymer nanoparticles to photobleaching and other deactivation processes appears to be reasonable, further improvements of long-term stability, ideally based on an understanding of the relevant steps, will likely be necessary. A different attractive prospect appears to be the further utilization of the per se high degree of dispersion of nanoparticles for the generation of hybrid structures, a concept known and proven for more traditional materials.

5. Abbreviations

ADMET	acyclic diene metathesis
AFM	atomic force microscopy
APS	ammonium peroxodisulfate
COT	cyclooctatetraene
DBSA	dodecylbenzenesulfonic acid
DLS	dynamic light scattering
DMF	dimethylformamide
DMSO	dimethyl sulfoxide
DTAB	dodecyltrimethylammonium bromide
EDOT	3,4-(ethylenedioxy)thiophene
EHEC	ethyl hydroxyethyl cellulose
FRET	fluorescence resonance energy transfer
GPC	gel permeation chromatography
ITO	indium tin oxide
MEH-PPV	poly[[2-[(2′-ethylhexyl)oxy]-5-methoxy-*p*-phenylene]vinylene]
OLED	organic light-emitting diode
OTAB	octyltrimethylammonium bromide
P2VP-BMA	poly(2-vinylpyridine-*co*-*n*-butyl methacrylate)
P4VP	poly(4-vinylpyridine)
P4VP-BMA	poly(4-vinylpyridine-*co*-*n*-butyl methacrylate)
PANI	polyaniline
PC	polycarbonate
PEDOT	poly[3,4-(ethylenedioxy)thiophene]
PEG	poly(ethylene glycol)
PEMA	poly(ethyl methacrylate)
PEO	poly(ethylene oxide)
PPE	poly(phenyleneethynylene)
PPV	poly(*p*-phenylenevinylene)
PPy	polypyrrole
PSS	poly(styrenesulfonate)
PVA	poly(vinyl alcohol-*co*-vinyl acetate)
PVME	poly(vinyl methyl ether)
PVP	poly(vinylpyrrolidone)
ROMP	ring-opening metathesis polymerization
SDS	sodium dodecyl sulfate
SEM	scanning electron microscopy
TEM	transmission electron microscopy
THF	tetrahydrofuran
TTAB	tetradecyltrimethylammonium bromide

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