

Fluorescent Conjugated Polymer Nanoparticles by Polymerization in Miniemulsion

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Abstract: Highly fluorescent conjugated polymer nanoparticles were prepared directly by polymerization in aqueous miniemulsion, employing Glaser coupling polymerization as a suitable step-growth reaction. A 4,4'-dinonyl-2,2'-bipyridine-modified catalyst was found to be suited for the polymerization in the aqueous heterophase system. Nanoparticles of poly(arylene diethynylenes) (arylene = 2,5-dialkoxy phenylenes and 9,9'-dihexyl fluorene) with molecular weights in the range of M_n 10^4 to 10^5 g mol⁻¹ and with sizes of ≤ 30 nm, as observed by TEM, result. *N,N'*-Di(4-ethynylphenyl)-1,7-di[4-(1,1,3,3-tetramethylbutyl)phenoxy]perylene-3,4:9,10-tetracarboxdiimide or 2,7-diethynylfluorenone was converted completely during the heterophase polymerization to afford colloidally stable nanoparticles of poly(arylene diethynylenes) with 0.1–2 mol % covalently incorporated perylene dye and 2–9 mol % of covalently incorporated fluorenone dye, respectively. Fluorescence spectroscopy of the aqueous dispersions reveals an efficient energy transfer to the dye in the nanoparticles, which enables a variation of the luminescence emission color between red (λ_{em} (max.) ca. 650 nm) and the green emission of the nanoparticles without dye.

Introduction

Nanoparticles of luminescent conjugated polymers, dispersed in water as a continuous phase, are finding increasing interest in materials science and biological systems. For example, they may contribute to resolve some key challenges in the processing and structuring of conjugated polymers, particularly to multilayer devices.¹ In this context, their compatibility with standard printing techniques is attractive. Because of their high degree of dispersion, nanoparticle dispersions are useful for the preparation of nanocomposites.² Most recently, the potential of nanoparticles of conjugated polymers for cell imaging has been recognized.³

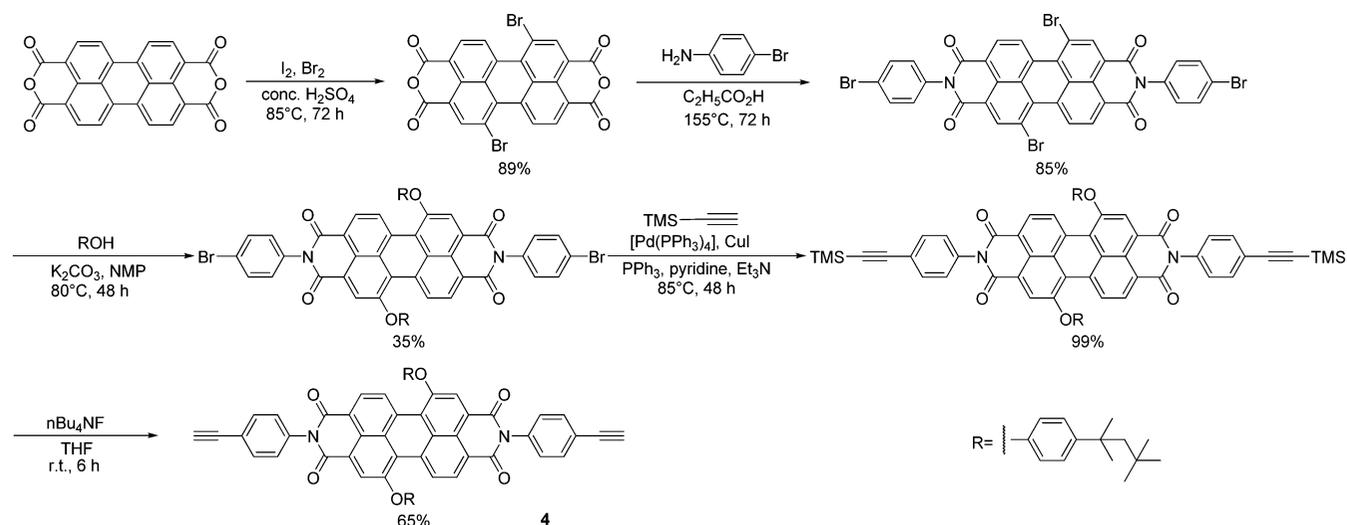
Aqueous dispersions of submicrometer polymer particles are conveniently prepared by emulsion polymerization processes, with mini- and microemulsion polymerizations as well-known variations of classical emulsion polymerization. However, polymerizations in disperse aqueous systems are traditionally a

realm of free-radical polymerization,⁴ while the preparation of luminescent conjugated polymers of interest requires catalytic step-growth polymerizations.⁵ To date, this has been circumvented by employing secondary dispersion techniques (i.e., dispersing solutions of preformed polymers in organic solvents in water).^{1–3} While this approach can be advantageous in terms of applying commercially available polymers, on the longer term it is desirable to also be able to prepare luminescent conjugated polymer nanoparticles by polymerization in disperse systems as this in principle provides access to a much broader scope of materials, for example, colloidally stable particles with sizes reasonably small for cell imaging^{3,6} or the preparation of ultrathin films^{5,7} (<ca. 30 nm),⁸ or structured particles, and is not limited to polymers with a high solubility in organic solvents.

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Scheme 1. Synthesis of Diethynyl Perylenediimide (4)



To date, catalytic polymerizations in emulsion have been restricted to chain growth polymerizations.^{9–11} By comparison, in step-growth reactions the active metal center is released from the polymer chain after each incorporation of a monomer unit. This can enhance deactivation, if the intermediates are water sensitive. This could be detrimental, as in step-growth polymerizations high conversions are a requirement for achieving reasonable molecular weights. The latter also requires strict stoichiometric balance for reactions based on A–B functional group coupling, which can be difficult to achieve in disperse systems in which all components have variable partition coefficients between the different phases present. Therefore, a high-yielding reaction, which is not sensitive to water, is required for the polymerization to achieve high molecular weights.

For electroluminescence¹² as well as photoluminescence, ability to adjust the emission wavelengths is very desirable. For a given polymer system, this can be achieved by blending with fluorescent dyes.¹³ An elegant approach to prevent microphase separation, which among others can deteriorate energy transfer to the dye, is its covalent incorporation during polymerization.¹⁴

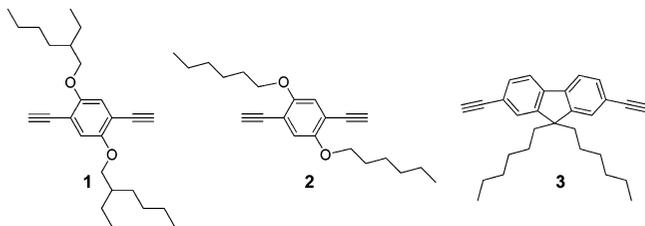
We now report on the direct preparation of luminescent high molecular weight conjugated polymer in the form of nanoparticles, with adjustable emission wavelength.

Results and Discussion

The Glaser reaction is a high-yielding oxidative coupling reaction of monosubstituted alkynes to the diethynyls under very mild conditions. Air can serve as the oxidant.¹⁵ The preparation of conjugated polymers by Glaser coupling has been demonstrated in organic solution.¹⁶ In terms of classical polycondensation, the reaction is akin to polymerization of an AB monomer (with the A and B functional group identical). Unlike A–A + B–B polycondensation, exact adjustment of stoichiometry, which could be particularly challenging in multiphase systems such as aqueous emulsions, is not an issue. These features prompted us to study nanoparticle synthesis by Glaser coupling.

Monomer Synthesis. 1,4-Diethynyl-2,5-bis(2-ethylhexyloxy)benzene (**1**), 1,4-diethynyl-2,5-dihexyloxybenzene (**2**), and 2,7-diethynyl-9,9-dihexylfluorene (**3**) were prepared similarly to published procedures. The acetylene moieties were introduced

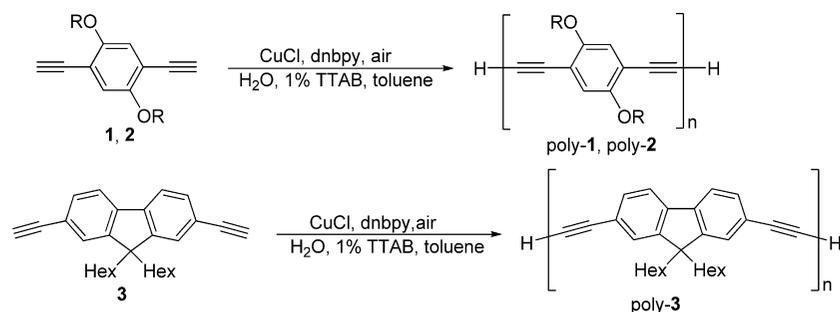
by Sonogashira coupling of the dibromo compounds with trimethylsilylacetylene (TMS–acetylene), followed by the cleavage of the TMS group.



To control the emission color of the conjugated polymer nanoparticles by covalent incorporation of a fluorescent dye, a diethynyl-substituted perylenediimide derivative (Scheme 1) and 2,7-diethynylfluorene (**5**)¹⁷ were prepared. Perylene dyes are known to be very photostable and emit with high quantum yields.¹⁴ Bromination of perylenetetracarboxylic acid dianhydride in concentrated sulfuric acid afforded the

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Scheme 2. Polymers Prepared in the Form of Nanoparticle Dispersions

Table 1. Polymerizations in Aqueous Miniemulsion^a

entry	monomer	monomer/catalyst	t [h]	M_n^b [g mol ⁻¹]	M_w^b [g mol ⁻¹]	$M_{n,NMR}^c$ [g mol ⁻¹]	DP _n ^c	particle size ^d [nm]
1-1	1	6.9	48	2.3×10^4	7.6×10^4	1.8×10^4	47	22 ± 11
1-2	1	6.8	48	4.1×10^4	2.5×10^5	5.7×10^4	150	27 ± 12
1-3	1	22.3	96	2.2×10^4	5.3×10^4	2.6×10^4	68	n. d.
1-4	2	5.1	96			9.4×10^4	290	31 ± 10
1-5	3	7.0	72	2.1×10^4	6.4×10^4	1.0×10^4	26	29 ± 11
1-6	3	21.9	120	3.4×10^4	1.1×10^5	1.3×10^4	34	n. d.

^a Reaction conditions: 25 °C (entry 1-2: 50 °C); 60 μmol of CuCl/dnbpy (1:1); 1 mL of toluene; 30 mL of 1% aqueous TTAB solution.

^b Determined by GPC in THF at 40 °C vs polystyrene standards. ^c Determined by ¹H NMR in CDCl₃ at 25 °C (entry 1-4: 100 °C in C₂D₂Cl₄).

^d Number average particle sizes determined by TEM.

disubstituted product. Imidation with 4-bromoaniline in propionic acid, followed by selective substitution of the perylene-bound bromide groups with 4-(1,1,3,3-tetramethylbutyl)phenolate, afforded the soluble dibromo-substituted perylenediimide. Catalytic coupling with TMS-acetylene and subsequent cleavage of the trimethylsilyl moiety with tetrabutyl ammonium fluoride afforded the diethynyl perylene-diimide **4**.

As reported by Würthner et al.,¹⁸ bromination of the perylene bisanhydride in concentrated H₂SO₄ is not regioselective, rather, a mixture of the desired 1,7- and the 1,6-substituted regioisomer was obtained. These isomers were reported to not be separable by column chromatography in the case of dibromoperylene bisimides.¹⁸ Analysis of the perylene dibromides (anhydride or imide) is hampered by their low solubility. In the final product (**4**), however, no undesired regioisomers were detected by 600 MHz ¹H NMR spectroscopy. Apparently, any regioisomers likely formed in the bromination step were removed by the column chromatographic purifications after the introduction of the bulky alkylphenoxy side groups.

Nanoparticle Preparation. A classical emulsion polymerization mechanism requires diffusion of monomer through the aqueous phase. This hampers its application to very hydrophobic monomers and can result in undesired composition gradients in the case of copolymers. Therefore, a miniemulsion technique was employed. Glaser coupling polymerization in miniemulsion requires a catalyst specifically suited for these conditions. Under standard Hay conditions¹⁹ (CuCl/tmeda as catalyst; tmeda = *N,N,N',N'*-tetramethyl ethylene diamine), the Glaser coupling reaction does not occur in the presence of substantial amounts of water.²⁰ All ligands commonly used in the Glaser reaction have a high water solubility, which would result in location of the catalyst in

the aqueous phase rather than in the organic droplets. In addition, the poor solubility of catalysts with these ligands in apolar organic solvents is problematic in its own right.¹⁵ From studies of various bidentate nitrogen ligands, we found 4,4'-dinonyl-2,2'-bipyridine (dnbpy)²¹ to afford a catalyst suitable for Glaser coupling polymerization in miniemulsion, in combination with CuCl. This lipophilic bipyridine derivative is capable of solubilizing the catalyst in the organic droplets.

For polymerization, a miniemulsion obtained by ultrasonication of an aqueous surfactant solution (tetradecyltrimethylammonium bromide, TTAB) with an organic phase containing the monomer and catalyst (toluene solution of CuCl/dnbpy 1:1) was stirred in air at room temperature. Note that during this procedure the small portion of toluene introduced with the catalyst is removed by evaporation as the azeotrope. Intensely colored dispersions were obtained (cf. Figure 2). Over a period of observation of more than one year, the dispersions were found to be colloiddally stable. No precipitate was observed in the dispersions, and no aggregation or other changes of the particles were observed in TEM images after one year of storage. For example, for a poly-**1** dispersion a particle size of 22 ± 11 nm was determined after polymerization and 23 ± 8 nm after one year of storage.

All three monomers studied were converted quantitatively to the corresponding poly(arylene diethynylene) nanoparticles, with functional group conversions >98% (Scheme 2). Polymer molecular weights are in the range 10⁴ to 10⁵ g mol⁻¹, as determined by both gel permeation chromatography (GPC) and ¹H NMR spectroscopic determination of the HC≡C— end groups (Table 1). Results of both methods are in reasonable agreement, considering that data from GPC are apparent molecular weights (referenced to polystyrene stan-

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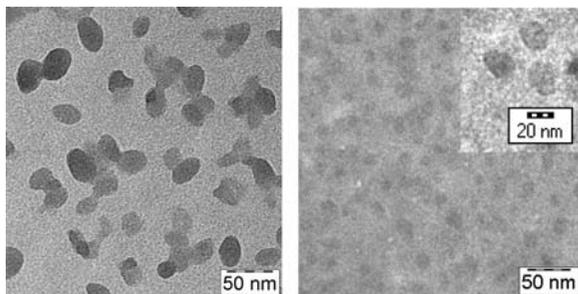


Figure 1. TEM image (left) and cryo-TEM images (right)²³ of poly-3 nanoparticles.

dards).²² Molecular weight determination of poly-2 was hampered by its very low solubility in organic solvents. A molecular weight of ca. $M_n 10^5 \text{ g mol}^{-1}$ was estimated by high-temperature NMR (in $\text{C}_2\text{D}_2\text{Cl}_4$ at 100 °C). Polymerization at an elevated temperature of 50 °C resulted in increased molecular weights as studied for poly-1 (entry 1–2). Following the reaction over time revealed that the polymerization is essentially completed after 24 h.

Particle sizes of the dispersions were studied by transmission electron microscopy (TEM; Figure 1 and Figure S1 in the Supporting Information). Number average particle sizes amount to 22–31 nm (Table 1). While the samples feature a certain particle size distribution, no larger particles (>100 nm) or significant aggregates were observed. Cryo-TEM on shock-vitrified samples, which reflects the structure of the aqueous dispersions, demonstrates more clearly the nonaggregated nature of the particles in the dispersions (Figure 1). The observed nonspherical shape of the poly-3 particles can be tentatively associated with the relatively high persistence length of conjugated polymers, which is on the same order of magnitude as the particle sizes. This may result in a nonspherical shape being energetically favored compared to a sphere, as it can better accommodate the conjugated segments of the polymer chains.

Polymerization of **1** at an elevated temperature of 50 °C (entry 1–2) had no significant effect on the particle shape or particle size.

Copolymerizations with the diethynyl perylenediimide dye **4** and diethynylfluorenone **5** proceeded analogously to the aforementioned homopolymerizations (Table 2) to afford colloidally stable dispersions (Figures 2 and 3). No significant undesired reduction of the high functional group conversion and polymer molecular weights was observed, which indicates that the reactivities of the ethynyl moieties of **4** and **5** are not unfavorably diminished compared to the main monomers, **1**, **2**, or **3**, respectively (vide infra), and that the catalyst and coupling reaction is compatible with the perylene moiety and vice versa. Particle sizes are also not affected by the presence of dye in the polymerization reaction (Table 2).

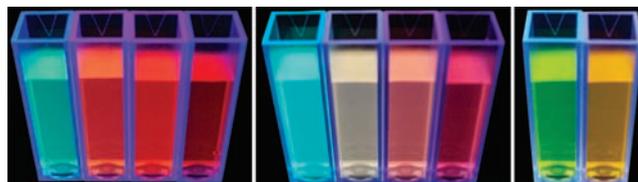
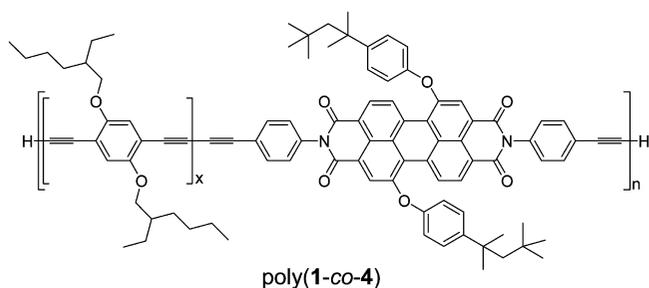


Figure 2. Dilute polymer dispersions of poly(1-co-4) with (from left to right) 0, 0.5, 1, and 2.1% incorporated dye; poly(3-co-4) with 0, 0.1, 0.2, and 0.8% incorporated dye; poly(2-co-4) with 0 and 0.4% incorporated dye under UV light ($\lambda = 366 \text{ nm}$).



Figure 3. Diluted polymer dispersions (from left to right) of poly-1, poly(1-co-5) (9.4%), and poly(1-co-4) (2.1%) under UV light ($\lambda = 366 \text{ nm}$).

Incorporation of the dye (**4**) into the polymer chain was studied by ^1H NMR spectra (Figure S2 in the Supporting Information). For poly(1-co-4) (entry 2–3), the aromatic perylene protons resonate at $\delta 9.69$, 8.67 , and 8.38 ppm . As expected, incorporation of the perylene dye into the polymer does not affect the shifts of these signals by comparison to monomer **4**, but they are significantly broadened. In addition to 1-ethynyl-2,5-bis(2-ethylhexyloxy)benzene end groups originating from the main monomer **1** ($\delta 3.34$), perylene imide-substituted $\text{HC}\equiv\text{C}$ end groups ($\delta 3.14$) are observed. The portion of the latter end groups is slightly higher than the molar incorporation of **4**, which indicates a slightly lower reactivity of end groups based on **4** by comparison to end groups from **1**. The incorporated amount of **4** as determined by ^1H NMR is identical to the composition of the polymerization reaction mixture within experimental error of the NMR technique; that is, the dye appears to be completely incorporated covalently into the polymer. Incorporation of dye was also demonstrated by chromatography, which is more sensitive than NMR for this purpose. Chromatography of poly(1-co-4) and for comparison a physical mixture of poly-1 and 0.01 mol % perylene (with respect to repeat units in **1**) on a TLC plate resulted in a clear separation of the perylene dye from the homopolymer, while no residual dye was observed in the copolymer (Figure S3 in the Supporting Information).

Copolymerizations with the diethynyl-substituted fluorenone (**5**) also afforded complete incorporation into the polymer chain, as concluded from ^1H NMR spectroscopy (Figure S4 in the Supporting Information). In this case, no ethynyl resonances of dye end groups were detected (monomer **5**: $\delta 3.17$ for $\text{HC}\equiv\text{C}$). Molecular weights and particle sizes of the diethynylfluorenone copolymers also do not differ significantly from the corresponding poly-1 homopolymers.

Table 2. Copolymerization of Perylene Dye (4) and Diethynylfluorenone (5) in Aqueous Miniemulsion^a

entry	monomer (mol % 4 or 5)	monomer/catalyst	t [h]	M_n^b [g mol ⁻¹]	M_w^b [g mol ⁻¹]	$M_{n,NMR}^c$ [g mol ⁻¹]	DP _n ^c	particle size ^d [nm]
2-1	1 (0.5% 4)	6.7	120	2.4×10^4	8.5×10^4	1.9×10^4	50	n. d.
2-2	1 (1.0% 4)	8.8	120	3.7×10^4	1.1×10^5	2.4×10^4	63	n. d.
2-3	1 (2.1% 4)	7.0	72	3.3×10^4	9.5×10^4	1.8×10^4	47	40 ± 16
2-4	2 (0.4% 4)	7.7	72			1.8×10^4	55	n. d.
2-5	3 (0.1% 4)	7.2	48	1.7×10^4	6.0×10^4	9.9×10^3	26	n. d.
2-6	3 (0.2% 4)	7.0	72	2.2×10^4	6.0×10^4	1.2×10^4	32	n. d.
2-7	3 (0.8% 4)	6.3	96	2.0×10^4	6.4×10^4	9.0×10^3	24	32 ± 11
2-8	1 (2.2% 5)	6.7	72	4.1×10^4	1.3×10^5	2.4×10^4	63	n. d.
2-9	1 (5.3% 5)	6.9	72	5.0×10^4	1.6×10^5	2.4×10^4	73	n. d.
2-10	1 (9.4% 5)	7.8	120	2.5×10^4	8.8×10^4	2.8×10^4	63	22 ± 7

^a Reaction conditions: 25 °C; 60 μmol of CuCl/dnbpy (1:1); 1 mL of toluene; 30 mL of 1% aqueous TTAB solution. ^b Determined by GPC in THF at 40 °C vs polystyrene standards. ^c Determined by ¹H NMR in CDCl₃ at 25 °C (entry 2-4: 100 °C in C₂D₂Cl₄). ^d Number average particle sizes determined by TEM.

Table 3. Optical Properties of Polymer Nanoparticles, Chloroform Solutions, and Films^a

	polymer (% dye)	λ_{abs} [nm]	λ_{em} [nm]	Φ_f [%]
aqueous dispersion	poly-1	434, 472	496	5
	poly-2	445, 488	501, 563	4
	poly-3	385, 413	502	11
	poly(1-co-4) (2.1%)	469	641	5
	poly(2-co-4) (0.4%)	446, 490	503, 621	4
	poly(3-co-4) (0.8%)	386, 413	634	6
solution	poly(1-co-5) (9.3%)	467	565	6
	poly-1	457	484	77
	poly-3	422	428	65
	poly(1-co-4) (2.1%)	457	483	53
	poly(3-co-4) (0.8%)	422	434	65
	film	poly-1		520
poly-3			507	13

^a λ_{abs} : wavelength of absorption maximum, λ_{em} : wavelength of emission maximum, Φ_f : fluorescence quantum yield. Polymer films were prepared from 10 g L⁻¹ chloroform solutions by spincoating.

Fluorescence Properties. UV/vis absorption and emission spectra of the nanoparticle dispersions and of polymer films and polymer solutions in chloroform for comparison were studied. Most notably, emission of the nanoparticles is red-shifted by comparison to polymer solutions (Table 3). This is particularly pronounced for the polyfluorene poly-3 (Figure 4), with a $\Delta\lambda = 74$ nm red-shift of the fluorescence maximum of the nanoparticles ($\lambda = 502$ nm) vs a corresponding polymer solution ($\lambda = 428$ nm). Such an effect is well-known from studies of bulk conjugated polymers. By comparison to the emission maximum observed in solution (0-0 transition), energy transfer from the excited state to lower band gap chromophores in the solid state results in longer wavelength fluorescence emission. Interchain interactions (e.g., aggregate formation by π -stacking) in the solid have also been reported to promote radiationless decay, at the expense of fluorescence quantum yields.²⁴

Overall, the fluorescence properties in terms of emission energy and quantum yields of the nanoparticles were found to resemble the bulk solid, as represented by the solution-cast film samples (Figure 4). In detail, comparing emission of nanoparticle dispersions of poly-1 and its less bulky-substituted analogue poly-2, a more intense red-shifted band

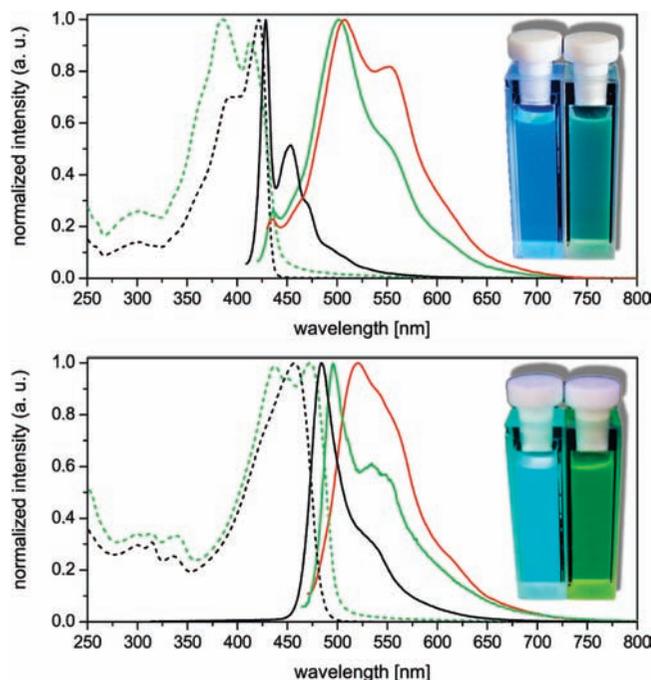


Figure 4. Absorption (dashed) and fluorescence (solid line) spectra of aqueous dispersions (green), chloroform solutions (black), and thin films (red) of poly-3 (top image, $\lambda_{exc} = 410$ nm) and poly-1 (bottom image, $\lambda_{exc} = 450$ nm). Insets: photographs of polymer solution (top) and nanoparticle dispersion (bottom).

is observed for the latter (Figure S5 in the Supporting Information). This agrees with the assumption that interchain interactions, which are less hindered by the less bulky alkyloxy side groups in poly-2, promote energy transfer to lower energy chromophores. “Isolation” of individual polymer chains by appropriate substituents is a concept for decreasing interchain interactions, which can result in solution-like properties in the solid.²⁵

An increased polymerization temperature of 50 °C for the preparation of poly-1 nanoparticles had no significant effect on the optical properties. Fluorescence spectra and quantum yields (6% for polymerization at 50 °C) are virtually identical to the material prepared at room temperature.

An effective energy transfer to polymer-incorporated dye is already evident from the appearance of the nanoparticle dispersions to the eye under UV light (Figures 2 and 3). The effect is more pronouncedly observed for films, obtained by simple drying of a drop of dispersion on a glass slide, under UV excitation (Figure 5).

- (22) For a discussion of GPC of rigid rod polymers, see: Grell, M.; Bradley, D. D. C.; Long, X.; Chamberlain, T.; Inbasekaran, M.; Woo, E. P.; Soliman, M. *Acta Polym.* **1998**, *49*, 439–444.
- (23) The occasional small light spots are due to beginning melting of the vitrified ice matrix under the electron beam.
- (24) (a) Nguyen, T.-Q.; Martini, I. B.; Liu, J.; Schwartz, B. J. *J. Phys. Chem. B* **2000**, *104*, 237–255. (b) Schwartz, B. J. *Annu. Rev. Phys. Chem.* **2003**, *54*, 141–172.

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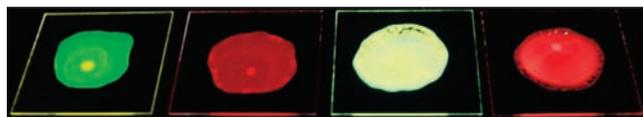


Figure 5. Films obtained by drop-coating of dispersions of (from left to right) poly-1, poly(1-co-4) (2.1%), poly-3 and poly(3-co-4) (0.8%) under UV light ($\lambda = 366$ nm).

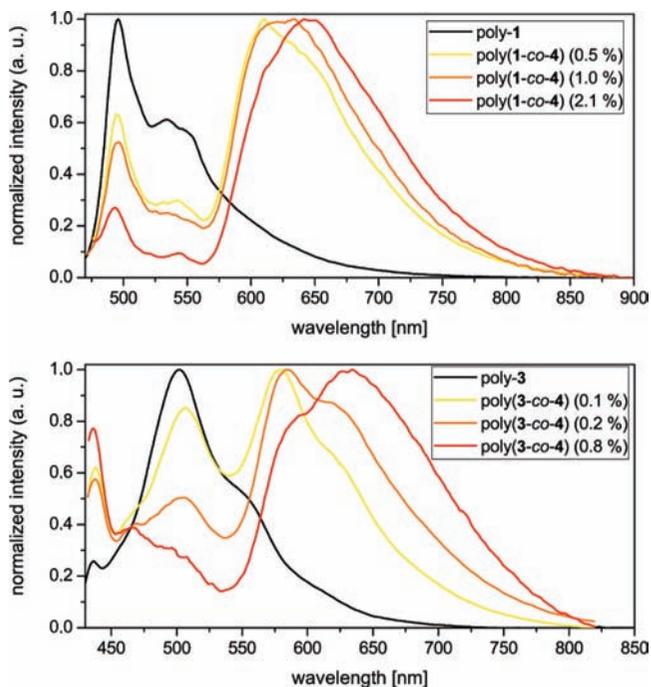


Figure 6. Fluorescence spectra of poly-1 and poly(1-co-4) nanoparticles (top, $\lambda_{\text{exc}} = 450$ nm) and of poly-3 and poly(3-co-4) nanoparticles (bottom, $\lambda_{\text{exc}} = 420$ nm) with various amounts of incorporated perylene dye.

Fluorescence spectroscopy of copolymer nanoparticle dispersions reveals the efficiency of energy transfer to the perylene-diiimide repeat units (Figure 6 and Figure S6 in the Supporting Information). Emission from the latter increases with increasing dye incorporation. At a molar incorporation of 0.8 mol % (poly(3-co-4)) or 2 mol % (poly(1-co-4)), emission occurs nearly exclusively from the dye. In detail, a slight bathochromic shift of the dye emission is observed with increasing dye incorporation. By clear contrast to the solid nanoparticles, no energy transfer to the perylene-diiimide repeat units is observed for copolymer solutions (Figure S7 in the Supporting Information). This is in agreement with theoretical considerations that energy transfer in conjugated polymers proceeds via a two-step mechanism, the initial exciton hopping along the polymer chain being limiting in solution.²⁶

Incorporation of the fluorenone derivative **5** into poly-1 results in a broadening of the fluorescence spectra at low concentrations (Figure S8 in the Supporting Information). At a concentration of around 9%, an orange emission with a maximum at 565 nm originating from the dye comonomer almost exclusively occurs (Figure 7). At the same time, the absorption spectra of these copolymers are largely identical to the homopolymer.

The incorporation of copolymerizable dyes results in an adjustability of the emission maximum of the nanoparticles, as demonstrated here by poly-1: 496 nm; poly(1-co-5): 565 nm, and poly(1-co-4): 641 nm (Figure 7; also cf. Figure 3).

The fluorescence properties of the dispersions were found to be essentially unaltered by storage for a period of more than a year (Figure S9 in the Supporting Information).

Summary and Conclusions

Nanoparticles of high molecular weight poly(arylene diethynylene)s can be accessed by Glaser polymerization in highly disperse aqueous systems, a catalytic step-growth reaction that does not require stoichiometric balance of reagents as in common $A_2 + B_2$ condensation. The catalyst system CuCl/dnbpy was found to be suited for promoting polymerization in the organic phase in the miniemulsion procedure employed, with air as the oxidant at room temperature. Particles of only ca. 30 nm size are obtained. A copolymerizable difunctional perylene-diiimide is covalently incorporated, without any undesired effect on the progress of the polymerization reaction or particle sizes. The nanoparticle dispersions are colloiddally stable, and their fluorescence properties are unaltered by prolonged storage. In nanoparticles of dye copolymers, an efficient energy transfer from the conjugated polymer backbone to the dye can occur, resulting in emission from the dye virtually exclusively for appropriate copolymer nanoparticles. This enables increasing fluorescence wavelength of the particles by dye incorporation.

The preparation of nanoparticles of fluorescent conjugated polymers directly by polymerization, in a disperse aqueous system, is a general and versatile approach to these types of materials, which are finding rapidly increasing attention. Among others, it is of interest for the generation of core-shell particles, with covalently bound hydrophilic moieties on their surface affording colloidal stabilization or particle recognition.

Experimental Section

Materials and General Considerations. 4,4'-Dinonyl-2,2'-bipyridine (97%) (Aldrich), tetradecyltrimethylammonium bromide (>98%) (Fluka), and CuCl (ACS grade) (Merck) were used as received. Nylon filters (0.45 μm pore size) were purchased from VWR.

NMR spectra were recorded on a Varian Unity INOVA 400, on a Bruker AC 250, or on a Bruker Avance DRX 600 spectrometer. ^1H and ^{13}C chemical shifts were referred to the solvent signal. Mass spectrometry was performed on a Finnigan MAT8200 EI-MS instrument. GPC was carried out on a Polymer Laboratories PL-GPC 50 with two PLgel 5 μm MIXED-C columns in THF at 40 $^\circ\text{C}$ against polystyrene standards. TEM images were obtained on a Zeiss Libra 120 instrument (acceleration voltage 120 kV). For cryo-TEM, a Gatan cryo-transfer attachment CT3500 was used. Dispersions were dialyzed for TEM analysis to remove any free surfactant and applied to a copper grid. Samples were not contrasted. Specimens for the cryo-TEM investigations were prepared in a Leica CPC instrument by freezing a thin film of the dispersion by plunging in liquid ethane. The thin film was created by dipping a small amount of the dispersion on a holey carbon film. A meniscus, thin enough for use in TEM, formed over the holes and was rapidly frozen to afford a vitrified sample. The sample was cryo transferred into the TEM and examined at a temperature around 90 K with minimal electron dose. Absorption spectra were recorded on a Varian Cary 50 spectrometer. Fluorescence spectra were obtained on a custom-made setup consisting of a xenon

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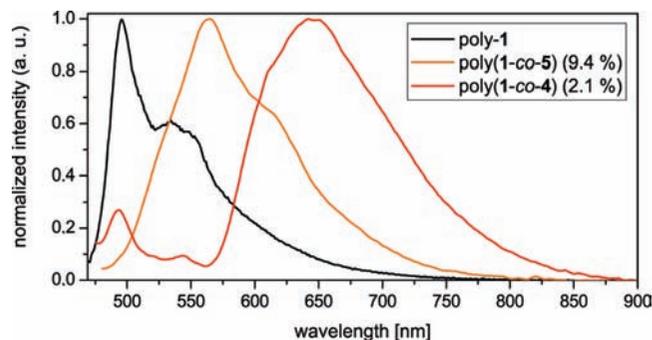


Figure 7. Fluorescence spectra ($\lambda_{\text{exc}} = 450 \text{ nm}$) of poly-1, poly(1-co-5), and poly(1-co-4) nanoparticles.

flash lamp, a monochromator (Oriel 77250 1/8M), a spectrograph, and a nitrogen-cooled CCD camera enabling photoluminescence detection from 310 to 940 nm.²⁷ Polymer film fluorescence spectra and fluorescence quantum yields were obtained on a Hamamatsu Absolute PL Quantum Yield Measurement System C9920-02. For measurements in solution, spectroscopic-grade chloroform (Uvasol, Merck) was used. Polymer films for fluorescence measurements were prepared by spincoating of a 10 g L^{-1} chloroform solution at 4000 rpm on a glass coverslip.

General Polymerization Procedure. CuCl and dnbpy were mixed with 0.5 mL of toluene and stirred until the solids had

dissolved completely. The green catalyst solution obtained was mixed with a solution of the monomers in 0.5 mL of toluene and immediately added to 30 mL of a 1% aqueous TTAB solution with a syringe. The mixture was ultrasonicated for 2 min (Bandelin HD 2200 with a KE76 tip operated at 120 W). The miniemulsion was stirred at room temperature in a Schlenk tube open to air for several days (for specific reaction times, cf. Tables 1 and 2). The polymer dispersions were dialyzed for 4 days to remove residual surfactant and catalyst, followed by filtering through a paper filter to remove any agglomerates.

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Supporting Information Available: Additional synthetic procedures, NMR spectrum of copolymer, additional fluorescence spectra and photograph of TLC of copolymer, and TEM image of polymer dispersion. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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