Synthesis of MDMO-PPV Nanoparticles Via In Situ Sulfinyl Precursor Route Polymerization in Miniemulsion

Anitha Ethirajan,* Lien D’Olieslaeger, Joke Vandenberghe, Laurence Lutsen, Marc D’Olieslaeger, Dirk Vanderzande, Thomas Junkers*

A facile route to synthesize poly[(2-methoxy-5-(3′,7′,7′-dimethyloctyloxy))-1,4-phenylene vinylene] polymer nanoparticles (NPs) using the miniemulsion technique in combination with the sulfinyl precursor route polymerization is presented. The reaction conditions involving high temperature are overcome by using ethylene glycol as a polar continuous phase. Particles can be easily transferred into the water phase without the need for additional surfactant. The characteristic UV–vis absorption and the strong fluorescence exhibited by the polymer along with the molecular weight obtained prove the success of the synthetic strategy. Such in situ synthesis of PPV in the form of NPs can be extended to other conjugated polymers, opening new doors for synthesizing luminescent NPs that have tremendous potential in biomedicine and printable electronics.

1. Introduction

Recently, semiconducting polymer nanoparticles (NPs) have gained tremendous interest as a new class of fluorescent nanomaterials that exhibit extraordinary photoluminescence, excellent photostability, and fast emission rates. Although fluorescent NPs based on inorganic semiconductors and small dye molecules are widely spread, the short excited-state lifetime, quantum yields approaching unity, a large absorption cross-section per particle and their non-toxicity makes semiconducting polymer NPs very appealing for biological imaging and biosensing applications. Also, such particles are highly interesting for optoelectronic devices owing to their interesting electronic properties in combination with ease in processability. Most polymer particles based on conjugated polymers are currently produced using preformed polymers, for example, using the miniemulsion technique in combination with solvent evaporation or by the precipitation method. Direct synthesis of conjugated polymer particles employing simple but yet efficient chemistries in heterogeneous systems have been reported for step-growth polymerization approaches. Previously, oil-in-oil emulsions (non-aqueous) using suitable block copolymeric surfactants were used to synthesize conjugated polymer particles. However, transfer of these particles to the aqueous phase was not reported. Aqueous miniemulsions were described by Mecking et al. for the synthesis of conjugated polymer particles employing Glaser, Sonogashira, and Suzuki–Miyaura reactions. For synthesis involving high temperatures and dry conditions,
non-aqueous media is, however, more suited. Polymerizable
miniemulsions of vinylic monomers in direct and
inverse miniemulsions have already been formulated using
non-aqueous polar and unpolar continuous phases.\[13\] Of
all the heterophase systems to synthesize NPs, miniemul-
sion offers reaction possibilities that are pragmatically
not possible with other approaches for the formation of
polymer NPs and functionalized hybrid NPs.\[14,15\]
Poly(p-phenylene vinylene) (PPV) and its derivatives are
a class of conjugated polymers with broad range of appli-
cations in optoelectronic devices and biosensors.\[16–19\]
PPV derivatives with backbone functionalization are very
interesting as they allow for good tunability of properties,
especially regarding solubility, which is often a problem
in wet-processing of conjugated materials. PPVs in general
can be synthesized either by direct step-growth routes or
by using the so-called p-quinodimethane based precursor
routes.\[20\] As the direct routes give mostly only access to
low-molecular-weight oligomers, the precursor routes are
usually more preferred due to their higher reproduc-
ability and ability to yield high molecular weights instant-
aneously. Furthermore, due to the chain growth nature
of the precursor routes, they allow for the synthesis of
complex functionalized PPV derivatives with ease. Among
the different well established routes following the pre-
cursor mechanisms the sulfanyl route offers polymers with
highest quality regarding control over the reaction
and regularity of the product.\[21\] Sulfanyl precursor poly-
merization follows a free-radical polymerization mecha-
nism (under certain reaction conditions also anionic
polymerization can occur, which is however in the pre-
sent context not the case). Thus, polymerizations are pro-
ceeding very fast, making them hence an ideal candidate
for the miniemulsion process.

Hence, in what follows, the sulfanyl route will be
explored in a heterophase system to produce NPs of a
common PPV derivative, poly[(2-methoxy-5-(3′,7′,-
dimethyloctyloxy)-1,4-phenylene vinylene] (MDMO-PPV).
To date, no in situ polymerization procedure towards PPV
NPs from precursor routes – and thus material of signifi-
cant molecular weight – exists. Also, in general no radical
polymerization was to date used to make conjugated NPs
(mostly since arylene vinylenes are the only kind of such
materials accessible from radical routes). Only NPs from
step-growth protocols have been reported in literature,
giving access only to low molecular weight PPV with
somewhat limited physical properties.\[22,23\]

2. Experimental Section

2.1. Materials

The precursor monomer was synthesized following literature
procedures.\[24\] All the other reagents and solvents used were
obtained from different commercial sources: ethylene glycol, tol-
ene and NatBuO from Sigma–Aldrich and the surfactant, Lute-
nosol AT50 from BASF, which is a poly(ethylene oxide)-hexadecyl
ether with an EO block length of about 50 units. Demineralized
water was used during the experiments.

2.2. Synthesis of MDMO-PPV NPs

MDMO-PPV polymer NPs were synthesized using the miniemul-
sion technique in combination with sulfinyl precursor route
polymerization. The precursor monomer (200 mg, 0.408 mmol)
dissolved in 0.3 g toluene was added to a solution of 3.5 g lutensol
AT50-ethylene glycol solution (0.8 wt%). After stirring for 1 h
under nitrogen flushing, the macroemulsion was subjected to
ultrasonication under ice cooling for 4 min at 50% amplitude in a
pulse regime (30 s sonication, 20 s pause) using a Branson 450 W
digital sonifer (1/8" tip). To this miniemulsion, a solution of
NatBuO in ethylene glycol (77.5 mg, 0.816 mmol, 2 equiv) that
was flushed with nitrogen for 1 h was added. Finally MDMO-PPV
NPs were formed by thermal elimination by stirring the sample
at 120 °C for 3 h. The sample was placed in an ultrasonication
bath to redisperse the aggregated particles (caused by thermal
treatment). The particles were then transferred from the eth-
ylene glycol to the water phase by centrifugation (14 000 rpm for
40 min) and redispersion. The particles were caracterized after
washing using demineralized water to remove the excess sur-
factant by multiple centrifugation and redispersion. NMR spec-
troscopy characterization of the obtained polymers yielded for
the precursor polymer 1 H NMR (300 MHz, CDCl3, δ): 6.9–6.7 (br m,
2H, Hα); 4.7–4.5 (br s, 1H, Ar-S(=O)R); 4.0–2.9 (br m, 7H, OCH3,
OCH2, Ar-S(=O)CH2-Ar); 2.7–2.6 (br d, 2H, S-OCH2(CH3)2CH3); 1.9–1.0 (br m, 20H, Hα); 1.0–0.8 (m, 12H, CH2, CH3). Fort he con-
jugated polymer after thermal elimination 1 H NMR (300 MHz,
CDCl3, δ): 7.5 (br, 2H, H olef. ); 7.2 (br, 2H, H ar ); 4.2–3.7 (br m, 9H, OCH3, CH2, OCH3); 2.0–1.0 (br m, 10H, Hα); 1.0–0.8 (m, 9H, CH3)
was obtained. Both peak assignments are typical for MDMO-PPV
obtained from the sulfanyl precursor route and virtually identical
with literature spectra.\[20\]

2.3. Experimental Characterization

The average size of the NPs was determined by dynamic light
scattering using a Brookhaven instruments zetapals. The sample
was diluted using demineralized water. The morphology of the
NPs was imaged using a TECNAI spirit TEM of FEI operating at
an accelerating voltage of 120 kV. The sample was prepared by
air drying the diluted sample in water on a carbon-coated copper
grid without any additional contrasting. The UV–vis absorption
spectrum of the conjugated polymer dissolved in chloroform was
obtained using the Agilent Cary500 Scan UV–vis–NIR spectro-
photometer. The emission spectrum of the conjugated polymer
dissolved in chloroform was obtained using the Horiba–Jobin
Yvon FluoroLog-3 spectrofluorometer.

Analysis of the MWDs of the polymer samples were
performed on a Tosoh EcoSEC operated by PSS WinGPC software,
equipped with a Plgel 5.0 μm guard column (50 × 8 mm),
followed by three Plgel 5 μm Mixed-C columns (300 × 8 mm) and
a differential refractive index detector as well as a UV detector.
using THF as the eluent at 40 °C with a flow rate of 1 mL min⁻¹. The SEC system was calibrated using linear narrow polystyrene standards ranging from 474 to 7.5 × 10⁶ g mol⁻¹, and toluene as a flow marker. Molecular weights reported herein thus represent only apparent molecular weights since the results are based on polystyrene calibration. Reliable Mark–Houwink parameters are not available for MDMO-PPV. Previous investigations with multicycle light scattering detection showed, however, that for the final conjugated polymer, apparent and true molecular weights are in reasonable agreement with each other.[25] ¹H NMR spectra were recorded with a Varian Inova 300 spectrometer at 300 MHz using a 5 mm probe.

### 3. Results and Discussion

MDMO-PPV polymer NPs were synthesized using the miniemulsion technique in combination with sulfinyl precursor route polymerization. In the precursor route (see Scheme 1), first the reactive monomer is formed upon addition of a relatively strong base to a substitute para-xylene bearing a polarizer (P) and a leaving group (L). The monomer, a p-quinodimethane species, spontaneously polymerizes after dimerization into a precursor polymer with a high conversion in a short time. The so-obtained precursor polymer is then converted into its conjugated form by means of a secondary elimination step, which is for the sulfinyl route a thermal conversion. Polymerization itself occurs rapidly even below room temperature, commonly within few minutes to full monomer conversion. Molecular weights that are accessible are high. Typical results (depending on reactant concentrations, additives and reaction media) cover materials in the range of several 10⁴–10⁶ Da. While the polymerization itself can be carried out at room temperature with ease, high temperatures are required to convert the substituted polymer into the conjugated PPV. Non-aqueous miniemulsion had thus to be employed in order to be able to convert the formed polarizer-substituted prepolymer into the final conjugated MDMO-PPV. In this work, ethylene glycol was used as the continuous phase due to high reaction temperature and a non-ionic surfactant based on ethylene glycol units as the hydrophilic moiety (Lutensol AT50) was used as a surfactant. The miniemulsion containing the precursor monomer/toluene droplets in ethylene glycol was first formed and then to this a second ethylene glycol solution containing the base (NatBuO) was introduced. The high interfacial area offered by the nanodroplets allows for efficient interaction between the reactants. Such an approach was also recently reported where synthesis of unsubstituted polythiophene with defined high molecular weight was achieved by employing ultrasonication. High interfacial area nanoentities allowed thereby for efficient interaction between the reactants which was followed by microwave assisted reaction in a heterophase system.[26] In the MDMO-PPV particle synthesis, polymerization proceeded directly upon mixing of the two solutions as was indicated by a color change of the dispersions. It should thereby be noted that the reaction – while being conducted at room temperature – would also occur when heating was applied to the dispersion; the polymerization is very robust in that respect. Heating was not used in the present case, since sulfinyl precursor polymerizations also in bulk are usually performed between 20 and 30 °C. Monomer conversions in precursor polymerizations are – as discussed above – typically very high and can be assumed to reach practically 100% due to the high reactivity of the active quinodimethane monomer. Isolated yields in bulk polymerization (after precipitation) are usually around 80% or better, which reduction can be explained by formation of small molecular weight side products during polymerization that is also observed in bulk polymerization. Since polymerization in the miniemulsion nanocontainers will certainly follow the same reaction mechanism, similar results in terms of conversion and yields can be generally expected. At this stage a small sample was taken for characterization of the precursor polymer (see below). Finally, MDMO-PPV NPs were formed by the subsequent post thermal elimination step by heating the precursor polymer particle dispersion at 120 °C for 3 h. During the thermal elimination step, a gradual change in the color from light yellow to orange and then intense red was observed – indicating successful formation of conjugated material. Also here, it is important to note that elimination can in principle also be performed at other temperatures. Conversion of the sulfinyl precursor polymer starts at temperatures as low as 80 °C. Higher temperature was used to speed up elimination since formation of MDMO-PPV is largely accelerated at 120 °C. During thermal elimination step partial aggregation of particles took place owing to the influence of high temperature on the non-ionic surfactant containing thermally labile ethylene glycol chains. By subjecting the sample solution to a mechanical agitation shortly using an ultrasonication bath, the aggregates were, however, conveniently redispersed. While redispersion proceeds without problems, nevertheless some material is lost during centrifugation. No yields of reaction for the entire process can thus be given. As discussed above, however,
yields in the ethylene glycol phase should be as high as in bulk polymerization.

The stable colloidal dispersion in the presence and absence of UV illumination is depicted in Figure 1. To achieve an aqueous dispersion of the MDMO-PPV particles, the as-synthesized particles were transferred into water phase by centrifugating and redispersing the obtained pellet in water. The NPs dispersed well in water without need for additional stabilizers or precipitation on the glass vial walls. The number-average particle size measured by DLS was about 237 nm with a polydispersity index of 0.2 (for details on the DLS measurements see Figure S1, Supporting Information).

The morphology of the particles studied using TEM clearly shows that the particles are spherical in shape and additionally reveal that they are not aggregated. The number average particle size measured by DLS (hydrodynamic diameter) are comparable to the average diameter obtained from TEM images. The apparent molecular weight of the conjugated polymer obtained in an representative experiment was about $M_n = 23\,500\,\text{g}\,\text{mol}^{-1}$ with a PDI = 3.4. The apparent molecular weight of the precursor polymer before the heat-treatment of the particles was about $M_n = 9700\,\text{g}\,\text{mol}^{-1}$ (PDI = 2.4). Both polymers were well soluble in organic solvents and no traces of aggregates could be observed by spectrosopy. The eluograms of precursor polymer and the conjugated MDMO-PPV are shown in Figure 2.

A smaller apparent molecular weight is observed for the precursor polymer compared with the conjugated material, which is typical for all precursor route PPV materials. This effect can be attributed to selective precipitation, but even more to the larger hydrodynamic volume of the stiff conjugated chains as compared with the precursor polymer. The difference in apparent chain length is thus mostly an artifact from direct polystyrene calibration of the SEC. More recent studies demonstrate that the $M_n$ obtained for the eliminated PPV from polystyrene calibration is close to the absolute molecular weight.\(^{[25]}\) For the analysis of molecular weights of the PPV materials, it should also be noted that UV detection was chosen over RI detection since relatively high amounts of surfactant were present in the product mixtures after dissolution of the particles in THF. As can be seen from the depicted traces, no clear determination of the high molecular weight fraction could be reached using RI detection. In the UV detector signal, the PPV-related polymer can be selectively traced, thus allowing for a more accurate determination of average molecular weights and dispersity. For the conjugated MDMO-PPV, no significant difference between RI and UV–vis detection was observed due to removal of the surfactant after precipitation of the polymer. It is important to stress that the process is easily reproducible and – as described above – also allows for variation in the polymerization procedure. Repetition of the emulsification/polymerization/redispersion protocol yielded almost the same result in terms of molecular weight (18 700 g mol\(^{-1}\) at PDI = 3.4 in the conjugated form) and optical properties of the material (see discussion below).

The success of the elimination step – that is the absence of non-eliminated sulfinyl groups on the backbone – was confirmed by NMR spectroscopy studies (see Figure 3) as well as by the observation of typical $\lambda_{\text{max}}$ in the UV spectrum of the product. Samples of the polymer particles were taken directly after polymerization and analyzed via NMR spectroscopy. A typical precursor MDMO spectrum is observed which is virtually identical to literature spectra for polymers made in bulk via the same route.\(^{[20]}\) In addition, intense resonances (marked with squares in the figure) result from leftovers of the lutensol AT50 surfactant that was used for the stabilization of the miniemulsion. Since precipitation of the polymer at precursor
level is difficult, the surfactant was not removed prior analysis. The peak marked with an asterisk results from residual CHCl₃. Further unassigned peaks in the spectrum result from impurities, which could also not be removed at this point in synthesis. Occurrence of the impurities poses, however, no problem and is commonly observed in precursor PPV polymerization. After elimination of the sulfinyl groups from the precursor, disappearance of the characteristic peaks at 4.6 and 2.7 ppm is observed. Concomitantly, a new peak arises at 7.5 ppm, marking the successful formation of the conjugated pi-system on the polymer backbone. The NMR spectroscopy analysis of the materials thus unambiguously confirms the successful synthesis of MDMO-PPV in the miniemulsion process. NMR spectroscopy is, however, limited with respect to determination of chain defects in the material, which can have severe impact on the optoelectronic properties. If too many defects are created (for example, by increased radical recombination events or inefficient propagation compared with initiation of chains), conjugation is partially broken – absorption and emission spectra of the polymers are altered.

Thus, the optical properties of the polymer were studied using UV–vis and fluorescence spectroscopy. The UV–vis absorption profile in Figure 4 (l.h.s.) exhibits an absorption maximum (λ_max) of 494 nm independently confirming the presence of the conjugated system characteristic to MDMO-PPV. At the same time the complete absence of the precursor units in the backbone is confirmed by the absence of its characteristic absorption band at 288 nm. The photoluminescence measured using the fluorescence spectroscopy is also presented in Figure 4 (r.h.s.). With the excitation wavelength (λ_exc) of 494 nm (thus at its absorption maximum), the polymer exhibits a distinct fluorescence emission maximum (λ_em) at 550 nm with a shoulder at around 600 nm. Both maximum absorption and emission maxima are very close to typical result for MDMO-PPV and thus unambiguously prove that the optical properties of the obtained material is competitive with the one obtained via homogeneous polymerization. From the spectra it can be concluded that the structural integrity of the polymers made in miniemulsion is thus very high, keeping the advantages of the sulfinyl precursor route over the other common polymerization routes such as Wittig polycondensation and Gilch polymerization. This is a very important observation, because device efficiencies, be it in light emitting diodes or in light harvesting applications, rely on low amounts of defects in the chains, which is reflected in high λ_max and well defined λ_em. Since the absorption and emission spectra are matching literature spectra, it can safely be assumed that the MDMO-PPV made in miniemulsion is widely comparable to MDMO-PPV synthesized in bulk also with respect
to other parameters and further characterization of the obtained MDMO-PPV with respect to its optical properties is not required since conventional MDMO-PPV from the sulfanyl route has been extensively studied before. This is of great importance when considering potential application of the water-dispersed conjugated material. From an engineering point of view, such dispersion can be used for green processing of PPV for example for printing purposes. Thus, in final applications, particles will be deposited in solid layers and it may be expected that the final characteristics of such films will not significantly differ from the characteristics of the bulk material.

4. Conclusion

In conclusion, the sulfanyl route in combination with the miniemulsion technique offers a convenient way to synthesize MDMO-PPV NPs. With the described method, conjugated NPs are for the first time available from direct radical polymerization in miniemulsion. The obtained particles can be easily transferred into the water phase without need for an additional surfactant and the procedure is well reproducible. The characteristic UV–vis absorption and the strong fluorescence exhibited by the polymer along with the molecular weight of $M_n = 23$ 500 g mol$^{-1}$ obtained proves the success of the novel synthetic strategy. The in situ synthesis of PPV derivative in the form of NPs can be extended to other conjugated polymer particles of the poly(arylene vinylene) type and opens new doors for synthesizing functional luminescent NP probes that have tremendous potential in the field of biomedicine. Since a non-ionic surfactant was used, the dispersion has good steric stabilization against any electrolyte addition which is crucial for biological applications. Also, dispersions of semiconductor NPs are very valuable in the field of printable electronics. The procedure described in here will also allow for the synthesis of multifunctional hybrid NPs that combine the functional advantages of different individual components.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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