

Department of Chemistry
University of Helsinki
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**ENHANCING THE PROCESSABILITY OF
POLY(BENZIMIDAZOBENZOPHENAN-
THROLINE) THROUGH CHEMICAL
MODIFICATION**

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ACADEMIC DISSERTATION

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ABSTRACT

Poly(benzimidazobenzophenanthroline) (BBL), which may be doped into a p- and n-type semiconductor, has been chemically modified to enhance its processability. In its pristine form BBL is processable only in some concentrated acids and nitromethane/Lewis acid solutions. The corrosiveness of these solvents and moisture sensitivity of the solutions severely limits the possibilities for the use of BBL as an electroactive material in organoelectronic devices and limit the possibilities for its post synthetic chemical modification.

In this work processable BBL derivatives have been prepared using two different approaches i) preparation of block-copolymers by attachment of water soluble polymers on BBL functional chain ends ii) attaching bulky side groups on one of the monomers and using that as a starting material in the polymerization reaction.

Short BBLs of DP 10 or 20 were prepared with functional chain ends and monofunctional poly(ethylene oxide) (PEO) or poly(N-isopropylacrylamide) of several different molecular weights were attached at the chain ends. Elemental analysis showed that the extent of chain end substitution varied quite a lot when PEO was used. It was also shown that thermogravimetric analysis (TGA) was not suitable to determine the fraction of PEO in BBL-PEO block-copolymers. However, the extent of chain end substitution using PNIPAM was evaluated using TGA. BBL-PEOs could be processed into aqueous dispersions at concentrations ≥ 1.5 mg/ml by means of ultrasonication, and these dispersions were proven to be colloiddally very stable. The dispersions could be used to spin- or drop cast films. At higher concentrations BBL-PEO dispersions were shown to form gels. The reason for the gelling is the packing of the polymer into nano-wire structures which then aggregate into 3D-network. SEM- and cryo-TEM imaging confirmed the existence of wire-type structures. Wire structures and gelation were also observed for aqueous dispersions of pristine BBL.

BBL-PNIPAM block-copolymers were found to be indispersible in water with PNIPAM fractions lower than 35 mass %. However, they gelled upon ultrasonication. With higher PNIPAM fractions the polymers were dispersible and did not form gels in any of the studied concentrations. Dispersibility in water and the colloidal stability of BBL-PEOs and BBL-PNIPAMs was attributed to electrostatic stabilization as the particles showed negative zeta-potentials. Dispersible BBL-PNIPAMs were more stable due the high amount of dissociative groups originating from the partial degradation of the amide moieties during the coupling to BBL.

One of the monomers used to prepare BBL, 1,4,5,8-naphthalenetetracarboxylic acid 1,8-monoanhydride, was successfully mono- and dibrominated. The bromine was then used as a functional group and replaced either directly with 2-ethyl-1-hexylamine or substituted with azide and reacted with 1-hexyne. The modified monomers were used in preparation of BBL. BBLs bearing either 2-ethyl-1-hexylamine or 4-butyl-1,2,3-triazole groups were found to be sparingly soluble in dimethylsulphoxide and *N*-methyl-2-pyrrolidone.

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LIST OF ORIGINAL PUBLICATIONS

This thesis is based on the following publications:

- I Sami-Pekka Hirvonen, Mikko Mänttari, Valter Wigren, Carita Kvarnström, Heikki Tenhu. **A novel method to prepare water dispersible poly(benzimidazobenzophenanthroline) (BBL) by partial substitution of chain ends with poly(ethylene oxide)** Colloid and Polymer Science, 2011, 28, 1065-1072
- II Sami-Pekka Hirvonen, Mikko Karesoja, Erno Karjalainen, Sami Hietala, Pasi Laurinmaki, Eeva-Kaisa Vesanen, Sarah Butcher, Heikki Tenhu. **Colloidal properties and gelation of aqueous dispersions of conductive poly(benzimidazobenzophenanthroline) derivatives** Polymer 2013, 54(2), 694-701
- III Sami-Pekka Hirvonen, Heikki Tenhu. **Modification of naphthalenic unit in BBL main chain** Synthetic Metals 2015, 207, 87-95
- IV Sami-Pekka Hirvonen, Teemu Rossi, Mikko Karesoja, Erno Karjalainen, Heikki Tenhu. **Thermally responsive particles of poly(benzimidazobenzophenanthroline) modified with poly(N-isopropylacrylamide)** Colloid and Polymer Science 2015, article online DOI 10.1007/s00396-015-3693-6

The publications are referred to in the text by their roman numerals.

Author's contributions to the publications. In paper I the author planned the syntheses, prepared the polymers and did the chemical characterization. In addition to those the manuscript was prepared by the author. In paper II the author prepared the polymers, measured the colloidal and rheological properties and prepared the manuscript. In paper III the author planned and performed the syntheses, characterized the products and prepared the manuscript. In paper IV the author planned the syntheses, prepared most of the BBL-PNIPA copolymers, measured their colloidal properties and prepared the manuscript.

ABBREVIATIONS

AFM	Atomic force microscopy
AlCl ₃	Aluminum trichloride
BBL	Poly(benzimidazobenzophenanthroline)
BTA	1,2,4,5-Benzenetetramine tetrahydrochloride
CDCl ₃	Deuteriochloroform
DMF	N,N-dimethylformamide
DMSO	Dimethylsulphoxide
DP	Degree of polymerization
D ₂ O	Deuterium oxide
d ₆ -DMSO	Deuterated dimethylsulphoxide
d ₃ -MeNO ₂	Deuteronitromethane
FeCl ₃	Iron trichloride
GaCl ₃	Gallium trichloride
G'	Storage modulus
G''	Loss modulus
HOMO	Highest occupied molecular orbital
HPLC	High performance liquid chromatography
HSQC	Heteronuclear single quantum coherence
kD	kilo Dalton
LA	Lewis acid
LCST	Lower critical solution temperature
LUMO	Lowest unoccupied molecular orbital
Me ₆ TREN	Tris[2-(dimethylamino)ethyl]amine
MSA	Methanesulphonic acid
MWCO	Molecular weight cut off
NMP	1-Methyl-2-pyrrolidone
NMR	Nuclear magnetic resonance
NTCA	1,4,5,8-Naphthalenetetracarboxylic acid
NTCA-Br	2-bromo-1,4,5,8-Naphthalenetetracarboxylic acid
NTCA-CN	2-cyano-1,4,5,8-Naphthalenetetracarboxylic acid
NTCA-MA	1,4,5,8-Naphthalenetetracarboxylic acid 1,8-monoanhydride
NTCA-2EHA	2,6-bis((2-ethylhexyl)amino)naphthalene-1,4,5,8-tetracarboxylic acid
NTCA-1HE-Click	2-bromo-6-(4-butyl-1H-1,2,3-triazol-1-yl)naphthalene-1,4,5,8-tetracarboxylic acid (6) and 2,6-bis(4-butyl-1H-1,2,3-triazol-1-yl)naphthalene-1,4,5,8-tetracarboxylic acid
OFET	Organic field-effect transistor
PANI	Poly(aniline)
PEO	Poly(ethylene oxide)

PMDETA	<i>N,N,N',N'',N''</i> -Pentamethyldiethylenetriamine
PNIPAM	Poly(<i>N</i> -isopropylacrylamide)
P ₃ HT	Poly(3-hexylthiophene)
RT	Room temperature
SbCl ₃	Antimony trichloride
SbCl ₅	Antimony pentachloride
SEC	Size-exclusion chromatography
SEM	Scanning electron microscopy
SOCl ₂	Thionylchloride
S/N-ratio	Signal-to-noise –ratio
TEM	Transmission electron microscopy
TGA	Thermogravimetric analysis
THF	Tetrahydrofuran
UV-vis	Ultraviolet-visible

1 INTRODUCTION

1.1 Conjugated polymers

Conjugated polymers are polymeric materials that have alternating single- and double bonds in their backbone. The overall structure of these polymers vary from poly(acetylene), which is the simplest possible, to complex fused ring and ladder type polymers. Two examples of conjugated polymers are presented in figure 1.

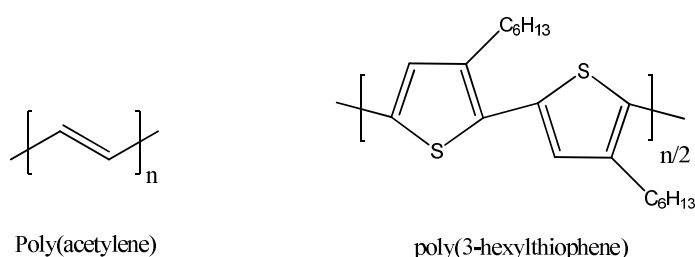


Figure 1. Structures of two well-known conjugated polymers

Polymers in this category have been studied increasingly ever since the semiconducting properties of poly(acetylene) were introduced to wider scientific community at the end of 70's by Shirakawa, Heeger and McDiarmid [1]. The conjugated structure of the backbone creates a π -orbital system that extends over the whole length of the polymer chain if there are no structural defects present and charge carriers created in this system are able to move along the chain and from one chain to another, which gives these materials their semiconducting properties.

The charge carriers are usually created by a process called doping, which in many cases is done by partial oxidation of the polymer using electrochemistry, free halogens or acids. Charge carriers can also be created by reducing the polymer either electrochemically using cathodic potential or chemically using reductive species such as potassium naphthalide. In some cases charge carriers are introduced in a process called photodoping in which absorbed energetic photons excite electrons into conduction band and no chemical dopant is needed. Doping of the polymer typically increases the conductivity by several orders of magnitude turning it from an insulator to a semiconductor. Depending on the method of doping semiconducting polymers are usually divided into two categories according to the type of the created charge carrier, which can be a hole or an electron. Oxidatively doped polymers have positive charge carriers (holes) and they are defined as p-type. Reductively or photodoped polymers have electrons as negatively charged

carriers and are categorized as n-type. Majority of semiconducting polymers can only be doped to p-type and they are usually relatively stable at ambient environment also in their doped form. Polymers chemically doped to n-type semiconductors are usually very prone to oxidation by atmospheric oxygen or moisture and can therefore be used only in well-sealed devices.

The possibility of replacing conventional inorganic semiconducting materials with organic ones has further increased the scientific efforts to develop new kinds of conjugated polymers with the possibility to tune the electronic properties for devices needing tailored HOMO and LUMO levels. These, and the HOMO-LUMO gap, commonly referred as band gap, are crucial for the effective function of some organoelectronic devices such as light emitting diodes and photovoltaics. Polymeric semiconductors have certain desirable properties that inorganic semiconductors do not have, such as solution processability at ambient environment and greater resistance to catastrophic breakage when bent or hit.

A common feature of all polymers consisting purely of a conjugated backbone is that they are poorly soluble as such. This is because a conjugated system prefers a planar conformation limiting the ability of different segments to twist and rotate through the single bond. The planarity of the structure decreases the entropy gain in dissolving as there are fewer possible conformations the chain can adopt in solution. Conjugated planar structures have also a strong tendency for pi-stacking further complicating the dissolution process. To overcome this, most semiconducting polymers have either been modified with bulky side chains which improve solubility as with poly(3-alkylthiophenes) or doped with an acidic species which yields a processable formulation such as a complex between poly(aniline) and poly(styrene sulphonic acid) which is electrostatically stabilized water based dispersion.

1.2 Poly(benzimidazobenzophenanthroline)

Poly(benzimidazobenzophenanthroline) commonly abbreviated as BBL is a conjugated ladder-type polymer having fully aromatic backbone, the structure shown in figure 2.

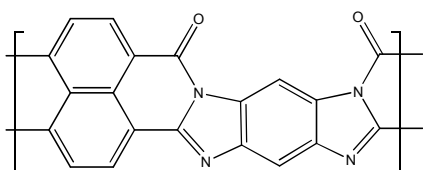


Figure 2. The chemical structure of BBL

BBL was first synthesized during the late 60's in the US as structural material in military avionics by Van Deusen [2, 3] followed by more thorough investigations by Arnold and Van Deusen [4, 5]. Due to the aromatic ladder-type structure it is very resistant against thermal and chemical degradation. It can be protonated by strong acids, is often processed as a solution in methanesulphonic acid and is unreactive toward bases if completely cyclized. Incomplete cyclization, which can be a result of the use of impure monomers, leads to chain scission in strongly basic conditions decreasing the molecular weight of the material [6]. BBL is thermally very stable and when heated in air it starts to oxidize slowly at temperatures above 500 °C but under nitrogen atmosphere thermal degradation starts above 700 °C. BBL is usually prepared by reacting 1,4,5,8-naphthalenetetracarboxylic acid and 1,2,4,5-benzenetetramine at elevated temperature in polyphosphoric acid, although it can also be prepared in melt. In the polymerization reaction a polyimide is formed first. This is followed by intrachain cyclization which forms the conjugated aromatic structure. Mechanistically the reaction is a polycondensation and does not allow for precise control over the molecular weights or molecular weight distributions. Thus the average degree of polymerization can be controlled to some extent by adjusting the stoichiometry of the starting materials.

Arnold and Van Deusen studied the properties of BBL on the early 70's using mainly films prepared either by casting from acid solutions [4] or collecting dispersed fibrous precipitates on a frit followed by drying [5]. Both of the methods were used to produce strong films. BBL can also be spun into fibers using methane sulphonic acid as solvent [4]. Sicree, Arnold and Van Deusen prepared BBL analogs using fused ring tetramines as the other monomer and showed that BBL has better film forming properties [7]. The scientific interest for BBL was renewed at early 80's as the conjugated structure suggested that it could be doped into a semiconductor. The studies on the semiconducting properties of BBL showed that the conductivity can be increased by several orders of magnitude from the initial insulating region of 10^{-12} S/cm of the pristine polymer to semiconducting region of 10^{-2} - 10^2 S/cm by doping either chemically [8, 9] or electrochemically [10-14]. Irvin et al. showed that electrochemical response of BBL films can be enhanced by increasing the film porosity by co-casting BBL with an ionic liquid in MSA [15]. Ion implantation of BBL films using Kr^+ or Ar^+ was shown to increase the conductivity up to 10^2 S/cm but high doses resulted in the degradation of the polymer ladder structure [16-21]. Unlike many conjugated polymers BBL can be chemically doped to both p-type semiconductor using strong acids or certain Lewis acids and to n-type using elemental potassium or potassium naphthalide. However, it is not doped effectively by I_2 or Br_2 [8] but can be processed into the semiconducting region using thermal annealing [8, 22]. BBL has also been shown to be photoconductive [23-29]. High electron affinity of BBL has been

utilized in binary blends of BBL and p-type conducting polymers as charge transfer between the polymers could be induced either by irradiation with light [30], electrochemically [31], or thermally [32], leading to significant increase in the conductivity of the blend. The blend of BBL and polypyrrole (PPy) was shown to exhibit conductivity up to 10^{-6} S/cm with very small proportion of PPy even before the light induced electron transfer [31]. Later, BBL-PEO block-copolymer was used in preparation of donor-acceptor composite layers with electropolymerized poly(azulene) films [33]. BBL has also been used in binary blends with graphene and graphene oxide but in these most of the electrical conductivity was attributed to an interpenetrating network of conducting graphene sheets [34]. Later BBL was used as a matrix material in photo reduction of graphene oxide in films made of BBL graphene oxide binary blends [35]. Since the initial studies on the semiconductive properties of BBL several studies were made during the 90's concentrating in the mode of conductivity, the effect of local defects [36] and trap states [37], the properties of excited states [38-40], and the conductivity and redox properties of different reduction sites [41, 42]. Hong et al. studied the electronic structures of n-doped BBL theoretically and proposed that up to 4 electrons could be added to each repeating unit [43]. The ladder type backbone forces the polymer into a coplanar structure which has been shown to result in non-linear optical properties [44].

The n-type conductivity properties, strict planarity of the chain and robustness of the polymer have been the main motivations in the studies of BBL despite the difficulties involved in processing it. So far BBL has been shown to function as electroactive material in different photovoltaic assemblies [36, 45-48], photodetectors [49, 50], capacitors [51] and different transistor assemblies [52-57]. The difficulty in producing nano-scale structures of BBL has been circumvented in some studies by preparing sandwiched structures of BBL and some other conducting polymers by means of spin coating, embedding of the films in epoxy matrix and use of a ultramicrotome in a process called nanoslicing to produce slices in which the polymers are in nanowire-like configuration [47, 58-60]. However, the inherent difficulties in processing the polymer and studying it in solution become obvious when the number of publications on BBL, which is well below one hundred, is compared to two other semiconducting polymers prepared more than twenty years ago, comparison presented in figure 3.

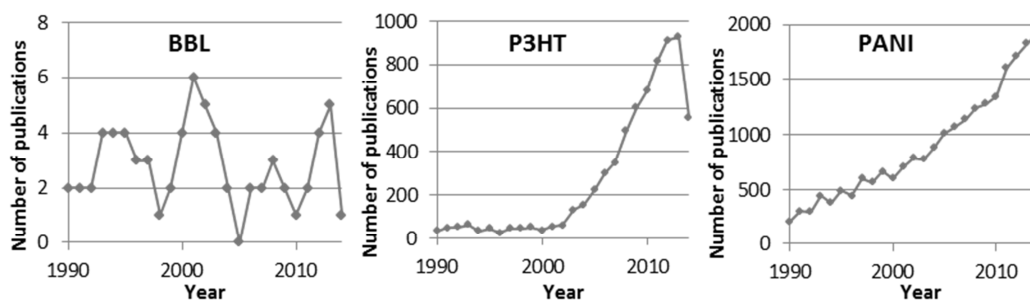


Figure 3. Number of publications per year on BBL, poly(3-hexylthiophene) and poly(aniline) between 1990 and 2014.

1.2.1 BBL in solutions

Despite of the relatively simple synthetic procedure needed for the preparation of BBL, the insolubility in non-acidic solvents severely limited the possibilities for research and so far no reports of BBL or its derivatives which are soluble in neutral solvents at room temperature can be found. BBL has been shown to pack with high local order into a orthorhombic unit cell [61] with strong van der Waals interactions due to π -stacking [62], which makes the dissolution process unfavorable in neutral solvents. BBL is slightly soluble in concentrated H_2SO_4 but the solubility decreases with increasing molecular weight. However, solutions up to 5 mass % can be prepared in MeSO_3H regardless of the Mw of the polymer [4]. The dissolution process is facilitated because concentrated strong acids protonate the carbonyl oxygen and imine nitrogen heteroatoms in the BBL chain. The protonation is accompanied by a change in color to deep red. Jenekhe and Johnson discovered that BBL can be dissolved in nitromethane / Lewis acid solutions [63]. It was shown that the ability of the LA used to dissolve BBL is not directly proportional to the Lewis acidity of the compound but rather follows empirically determined order $\text{GaCl}_3 > \text{AlCl}_3 > \text{FeCl}_3 > \text{SbCl}_5 > \text{SbCl}_3$. There is a stoichiometric threshold ratio of 4/1 between the LA and BBL repeating unit for effective dissolution and with lower ratios insoluble gels are formed. A theoretical upper limit for BBL concentration is set by the solubility of the LA used and in the case of AlCl_3 this is approximately 20 wt. %. Unlike in protonic acid solutions, in nitromethane / LA –solutions BBL enters into a liquid crystalline phase above concentrations of 8-9 wt. %, the threshold depending slightly on the LA used [63]. As LAs used to dissolve BBL were ineffective to dope it into a semiconductor, formation of a charge transfer complex in which electrons are transferred from the π -orbital system to the LA was ruled out. Instead, Jenekhe and Johnson proposed that electron donor-acceptor complex is formed between the LA and carbonyl oxygens and imine nitrogens. Using AlCl_3 as the LA Roberts and Jenekhe studied the mechanism of the solubilization by means of ^{27}Al -NMR spectroscopy and were able to show that of the AlCl_3 in the solution 3.6 moles were bound to

BBL and 0.96 moles remained unbound for a mole of BBL repeating units [64]. They attributed the apparent molar ratio of less than 4 LAs for each BBL repeating unit to either inaccuracies in the integration of the signals or the possibility that not every repeating unit needs to have all of the sites occupied for effective dissolution. To this date the most common solvents used for dissolution and processing of BBL are MSA and MeNO₂/AlCl₃.

1.2.2 BBL formulations processable in neutral solvents

BBL as such is completely insoluble in neutral solvents but there are a few reports showing it can be processed into dispersions in water or some organic solvents such as chloroform and methanol. Janietz and Sainova prepared a water based dispersions by adding a dilute solution of BBL in methanesulphonic acid into an aqueous solution of a non-ionic surfactant under ultrasonication [65]. The high shear forces from the ultrasonication prevent the formation of large aggregates upon deprotonation of the BBL chains and it precipitates into small particles which are rapidly covered by the surfactant preventing them to coalescent and precipitate out. They proved that different non-ionic surfactants, such as Tween 80 and Brij 98, can be used to produce a stable BBL dispersion with a typical particle size ranging between 50-150 nm and these dispersions can be spin-coated to semiconducting films of BBL as parts of functioning OFETs. Briseno et al. prepared BBL nanobelts by adding drop-wise a dilute solution of BBL in MSA into chloroform/methanol solution under vigorous stirring [66]. If the methanol concentration is suitably low, BBL packs into nanobelts rather than forms larger fibers because of the relatively slow deprotonation and loss of solubility of the BBL chains. After subsequent washing the nanobelts could then be transferred to water, ethanol, methanol and chloroform to yield BBL-nanobelt dispersions. It was also shown that in the nanobelts the individual BBL chains pack having the polymer long axis parallel to the belt axis. The nanobelts could be used to prepare n-channel OFET and the semiconductive properties of BBL were preserved in the belt structure.

1.2.3 Main chain modification of BBL

There have been very few reports on modifying the repeating units of BBL itself apart from the study of Sicree et al. [7] in which BTA was replaced with fused ring tetramines. In their noteworthy report Irvin et al. describe the synthesis of BBL analog, in which the benzenetetramine was replaced with pyridine tetramine (figure 4). The authors expressed their scepticism on the possibility of derivatization of the naphthalenic part of the repeating unit [51]. A report has been published which were BBL-like small molecular

compounds consisting of essentially one repeating unit [67]. No true polymers or oligomers have been reported so far.

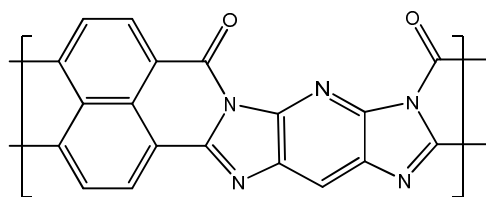


Figure 4. BBL in which the benzene ring of the BTA part is replaced by pyridine

1.3 POLY(N-ISOPROPYLACRYLAMIDE)

Poly(N-isopropylacrylamide) (figure 5) is an acrylic water soluble polymer well known for its behavior in aqueous solutions. Atactic PNIPAM exhibits a lower critical solution temperature (LCST) which is around 32 °C, first reported at late 60's by Heskins and Guillet [68]. Below this temperature the polymer is well soluble in water but as the temperature is increased above the LCST the polymer goes through a coil-to-globule transition and loses its solubility. Upon cooling below the LCST the polymer regains its solubility and returns in the solution phase. LCST of PNIPAM can be changed by copolymerization with other monomers [69, 70] and co-polymerizations with acrylic acid (AA) induce an elevation of LCST when the AA is not in a protonated form [71, 72]. The repeating units of PNIPAM carry an amide bond which can be hydrolyzed in acidic or basic conditions, and a partial hydrolysis of the polymer chain results in a copolymer of N-isopropylamide and acrylic acid.

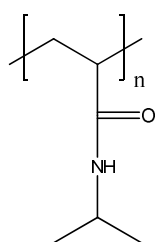


Figure 5. The chemical structure of poly(N-isopropyl acryl amide)

PNIPAM has been used as thermally responsive polymer in numerous applications in which some predetermined response has been induced by change of temperature across the LCST.

2 OBJECTIVE OF THE STUDY

The objectives of this study were to prepare new compositions of semiconducting polymers that are processable in water or neutral organic solvents. At the beginning of the study a novel poly(aniline)-poly(2,6-dimethylphenylene-1,4-oxide) sulphonic acid complex, which is dispersible in water, was developed and patented [73]. The structure of the prepared complex is presented in figure 6.

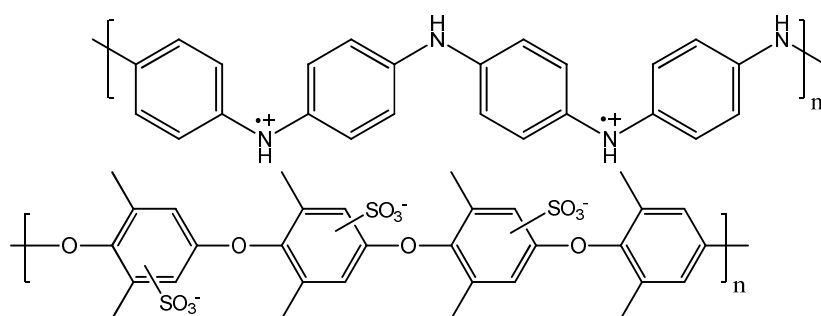


Figure 6. poly(aniline)-poly(2,6-dimethylphenylene-1,4-oxide) sulphonic acid complex

After this the course of the study was changed to a n-type semiconducting polymer, poly(benzimidazobenzophenanthroline). The primary goal for this was to modify the polymer in such a way that it is processable from water. Secondary goal was to introduce processability in other neutral solvents and to study the effects of the modifications on the electronic levels of the polymer.

3 EXPERIMENTAL

The synthesis of the monomers and polymers are described only briefly in this section. More detailed descriptions can be found in the original publications included in the appendices.

3.1 INSTRUMENTATION

^1H -, ^{13}C and HSQC –spectra were recorded using Bruker Avance II NMR-spectrometer operating at 500 MHz. All spectra were recorded at 20 °C unless stated otherwise.

Thermogravimetric measurements were performed using Mettler Toledo TGA 850 instrument and 70 μL Al_2O_3 crucibles. Samples were heated from 25 °C to 850 °C with heating rate of 10 °C/min under nitrogen flow of 50 ml/min.

Intrinsic viscosities were determined using Lauda S5 automated measuring unit with an Ubbelohde-type flow viscometer in a temperature controlled bath at 20.0 °C. Methanesulphonic acid was used as solvent.

For ultrasonication Hielscher UP400S instrument was used.

Dynamic light scattering was measured at 90° angle in a temperature controlled bath at 20 °C using Coherent SAPPHIRE 488-100 laser operating at 488 nm together with Brookhaven Instruments Corporation goniometer assembly. Data was processed using BIC dynamic light scattering software and CONTIN analysis.

Zeta-potentials were determined using Malvern Nano – ZS instrument.

Chromium and gold films were prepared using Edwards E306 A vacuum coater and plasma cleaning with Harrick Plasma Cleaner. Spin coating device used was home made. For film morphology and thickness characterization Veeco diCaliber atomic force microscope (AFM) and Nanofilm Ep3 Spectroscopic Imaging Ellipsometer were used.

SEM images were recorded with Hitachi S-4800 field emission Scanning Electron Microscope with 1kV acceleration voltage and current of 10 μA . Vitrified samples were observed using a Gatan 626 cryo-holder maintained at -180 °C in a FEI Tecnai F20 transmission electron microscope operated at 200 kV (Biocenter Finland National Cryo-TEM Facility, University of

Helsinki). The images were recorded with a Gatan US4000 CCD camera at a magnification of 68,000 \times and 3 μ m underfocus.

3.1.1 MATERIALS

1,4,5,8-Naphthalenetetracarboxylic acid 1,8-monoanhydride, fuming sulfuric acid containing 65 % of SO₃, Br₂ reagent grade, NaCN Puris grade, polyphosphoric acid (115 % on H₃PO₄ basis), NaCl reagent grade, N,N,N',N'',N''-pentamethyldiethylenetriamine, Cu(I)Br, Cu(II)Br₂, LiBr, 2-bromo-2-methylpropionic acid, 1,2,4,5-benzenetetramine tetrahydrochloride technical grade were purchased from Sigma-Aldrich. N-isopropylacrylamide was obtained from Acros Organics. DMF and TFH were HPLC grade and supplied by Chromanorm. d₃-MeNO₂ used in the preparation of NMR samples was supplied by Aldrich. D₂O and d₆-DMSO were supplied by Euriso-top. Silicagel 60, technical grade and KOH were supplied by Fluka. Alumina used was aluminum oxide supplied by Merck. Poly(ethylene oxide) monomethylether (PEO-MME) Mw 550 g/mol or 750 g/mol were obtained from Fluka and Mw 1900 g/mol and 2000 g/mol from Polysciences and Aldrich, respectively.

3.2 PREPARATION OF MONOMERS

3.2.1 Mono- and di-brominated NTCA

Bromination of 1,4,5,8-Naphthalenetetracarboxylic acid was performed in fuming sulphuric acid containing 65 % of SO₃. The reaction was carried out at room temperature and 40 °C and reaction time was 48 h. Depending on the reaction temperature and time NTCA can be mono- or dibrominated. In a typical monobromination 5.36 g (18.73 mmol) of 1,4,5,8-naphthalenetetracarboxylic acid 1,8-monoanhydride was slowly dissolved into 50 ml of fuming sulphuric acid at room temperature (22 °C). Vigorous magnetic stirring was used to limit the formation of large aggregates. 3 mg of I₂ and 3.3 g (20.7 mmol) of Br₂ were added. Reaction was continued for 48h at room temperature.

Dibrominated product was prepared by dissolving 5.36 g (18.73 mmol) of 1,4,5,8-naphthalenetetracarboxylic acid 1,8-monoanhydride in fuming sulphuric acid and adding 3 mg of I₂ and 3.3 g (20.7 mmol) of Br₂. Temperature was increased to 40 °C and the reaction continued for 48 h after which 1 ml of Br₂ was added and reaction continued for 24 h.

Both products were recovered by preparing an ice bath where 600 ml of crushed ice had been cooled to approximately -150 °C with liquid N₂. After cooling the reaction mixture was poured onto the ice very slowly and the ice was let to melt. The product was then recovered using suction filtration, washed repeatedly with water and dried under dynamic vacuum.

3.2.2 Synthesis of 2-cyano-1,4,5,8-naphthalenetetra-carboxylic acid

1.00 g (2.61 mmol) of 2-bromo-1,4,5,8-naphthalenetetracarboxylic acid was dissolved into 50 ml of DMF in a 100 ml flask equipped with magnetic stirring. 0.14 g (2.8 mmol) of NaCN was added. The color of the solution changed from light orange into black within 2 minutes. Temperature was adjusted to 50 °C and the reaction continued for 16 h. Unlike brominated NTCA the CN-derivative does not precipitate from acidic water and is poorly soluble in chlorinated solvents and ether, so following protocol was used for recovery. The volume of the reaction mixture was decreased to 30 ml using rotary evaporator and it was poured into a separation funnel having 100 ml of acidified brine (10 ml 1M HCl, 90 ml brine) and 100 ml of THF. The funnel was shaken vigorously at which point some NaCl precipitated. The aqueous phase was only lightly colored and the THF phase had turned almost completely black. Aqueous phase was discarded and the THF phase washed three times with 100 ml of acidic brine. The THF phase was recovered and the solvent evaporated which yielded 0.8 g of tar-like product still containing residual solvents.

3.2.3 Synthesis of tetramethyl 2,6-dibromonaphthalene-1,4,5,8-tetracarboxylate

12.36 g (100 mmol) of SOCl₂ was slowly dissolved into 100 ml of DMF. After 30 min 4.0 g (8.66 mmol) 2,6-dibromo-1,4,5,8-naphthalenetetracarboxylic acid was slowly added resulting in a red solution. After 40 min 10 ml of MeOH was added during 2 h to avoid excess heating and the reaction continued for 5 h. The volume of the solution was decreased to 40 ml using rotary evaporator and the solution was slowly poured into 400 ml of distilled water. The product was recovered as yellowish precipitate using suction filtration, washed repeatedly with water and dried under dynamic vacuum. The yield was 2.7 g (60 %)

3.2.4 Synthesis of tetramethyl 2-azido-6-bromonaphthalene-1,4,5,8-tetracarboxylate and tetramethyl 2,6-diazidonaphthalene-1,4,5,8-tetracarboxylate

2.00 g (3.86 mmol) of tetramethyl 2,6-dibromonaphthalene-1,4,5,8-tetracarboxylate was dissolved into 50 ml of DMF and 0.552 g (8.50 mmol) of NaN_3 was slowly added. Temperature was increased to 40 °C and the reaction continued for 16 h. The volume of the reaction mixture was then decreased to 30 ml using rotary evaporator and the reaction mixture was poured into 200 ml of distilled water. The precipitated product was collected using suction filtering, washed repeatedly with water and dried under dynamic vacuum. Yield was 0.8 g (47%).

3.2.5 Synthesis of 2-bromo-6-(4-butyl-1H-1,2,3-triazol-1-yl)naphthalene-1,4,5,8-tetracarboxylic acid (6) and 2,6-bis(4-butyl-1H-1,2,3-triazol-1-yl)naphthalene-1,4,5,8-tetracarboxylic acid (NTCA-1HE-Click)

0.80 g (1.81 mmol) of tetramethyl 2,6-diazidonaphthalene-1,4,5,8-tetracarboxylate, 0.656 g (8 mmol) of 1-hexyne and 0.315 g (1.82 mmol) of PMDETA were dissolved into 30 ml of DMF in a 50 ml round bottom flask. A stopcock was attached and the reaction mixture freeze-thawed for 3 times. 260 mg (1.8 mmol) of Cu(I)Br was added on the frozen sample after which the flask was purged with nitrogen three times while frozen and filled with nitrogen. The flask was heated to 50 °C in an oil bath and reaction continued for 16 h. The reaction mixture was poured into 200 ml of diethyl ether and washed 5 times with 0.1 M HCl and 3 times with distilled water. The ether fraction was collected and the ether removed with rotary evaporator. The product still containing the methyl ester groups was then dissolved in 30 ml of DMSO and 1 g of KOH and 5 ml of water were added. The reaction was continued at 50 °C for 48 h. The reaction mixture was cooled to RT, poured into 100 ml of 1 M aqueous HCl and extracted 5 times with 100 ml of diethyl ether. The ethereal fraction was then dried over anhydrous Na_2SO_4 and the ether removed with rotary evaporator to yield 0.52 g (52 %) of the product. $^1\text{H-NMR}$ of the product showed that despite long hydrolysis there still was on average 0.3 methyl ester groups per molecule.

3.2.6 Synthesis of 2,6-bis((2-ethylhexyl)amino)naphthalene-1,4,5,8-tetracarboxylic acid (NTCA-2EHA)

2.00 g (3.58 mmol) of 2,6-dibromo-1,4,5,8-naphthalenetetracarboxylic acid was added into 100 ml of DMSO at 50 °C which gave a deep red suspension. 1.46 g (26 mmol) of KOH was added and the mixture stirred for 1 h. 1.24 g (9.59 mmol) of 2-ethyl-1-hexylamine was added into the suspension and within 30 s the reaction mixture turned to clear red-yellowish solution. The reaction was continued for 18 h after which the solution was poured into 300 ml of H₂O. The product was collected as an orange precipitate using suction filtering, washed repeatedly with 0.1 M HCl solution followed by repeated washing with water. The product was dried under dynamic vacuum. Yield was 1.82 g (91 %).

3.3 PREPARATION OF THE POLYMERS

3.3.1 Preparation of poly(N-isopropyl acryl amide)

The general protocol for the preparation follows the syntheses described in [21] and was done as follows. N-isopropylacrylamide, bromo-2-methylpropionic acid, CuBr and CuBr₂ were dissolved in 200 ml of ion-exchanged water in a two necked flask with magnetic stirring at 0 °C. 1.5 times Me₆TREN needed was dissolved in 1.5 ml of ion-exchanged water in a vial and both the flask and the vial were nitrogen purged for 1 h. 1 ml of the Me₆TREN solution was removed from the vial using thoroughly nitrogen purged syringe and needle and injected in the monomer solution. Nitrogen flow in the flask was maintained throughout the reaction. Details of the individual reactions are summarized in table 1 of paper IV. The reaction was stopped after 90 min by opening the flask to ambient atmosphere and 20 ml of THF was added. The reaction mixture was poured in 1 L of THF and the solution passed through silica/alumina column to remove the copper. The solution was then concentrated to a volume of 100 ml using rotary evaporator and dialyzed against water for 4 days using dialysis tubes having MWCO of 3500 g/mol. After dialysis the solution was freeze-dried to recover the dry polymer. The PNIPAM having Mn of 2400 could not be dialyzed so it was precipitated from ion-exchanged water by heating, filtered out and re-dissolved followed by second precipitation and recovery by suction filtration after which the polymer was dried under dynamic vacuum.

3.3.2 Preparation of poly(benzimidazobenzophenanthrolines)

Predetermined amounts to match the desired BBL DP of 1,4,5,8-naphthalenetetracarboxylic acid 1,8-monoanhydride and 1,2,4,5-benzenetetramine tetrahydrochloride were weighed in a two necked round bottom flask and 50 g of polyphosphoric acid added. Nitrogen flow was adjusted and the flask heated to 100 °C at which point mechanical stirring was started. Evolution of HCl caused some foam formation and after the foaming had stopped the temperature was adjusted to 120 °C and the reaction continued for 16 h followed by 6 h at 180 °C.

The reaction temperature was decreased to 100 °C and the reaction mixture poured into 3 L of 1 M aqueous Na₂CO₃ solution under vigorous stirring. The product precipitated as flakes which were then suction filtered and washed repeatedly with water. The products were then either dried under dynamic vacuum or stored under water.

3.3.3 Poly(benzimidazobenzophenanthrolines) modified with bromine (BBL-Br)

0.392 g (1.02 mmol) of monobrominated NTCA and 0.300 g (1.02 mmol) of 1,2,4,5-benzenetetramine tetrahydrochloride were weighed in a flask and 40 g of polyphosphoric acid was added. The reaction mixture was heated to 100 °C under N₂ flow and mechanical stirring was started. After 2 h the temperature was increased to 120 °C and the reaction continued for 16 h. The reaction temperature was increased to 180 °C for 2 h after which it was decreased back to 120 °C. The hot reaction mixture was then slowly poured into Na₂CO₃ solution (65 g Na₂CO₃ in 3 L of distilled water). After 24 h the product had settled on the bottom so the excess liquid was discarded and the precipitate recovered using suction filtration, washed repeatedly with water and stored under water or dried under dynamic vacuum.

3.3.4 Poly(benzimidazobenzophenanthroline) modified with cyano group (BBL-CN)

0.400 g (0.99 mmol, corrected for solvent residues) of cyano modified NTCA and 0.290 g (0.99 mmol) of 1,2,4,5-benzenetetramine tetrahydrochloride were weighed in a flask and the reaction carried out as for the monobrominated BBL. After the product had settled on the bottom the excess liquid was poured out and the suspension containing the product moved into a dialysis tube and dialyzed against water for 48 h (4 * 3L). The dialyzed suspension was then freeze-dried.

3.3.5 Synthesis of BBL-1HE-Click

0.400 g (0.71 mmol) of NTCA-1HE-Click and 0.208 g (0.71 mmol) of BTA were weighed in a flask and 50 g of PPA was added. Nitrogen flow was adjusted in the flask, the temperature increased to 100 °C and mechanical stirring started. After the initial foaming had stopped the temperature was set to 120 °C for 18 h with vigorous (418 rpm) stirring followed by 2 h at 180 °C. Temperature was decreased to 120 °C and the reddish reaction mixture poured into aqueous Na₂CO₃ solution (60 g / 3 L). The initially black suspension was let to settle for 40 h after which a black precipitate had settled on the bottom. Excess liquid was poured off leaving 300 ml of suspension which was let to settle for another 48 h. After pouring off the clear liquid about 50 ml of black suspension was recovered, which was then dialyzed against water for 48 h (4*3 L) and freeze-dried. The yield was 0.350 g (85 %).

3.3.6 Synthesis of BBL-2EHA

0.486 g (0.87 mmol) of NTCA-2EHA and 0.248 g (0.87 mmol) of BTA were dissolved into 50 ml of m-cresol. Nitrogen flow and magnetic stirring were adjusted and the temperature was increased to 160 °C and the reaction continued for 18 h. The reaction mixture was cooled to room temperature and poured into 200 ml of MeOH at which point a black precipitate formed. The precipitate was collected with suction filtering, washed repeatedly with MeOH and water and dried under dynamic vacuum. The yield was 0.260 g (50 %).

3.3.7 Preparation of BBL-PEO block-copolymers

Predetermined amounts to match the desired BBL DP of 1,4,5,8-naphthalenetetracarboxylic acid 1,8-monoanhydride and 1,2,4,5-benzenetetramine tetrahydrochloride were weighed in a two necked round bottom flask and 50 g of polyphosphoric acid added. Nitrogen flow was adjusted and the flask heated to 100 °C at which point mechanical stirring was started. Evolution of HCl caused some foam formation and after the foaming had stopped the temperature was adjusted to 120 °C and the reaction continued for 16 h followed by 6 h at 180 °C. Temperature was decreased to 120 °C and predetermined amount, at least 4 times excess in respect to the theoretical amount of carboxylic acid chain ends, of poly(ethylene oxide) monomethylether added and the reaction continued for 18 h. The reaction temperature was decreased to 100 °C and the reaction mixture poured into 3 L of 1 M aqueous Na₂CO₃ solution under vigorous

stirring. Stirring was continued for 1 h after which the product was recovered as dark blue/black paste using suction filtration and washed repeatedly with water. In order to remove unreacted PEO the products were then dialyzed against water 3*4L in dialysis tubes having MWCO of 6-8 kD or 12-14 kD. The dialyzed products were stored as suspensions.

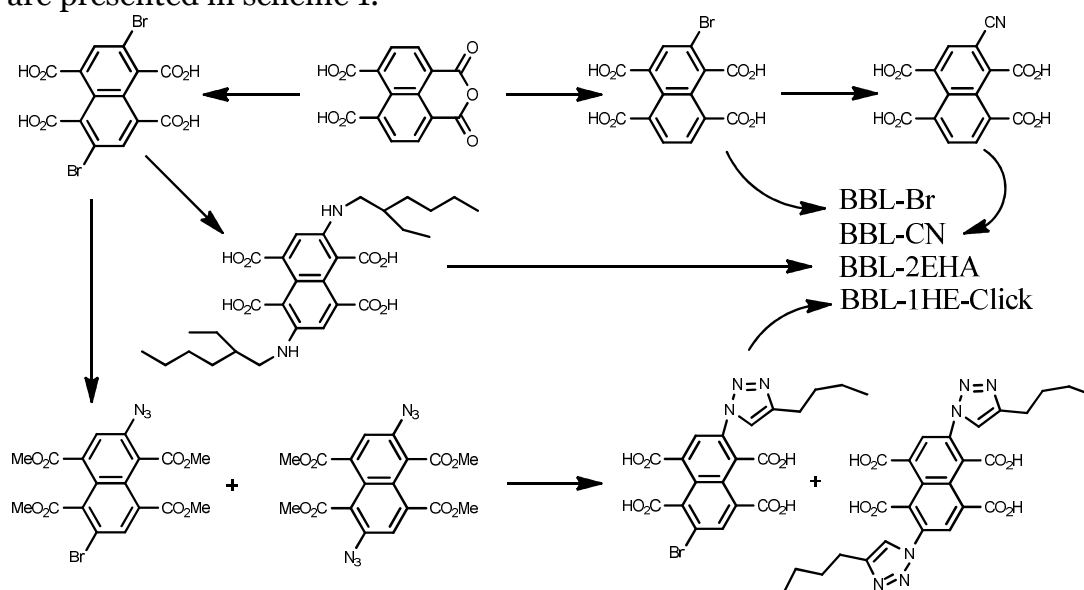
3.3.8 Preparation of BBL-PNIPAM block-copolymers

Predetermined amounts to match the target DP of the BBL block of 1,4,5,8-Naphthalenetetracarboxylic acid 1,8-monoanhydride and 1,2,4,5-benzenetetramine tetrahydrochloride were weighed in a 2-neck flask and 50 g of polyphosphoric acid added. Nitrogen flow was adjusted and the flask heated to 100 °C at which point mechanical stirring was started. After the foaming had stopped the temperature was increased to 120 °C and the reaction continued for 16 h. The reaction temperature was increased to 180 °C for 4 h and decreased back to 120 °C. At this point the PNIPAM was added and the reaction continued for 18 h. The reaction mixture was then poured into aqueous Na₂CO₃ solution (65 g in 3 L) under vigorous stirring. The copolymer settled over night onto the bottom and most of the liquid could be decanted out. The volume of the resulting dispersion was then decreased to 200 ml using rotary evaporator and dialyzed against water (4*3L) in MWCO 14-16k dialysis tubes. As the volume of the dispersion increased during the dialysis it was again decreased with rotary evaporator and the dialysis continued. After the dialysis the volume of the dispersions were decreased to 40-150 ml and the products stored as dispersions.

4 RESULTS AND DISCUSSION

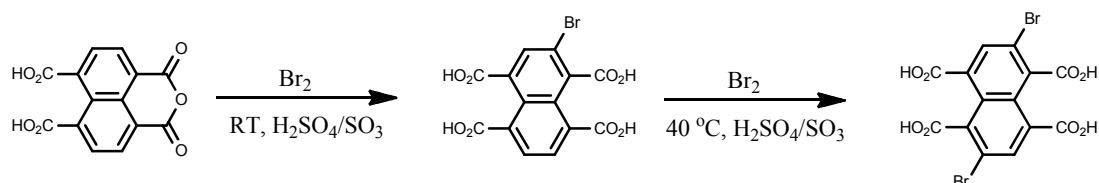
4.1 Synthesis of the monomers (paper III)

1,4,5,8-naphthalenetetracarboxylic acid was chosen to be modified because it is chemically robust and the bromination reaction is facile. As the reactions to replace aromatic bromine are well established four different derivatives were prepared and used as monomers. Simplified routes to each monomer are presented in scheme 1.



Scheme 1. Preparation and structures of the derivatized NTCAs.

1,4,5,8-naphthalenetetracarboxylic acid was mono- and dibrominated in fuming sulphuric acid according to the method by Piyakulawat et al. [74]. The extent of the bromination was dependent on the reaction time and temperature and the products could be recovered in good yields, the reactions are presented in scheme 2.



Scheme 2. Bromination of NTCA

The extent of bromination could be verified using proton NMR by comparing the relative integrals of the protons next to the brominated and un-brominated sites, figure 7.

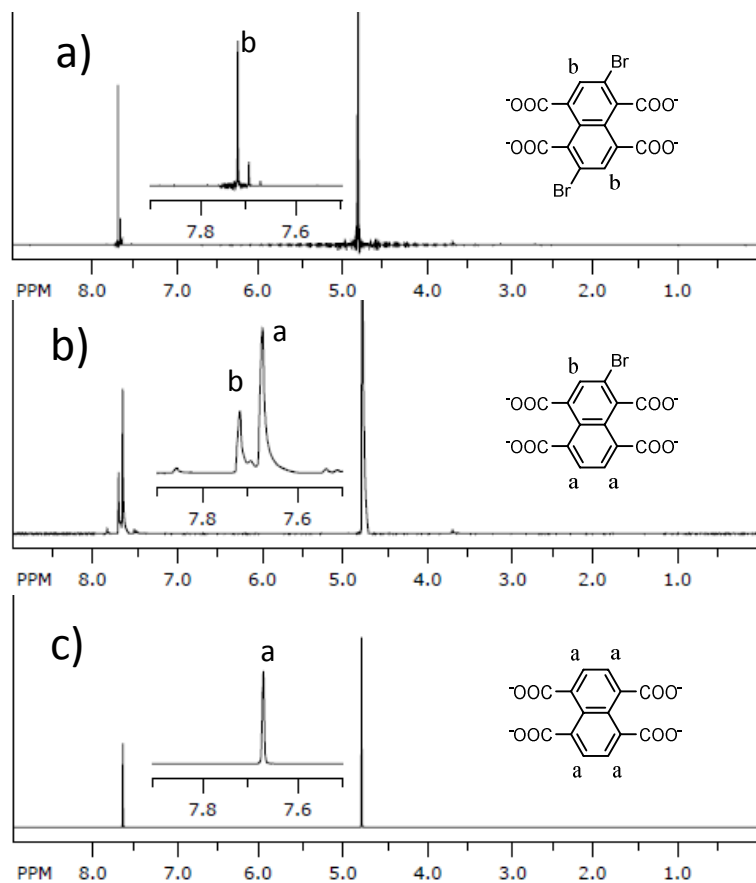


Figure 7. ^1H -spectra of NTCA (c), monobrominated NTCA (b) and dibrominated NTCA (a) recorded in D_2O / KOH.

The bromine could be replaced with a strong electrophile and at first cyanide ion was used in DMF. Addition of NaCN to a solution of brominated NTCA was accompanied by a fast color change from red to black and this was observed for mono- and di-substituted NTCA. The purification of the cyano modified NTCAs was not as straight forward as with the brominated ones as the products could not be precipitated in acidic water. Finally, the only practical way to recover the product was to extract it into THF from acidic brine and removing the solvent using rotary evaporator, which unfortunately leaves some residual solvents in the product. Attempt to recover NTCA-CN as pure product by drying it from DMF solution at 100 °C under dynamic vacuum for 16 h yielded black hard and solid material which according to ^1H -NMR still contained slightly over 30 % mol/mol of DMF. After the preliminary polymerizations using the cyano modified NTCAs as monomers it was found out that the products obtained using NTCA with two cyano moieties were completely insoluble in $\text{MeNO}_2/\text{AlCl}_3$ and could not be characterized by NMR. Therefore only preparation and purification of NTCA bearing one cyano group was pursued. The replacement of Br with CN was best observed in ^1H -spectrum as the signal from the proton next to the modified site changed from 7.60 ppm to 7.76 ppm (III, figure S7).

Substitution of the bromine with N_3 could be achieved using the same method and the product could be precipitated in acidic water. However, the product is still much more soluble in water than the starting material and only around 40 % of the product could be recovered. Furthermore, the free carboxylic acid complexes with both, the catalyst amine and copper in the subsequent click-reaction, making the purification of the product extremely difficult and lowering the yield to 5-10 %. Therefore the carboxylic acid groups were protected by turning them to methyl esters. It was not possible to duplicate the methylation reaction in H_2O using Me_2SO_4 as methylating agent as described by Christofi et al. [75]. The precipitated product was incompletely methylated and change of solvent to DMF led to side reactions. Instead, fast and almost complete methylation was achieved by reaction of the brominated NTCAs with thionylchloride followed by a reaction with MeOH. The extent of methylation was estimated using 1H -spectra (III, S3). Thus obtained tetramethyl 2,6-dibromonaphthalene-1,4,5,8-tetracarboxylate was then dissolved into DMF and reaction with NaN_3 followed by purification afforded the azide functionalized NTCA. Attachment of the azide was observed as an addition of a sharp new absorption band in IR-spectroscopy at 2123 cm^{-1} , typical for N_3 -group (III, S4). After the subsequent azide-alkyne Huisgen cycloaddition with 1-hexyne the band was found to disappear from the spectra indicating a complete reaction. Purification of the product was found to be tedious as the copper-amine-complex formed an insoluble precipitate trapping some of the product in it decreasing the yield to rather moderate 50 % even after multiple extraction steps. Hydrolysis of the esters using KOH and H_2O in DMSO, precipitation in H_2O and washing with dilute HCl afforded the product in acid form. 1H -NMR analysis of the reaction product is presented in figure 8.

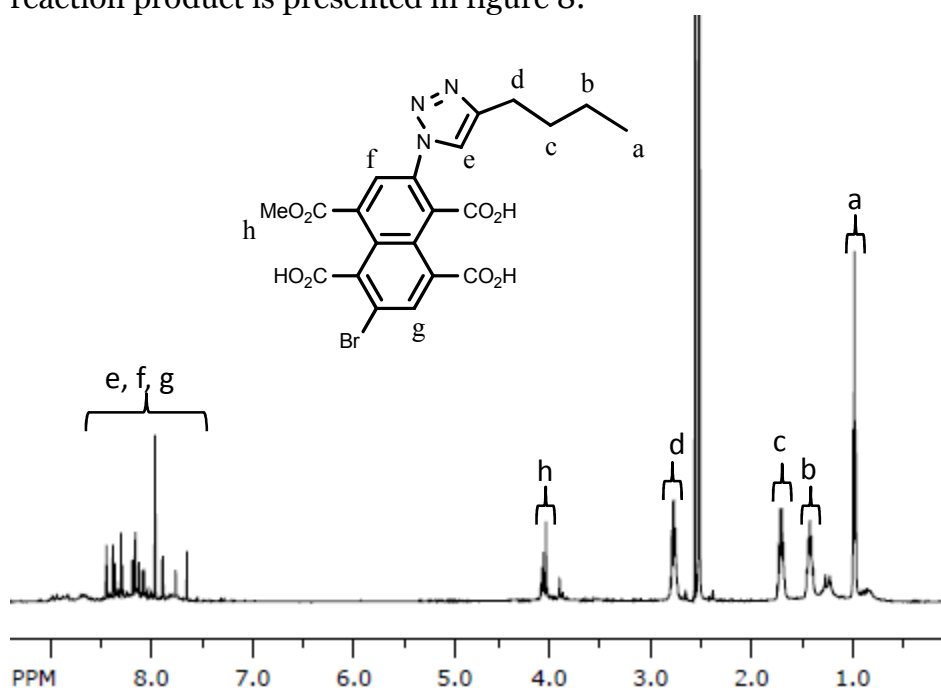


Figure 8. 1H -NMR-spectrum of the hydrolyzed click product in d_6 -DMSO

Signals of the aliphatic protons are clearly resolved in the ^1H -spectrum indicating the attachment of the 1-hexyne on the functionalized NTCA. Aromatic and triazole-ring protons are observed as a multiplet and differentiation between them could not be achieved. It was also discovered that the hydrolyzation reaction did not proceed to completion despite a rather long reaction time but on average 0.3 methyl groups per molecule. Despite the reaction between NTCA- Br_2 and NaN_3 seeming to be fast it was found not to go into completion. The relative areas of the integrals showed that only approximately 25 % of the product was in fact di-coupled and the rest 75 % was mono-coupled. Separation of the two products was considered to be unfeasible because of two reasons i) column chromatography resulted in significant losses of the product ii) the amount of the material was rather small. Using the mixture of the two products as a monomer would still work as a proof of concept and the mixture was used in the polymerization reaction.

Substitution of the bromine using 2-ethyl-1-hexylamine was achieved using very simple reaction between the reactants in DMSO using KOH as catalyst. NTCA- Br_2 as such is only slightly soluble in DMSO and the fast change of the suspension into clear solution upon addition of 2-ethyl-1-hexylamine indicates that the substitution of Br with an alkyl amine proceeds readily. Purification of the product is straight forward as pouring the reaction solution into excess water precipitates the product. Suction filtering and washing with dilute HCl and water afforded the product with a very good yield. ^1H -NMR was used to confirm that the reaction was successful and to check the degree of substitution, figure 9. Integration of the signal areas confirmed full disubstitution.

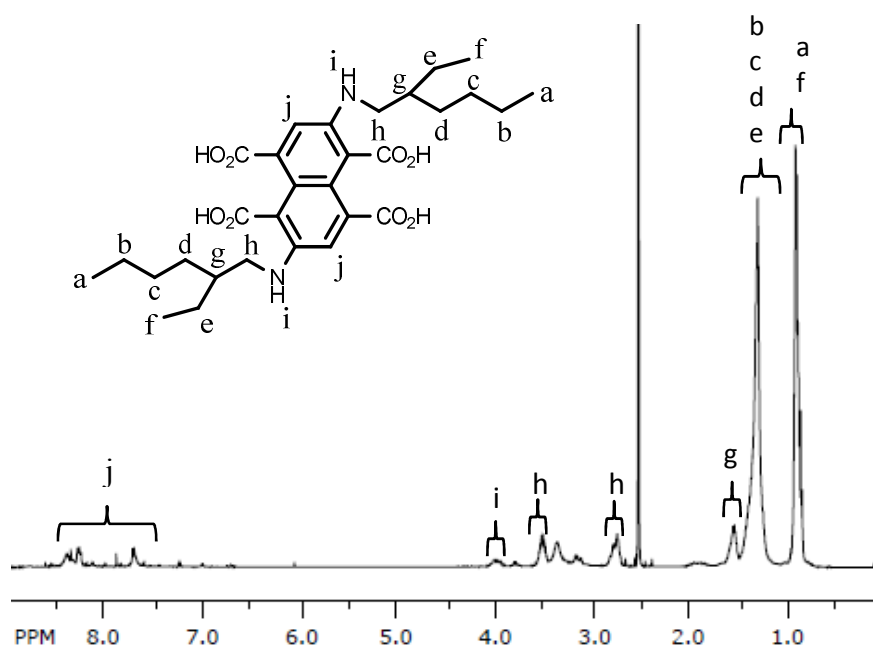


Figure 9. ^1H -NMR-spectrum of NTCA-2EHA in d_6 -DMSO

4.2 SYNTHESSES OF THE POLYMERS

4.2.1 Synthesis of BBL-PEOs (papers I and II)

Due to the high temperatures needed for the cyclization of the pre-polymer to BBL it was feasible to prepare the BBL-PEO block-copolymers by first synthesizing the BBL block of desired average length and end groups and then react it with PEO bearing just one functional group. Due to the abundance of hydroxyl-mono-functional PEOs of various molecular weights and the ease of preparing BBLs that have carboxyl groups at chain ends by using a slight excess of NTCA, the PEOs were attached using ester formation between the two polymers. The esterification reaction could be carried out in the same reaction medium as the preparation of the BBL itself and the recovery of the desired product by pouring the reaction mixture into aqueous Na_2CO_3 solution followed by dialysis removes all of the unreacted starting materials while preserving the product as a suspension. The size of the BBL block is denoted as an average value determined by the ratios of the monomers. The DP was varied between 5 and 20.

4.2.2 Synthesis of BBL-PNIPAM polymers (paper IV)

BBL-PNIPAM block-copolymers were synthesized in PPA using the same protocol which had been used previously to prepare BBL-PEOs with one modification of changing the excess monomer to BTA. Amine chain ends were in this case desired as ATRP provided a straight forward synthesis of PNIPAM with a carboxylic acid function at the chain end. One of the concerns about PNIPAM is the fact that it is an acrylate polymer bearing a hydrolysable bond in the side group of every repeating unit. However, as there should be very little of water available despite the otherwise harsh conditions only marginal degradation was expected, especially as the PNIPAM chain starts to thermally degrade at temperatures over 300 °C. Preliminary trials with high Mw PNIPAMs showed that little or none of the PNIPAM was incorporated in the BBL. This was probably because of very low concentration of the reactive PNIPAM chain ends per unit mass and therefore PNIPAMs having M_n of 10 000 g/mol or less were used in the rest of the substitution reactions.

4.2.3 Synthesis of BBL-Br (paper III)

BBLs bearing bromine on the naphthalenic unit were prepared in order to verify the polymerizability of the modified monomer. The reaction medium used was PPA as it was expected that brominated NTCAs are soluble in it. Monobrominated NTCA was found to form polymer using the same protocol as with unmodified BBL and after the cyclization step formed a deep red solution very similar to pristine BBL. After neutralization of the acid the product was observed to be black-grey instead of the black-blue of pristine or chain end modified BBL. Dibrominated NTCA was found to be un-polymerizable in PPA as it did not dissolve into the medium but stayed as separated particles on the surface. Increase of the temperature up to 140 °C or attempts to mechanically mix the substance in did not yield any improvement. The reaction was tried twice unsuccessfully and then discarded.

4.2.4 Synthesis of BBL-CN (paper III)

Cyano modified NTCAs always contained some residual solvents from the synthesis and the amounts of these were determined from ^1H -spectrum and taken into account when calculating the actual amount of the monomer in the synthesis. Cyano modified NTCAs were found to be soluble into PPA but BBLs prepared using the di-functionalized monomer were practically insoluble in $\text{AlCl}_3 / \text{MeNO}_2$. It is not known if this is an intrinsic property of the polymer or caused by cross-linking because of hydrolyzation of some cyano groups to carboxylic acids. However, as other known solvents are strong acids and would hydrolyze the cyano groups, characterization of the material was not possible and the research efforts were concentrated in BBL-CN having only one cyano-group per repeating unit.

4.2.5 Synthesis of BBL-1HE-Click (paper III)

NTCAs modified using azide-alkyne Huisgen cycloaddition were found to be soluble in PPA probably because of the polar triazole-ring, and the polycondensation reaction and the recovery of the product could be performed using the same protocol as previously for other modified BBLs. Due to the fact that the modified NTCA monomer was a mixture of mono- and di-coupled species some mismatch in stoichiometry was expected despite the best efforts to equimolarity. BBL-1HE-Click was found to aggregate into very small particles which separated slowly to the bottom of the beaker. The precipitated material was too fine to be separated using

suction filtering and was therefore dialyzed against water to remove any remaining impurities and then freeze-dried.

4.2.6 Synthesis of BBL-2EHA (paper III)

Polycondensation using NTCA-2EHA as one of the monomers was first tried twice in PPA but it was found to be insoluble and increase in temperature or mechanical mixing did not bring any improvement. Therefore m-cresol was tried as it has been proved a suitable reaction medium for other similar systems. Both of the monomers were found to be soluble in m-cresol and the polycondensation reaction was conducted at 160 °C. Based on previous experience with unmodified BBLs which turn slowly deep red at temperatures between 120-160 °C, indicating the proceeding of intrachain cyclization at temperatures lower than the much used 180 °C, it was approximated that 18 h at 160 °C should be sufficient for the polycondensation and the following cyclization. The product was precipitated in MeOH and was recovered using suction filtration as black powder. Despite being extensively washed with MeOH and water followed by drying under dynamic vacuum, some m-cresol was still retained in the dried product and this might be because it can penetrate into the structure between the chains, a property that has been used for secondary doping with poly(aniline) [76-81].

4.3 NMR characterization of BBLs (papers II, III and IV)

The NMR characterization of pristine BBL was done in d_3 -MeNO₂ / AlCl₃ – solution which can dissolve BBL in sufficient concentrations of 4-8 mg/mL for common experiments. FeCl₃ was first tested as Lewis acid but it caused broadening of proton signals to cover several ppms and was discarded. Addition of AlCl₃ shifted the signals several ppms upfield but the actual shape of the signals remained largely unaffected. The differences in the concentration of the Lewis acid in different samples resulted in slightly different downfield shifts but these were compensated by using the MeNO₂ as internal standard set always at 4.37 ppm. ¹H-spectrum of BBL shows 6 signals in the aromatic region (figure 10 a). However, the assignment of these cannot be done relying on the proton signals alone, as they differ significantly from the calculated values due to the coordination of the Lewis acid to carbonyl oxygens and imine nitrogens. HSQC-spectrum (figure 10 b) shows that 5 of these signals have correlation to a carbon while the signal at 8.22 ppm does not have a correlation and is caused probably by coordination of protons from HCl in the sample from hydrolysis of the AlCl₃ due to residual moisture. Protons of the BTA ring give three signals instead of two because of the possible trans- and cis-benzenoid conformations.

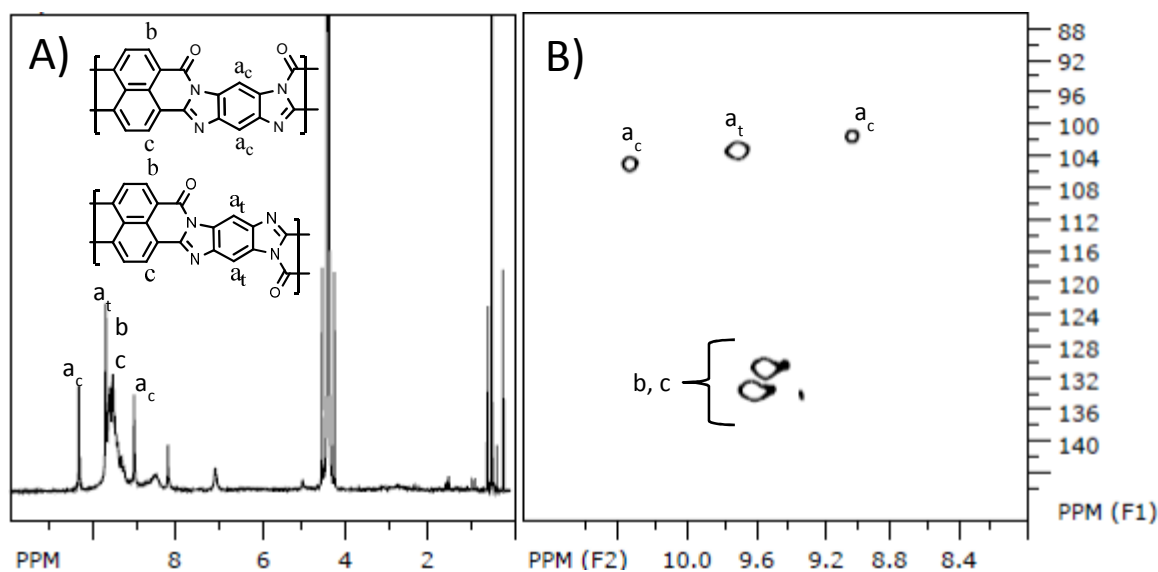


Figure 10. NMR-spectra of BBL in d_3 -MeNO₂/AlCl₃, A) ¹H-spectrum, B) HSQC-spectrum

¹H-NMR-spectra of BBL-PEOs were recorded in a mixture of D₂O and H₂O as the dried polymer could not be re-dispersed in D₂O. Spectra were also recorded in d_3 -MeNO₂ / AlCl₃ -solution. ¹H-spectra recorded in aqueous dispersions show essentially signals originating from PEO between 3.60-3.80 ppm. The absence of the proton signals of BBL was not surprising as it is expected to be embedded in particles. However, the spectra recorded in d_3 -MeNO₂ / AlCl₃ show essentially the signals of BBL protons and the spectrum is very similar to that of pristine BBL. It may be that the signals from PEO protons are masked under the solvent signal.

¹H-NMR-spectra of BBL-PNIPAMs were recorded in D₂O dispersions prepared using dried polymers. The poor re-dispersibility of the polymers limited severely the signal intensities except for BBL10-PNIPAM21 which seemed to re-disperse well. Reasonable spectra could be obtained from BBL10-PNIPAM79 and BBL10-PNIPAM21 (figure 11) which both showed significant degradation of the isopropyl acryl amide part of the PNIPAM chains. The degradation of these resulted also in splitting of the proton signals probably due hydrogen bonding between carboxylic acids of degraded parts and the amide of still intact groups. Integration of the signals and comparison of the areas of the methyl protons of the isopropyl units and the main chain CH₂ and CH units gave an estimation of the degradation, which was found to be 30-60 %.

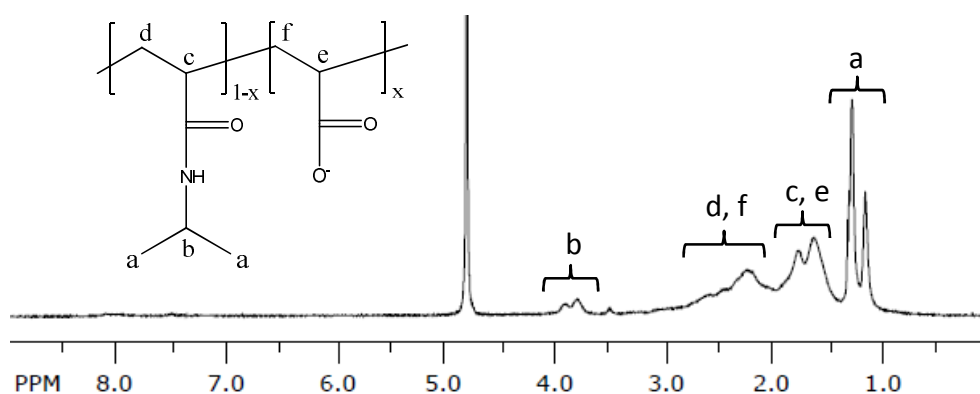


Figure 11. ¹H-NMR-spectrum of BBL10-PNIPAM21 in D₂O

NMR characterization of BBLs bearing Br or CN on the main chain was performed in d₃-MeNO₂ / AlCl₃ solution as well because these polymers have solubilities very similar to pristine BBL, although BBL-CN is the least soluble of the three. The ¹H spectra of both of the polymers (figure 12) are very similar and differ markedly from the spectra of pristine BBL. The well resolved three separate signals of the BTA protons cannot be observed anymore and the effect of the cis- and trans-benzenoid conformations is absent.

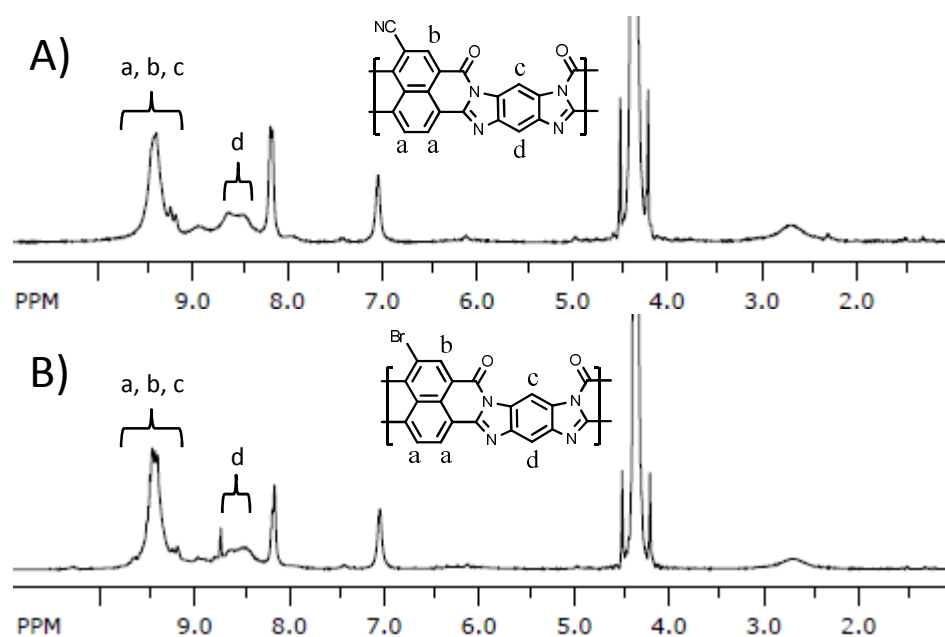


Figure 12. ¹H-spectrum of BBL-CN (A) and BBL-Br (B) in d₃-MeNO₂/AlCl₃

BBLs modified with side chains are sparingly soluble into DMSO which facilitated their NMR characterization in d₆-DMSO. The chemical shifts were expected to match the theoretical ones more closely as they would not be affected by coordination of a Lewis acid like in the other BBL samples. ¹H-spectrum (figure 13) of BBL-1HE-Click shows signals in the aliphatic and aromatic region. The signals are broadened which is typical for polymers but

makes the assignment challenging. Using data from HSQC spectrum it was possible to verify that the material contains aliphatic butane chains attached to the triazole-rings. Due the multiplicity of the signals one can assume that the side chains have thermally degraded to some extent and it would be useful to study the possibility to prepare the polymer in m-cresol which does not seem to degrade the side chains of BBL-2EHA. The aromatic signals are broadened to such an extent that they cover the region from 6.90 to 8.10 ppm. Because of the broadening no correlation signals were observed in the HSQC-spectrum and individual protons were not assigned. The signal intensities were limited by the solubility of BBL-1HE-Click in d_6 -DMSO at room temperature which was less than 2 mg/mL.

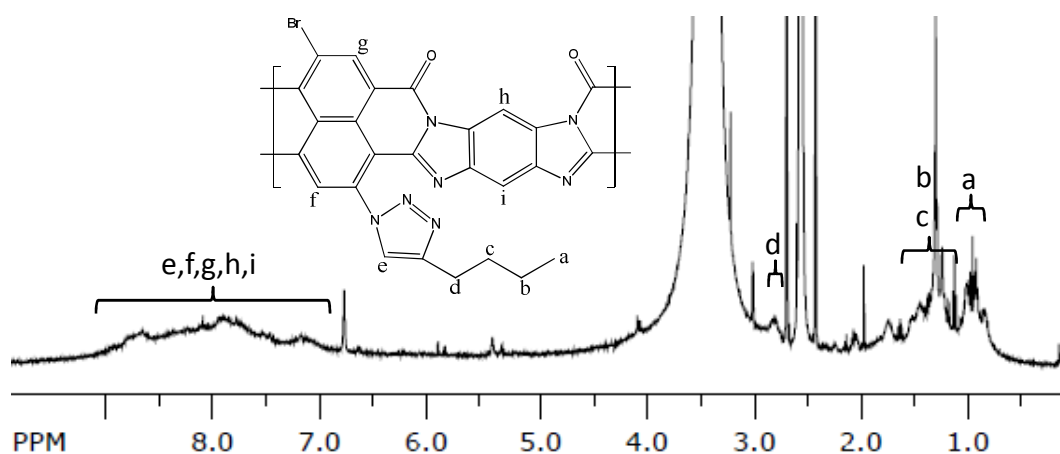


Figure 13. ^1H -NMR-spectrum of BBL-1HE-Click in d_6 -DMSO.

BBL-2EHA has solubility of 4-5 mg/mL in DMSO which facilitated better S/N-ratio in the NMR-spectra. ^1H -spectrum of the polymer shows signals of both, the aliphatic protons of the side chain and the aromatic protons of the BBL main chain (figure 14). ^1H -spectrum also shows signals from residual m-cresol which was not removed despite thorough drying of the material. The signals from the polymer are broadened but still allow for assignment using data from HSQC-spectrum (III, S13).

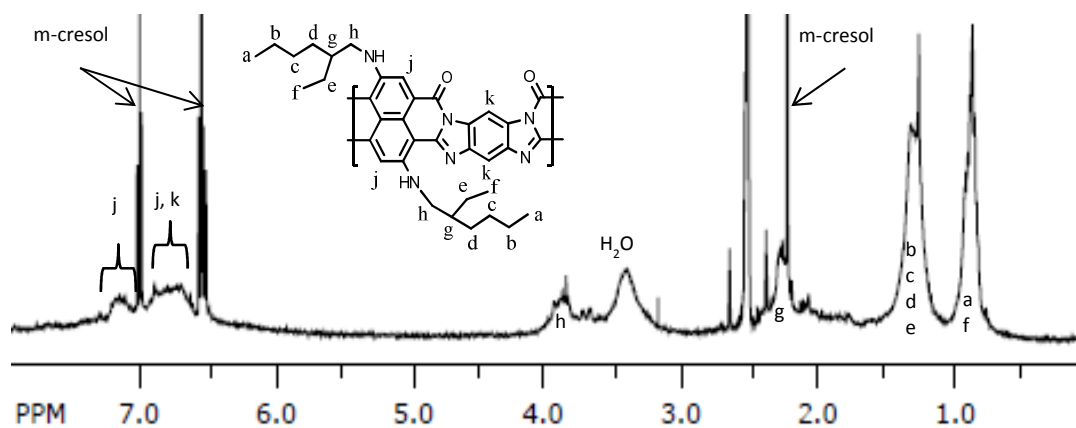


Figure 14. ^1H -NMR-spectrum of BBL-2EHA in d_6 -DMSO.

4.4 THERMOGRAVIMETRIC AND ELEMENTAL ANALYSIS OF BBL, BBL-PEO AND BBL-PNIPAM (PAPERS II AND IV)

Due to the poor solubility of BBL or BBLs modified with PEO or PNIPAM, the amount of the incorporated water soluble polymer could not be evaluated using $^1\text{H-NMR}$ or SEC. BBL is reportedly very stable thermally and this was also confirmed in this study as pristine BBL started to thermally degrade significantly at temperatures above 550 °C and retaining close to 95 % of the original mass at 600 °C. PEO starts to degrade around 300 °C and is practically completely degraded at 440 °C. PNIPAM follows rather similar degradation profile and is practically completely degraded at 450 °C. The apparently almost complete degradation of PEO and PNIPAM before the onset of BBL thermal degradation was used to evaluate their relative amounts in the block-copolymers. In general it was found that only a portion of all the reactive groups at the chain ends reacted with either PEO or PNIPAM reactive groups. The TGA determined mass fraction of PEO in BBL-PEOs was found to depend strongly on the M_w of PEO, ranging from 10 % with PEOs having DP of 12-17 to 15-20 % with PEOs having DP of 43-45, figure 15 A. BBL-PNIPAMs show much larger mass losses, up to 50 %, in the temperature range of 200-600 °C. Although the recorded mass losses for BBL-PNIPAMs were in some cases twice as high (16-49 %) when compared to BBL-PEOs, the chain end substitution was still far from complete.

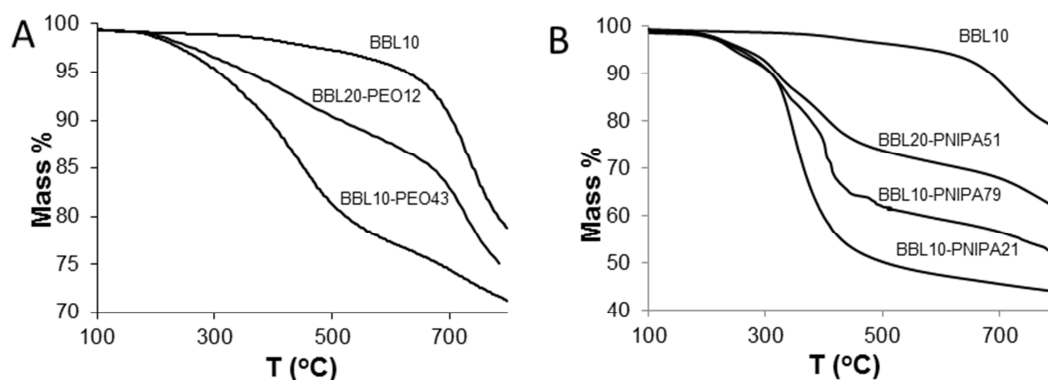


Figure 15. TGA curves of short BBL and A) selected BBL-PEOs, B) selected BBL-PNIPAMs. The numbers in the curve entries indicate the DP of the polymer blocks.

PEO is solely composed of hydrogen, carbon and oxygen whereas BBL has also nitrogen incorporated in its backbone. This makes it feasible to determine the relative amounts of each polymer using the ratio between carbon and nitrogen obtained using elemental analysis. The elemental analysis results are much closer to the theoretical values, which are calculated assuming 100 % substitution of the chain ends, the difference being usually less than 10 %. Elemental analysis could not be used in similar way to evaluate the relative ratios of BBL and PNIPAM due to the

degradation of the PNIPAM chain in the coupling of the polymers because this changes the C/N-ratio of PNIPAM.

4.5 PROPERTIES OF BBL AQUEOUS DISPERSIONS (PAPERS I, II AND IV)

BBL and its derivatives were found to be dispersible in water if prepared using the protocol described in the experimental section and stored in water. Drying of the material renders it indispersible in all cases but one.

4.5.1 BBL and BBL-PEO dispersions (paper I)

BBL-PEOs prepared and recovered as paste-like suspensions were found to be processable into aqueous dispersions by means of ultrasonication. These dispersions have long shelf-life, measured in years and BBL-PEO can be processed into even thin films by means of spin-coating. The origin of the good colloidal stability of BBL-PEOs was found to be a combined effect of electrostatic stabilization provided by unreacted carboxylic acids in the BBL chain and steric stabilization provided by the PEO chains. All the BBL-PEOs were found to form negatively charged particles in water and the measured ζ -potentials showed values varying between -51 and -32 mV. Titration of dilute BBL-PEO dispersions with NaCl solution precipitated the dispersed material quite readily at rather low salt concentrations of 1.5-4 mM. The high sensitivity to increased ionic strength indicates that the dispersibility of these polymers is mainly attributed to the electrostatic interactions and the PEO chains provide only modest additional stabilization. Tolerance to increased ionic strength could be slightly enhanced by addition of the well-known non-ionic surfactant Brij-98. However, when compared to dispersions prepared using unmodified BBL the BBL-PEOs show superior stability. In dispersions prepared using unmodified BBL the material precipitates readily at NaCl concentration of 1 mM and addition of surfactant does not enhance the colloidal stability. Furthermore, the dispersed BBL precipitates in a matter of days in contrast to the BBL-PEOs which remain dispersed for at least 6 years. The electronic properties of films prepared using BBL-PEO dispersions were found to have electronic properties similar to pristine BBL [82].

The original assumption was that the BBL-PEOs form compact particles composed of a BBL core and PEO corona as soon as they are transferred to the aqueous phase from PPA. The particle sizes and distributions were studied using dynamic light scattering and the results showed very broad particle size distributions ranging from some tens of nanometers to over one

micrometer and most of the particles were found to be in the range of 50-250 nm. While studying the properties of the BBL-PEO dispersions one sample having a concentration of 4 mg/ml was accidentally left to stand after ultrasonication and was found to have gelled in the vial after 4 days. This was completely unexpected and prompted for a study of rheological behavior of the dispersions in higher concentrations. All of the BBL and BBL-PEO dispersions were found to gelate after the particles were dispersed in water using ultrasonication in a concentration range of 1-5 mg/mL. The gelation process was observed using time sweep with small amplitude shear. After the pre-shear was ceased the storage modulus (G') started to increase almost immediately and surpassed the loss modulus (G'') by an order of magnitude, figure 16.

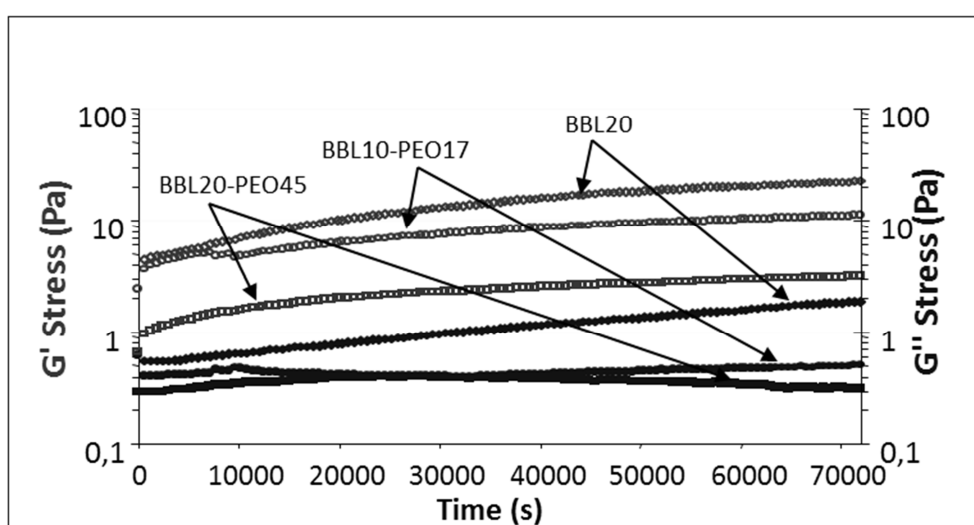


Figure 16. Storage (G' , open symbols) and loss (G'' , closed symbols) moduli of BBL and BBL-PEO polymers as a function of time using small amplitude oscillating shear. The numbers in polymer entries indicate the DP of the individual blocks. The polymer concentration was set to 2.00 mg/mL.

The force needed to break the gels was recorded in order to study the relationship of the toughness of the gel and the composition of the polymer. As the total polymer concentration is considered, the gels formed from pristine BBL dispersions are the toughest and the toughness increases slightly with molecular weight as shown for BBLs DP 10, 20 and high Mw (figure 17 B).

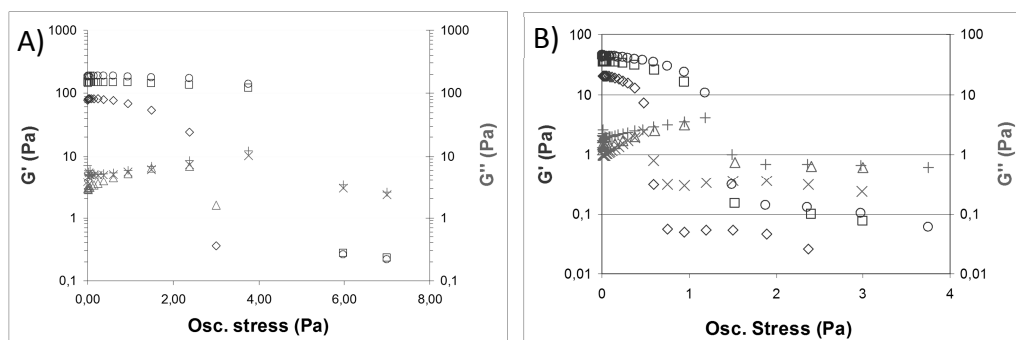


Figure 17. Storage (G') and loss (G'') moduli of BBL and BBL-PEO polymers as a function of increasing oscillating stress. A) BBL10-PEO17 (o,x), BBL20-PEO17 (□,+), and BBL20 (◇,△). B) BBL-high Mw(o,+), BBL20 (□,△), BBL10 (◇,×). BBL concentration was adjusted to 5.00 mg/mL for all samples.

The gelling behavior of the dispersions does not accommodate well a hypothesis of only compact particles and therefore the shape of the particles was studied using SEM and cryo-TEM. SEM images recorded of dried dilute dispersions of BBL and BBL-PEO showed grain-like particles and nano-wire type structures for both.

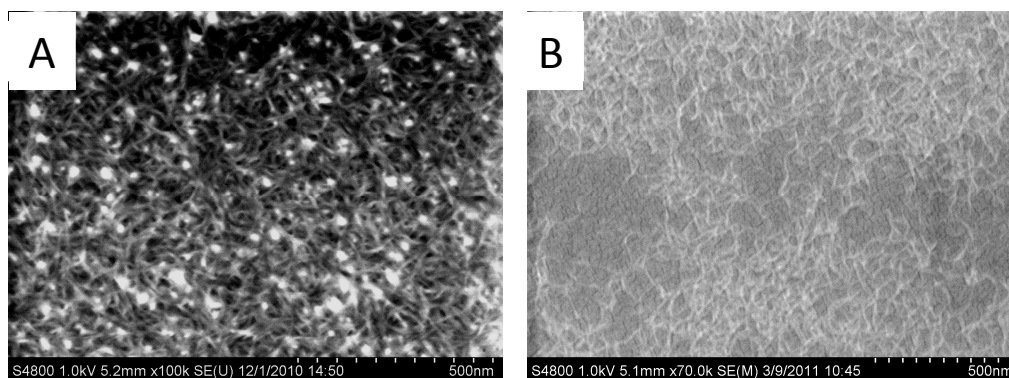


Figure 18. SEM images of dried samples: A) BBL20 B) BBL20-PEO10.

BBL has been previously shown to pack into nanobelt -type aggregates with lengths of 20-150 μm and widths of 200 nm - 1 μm [66]. It was difficult to identify the actual thickness and length of the nanowires based on SEM images alone, and cryo-TEM was employed so the nanowires would not be distorted by drying. Cryo-TEM imaging (figure 19) showed that the wires have an average thickness of approximately 3 nm and lengths exceeding one micrometer making the dimensions two orders of magnitude smaller than the previously reported ones. The assembly of BBL and BBL-PEOs into nano-wire type structures is unique to the preparation protocol developed in this work and such is not reported by others. It is feasible to assume that after the purification the nano-wires are packed in larger aggregates and ultrasonication breaks up these structures. The individual nano-wires then

form a looser network as soon as the agitation is stopped and this is observed as gelling.

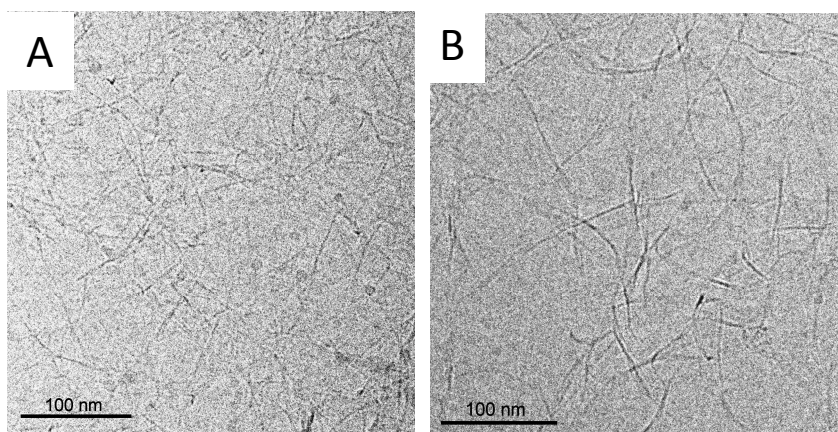


Figure 19. Cryo-TEM images of vitrified samples: A) BBL10-PEO17 B) BBL high M_w

4.5.2 AQUEOUS BBL-PNIPAM DISPERSIONS (PAPER IV)

BBL-PNIPAMs were distinctly divided into two categories after the purification. Polymers having BBL block sizes of over 10 repeating units precipitated during purification. Also, the material dispersed using ultrasonication at low concentrations ≥ 1.5 mg/mL, precipitated within 1h at room temperature. Polymers having BBL block sizes of 10 repeating units or less formed suspensions during purification and did not show any tendency to precipitate during extended storage time (1.5 years). BBL-PNIPAMs with BBL block of DP 10 differ markedly from dispersions prepared using BBL-PEOs as they do not show any tendency for gelation in the studied concentration range of 0.01-20 mg/mL. However, the originally indispersible BBL-PNIPAMs with BBL blocks of over 10 repeating units form stable gels upon sonication at higher concentrations (7-13 mg/ml). The gelling is most likely caused by formation of a network of nano-wires which then acts as a physical scaffold preventing the material to assemble into more compact structure and to precipitate. BBL4-PNIPAM21 showed some tendency for gelation after ultrasonication in a concentration of 22.4 mg/mL.

The LCST behavior of PNIPAM in the temperature range of 0-65 °C was lost upon preparation of the block copolymers. Furthermore, the dispersions of BBL-PNIPAMs were found to be highly tolerant to an increase in the ionic strength and depending on the composition of the polymer the dispersions were found to be stable in NaCl concentrations from 80 to 900 mM at room temperature. The thermal responsiveness of BBL4-PNIPAM21 and BBL10-PNIPAM-79 was regained by adjusting the ionic strength of the medium with NaCl to 80 and 90 mM, respectively. However, due to the high proportion of

acrylic acid units in the PNIPAM chain the temperature needed to induce the phase separation was 65 °C instead of the 32 °C typical for unmodified PNIPAM. Thermal responsiveness of BBL10-PNIPAM21 was regained by dispersing the polymer into buffer solution with pH 4.7, 4.6 and 4.5. The speed of the phase transition at 65 °C was dependent on the pH being faster in lower pH.

The two different dispersion behaviors, apparent indispersibility and gelling in higher concentrations of the BBL-PNIPAMs with BBL block size of over 10 repeating units and the readily forming stable dispersions of BBL-PNIPAMs with shorter BBL block leads one to a conclusion that upon increasing PNIPAM content the shape of the formed particles changes. Polymers with low PNIPAM content packs into nano-wires capable of forming physical networks in dispersed phase resembling the behavior of BBL-PEOs or pristine BBL. Polymers with higher (over 35 mass %) PNIPAM content packs in more compact particles that do not form networks.

4.6 OPTICAL PROPERTIES OF BBLs

Optical properties of BBL and BBL derivatives were studied using UV-Vis spectrometry. Measurements were conducted preferably in neutral solvents but as many of the prepared materials are truly soluble in MeSO₃H spectra of all of the BBLs were recorded also in it to make them more comparable. It was observed that aqueous dispersions of BBLs are not fluorescent under illumination of UV light at 366 nm but solutions prepared in MeSO₃H show red-orange fluorescence. Organosoluble BBLs show orange-green fluorescence and some solvatochromatism in DMSO and NMP. This however, was not studied further. P-doped BBL has been reported to emit around 590 nm under UV illumination [83].

4.6.1 UV-Vis-spectrometry of aqueous BBL dispersions (papers I, II, III and IV)

The recorded UV-Vis spectra of BBL, BBL-PEO and BBL-PNIPAM dispersions all show strong absorptions in the visible region and are deep-blue in color. They show a broad absorption maximum at approximately 570 nm assigned to π - π^* -transition and a narrower maximum at 350 nm assigned to n - π^* -transition. The relative intensities of the two absorption maxima vary and the n - π^* -absorption is clearly more intense for the BBLs modified with PEO when compared to unmodified BBL. Also, the relative intensity of the absorption at 350 nm increases as the molecular weight of the PEO increases and this can be attributed to higher mass fraction of PEO

in the block-copolymer. There was no significant red or blue shift in the absorption maximum at 570 nm and the actual values varied from 568 to 575 nm without correlation to the PEO Mw or its mass fraction. UV-vis spectra of BBL and several BBL-PEOs are presented in figure 20.

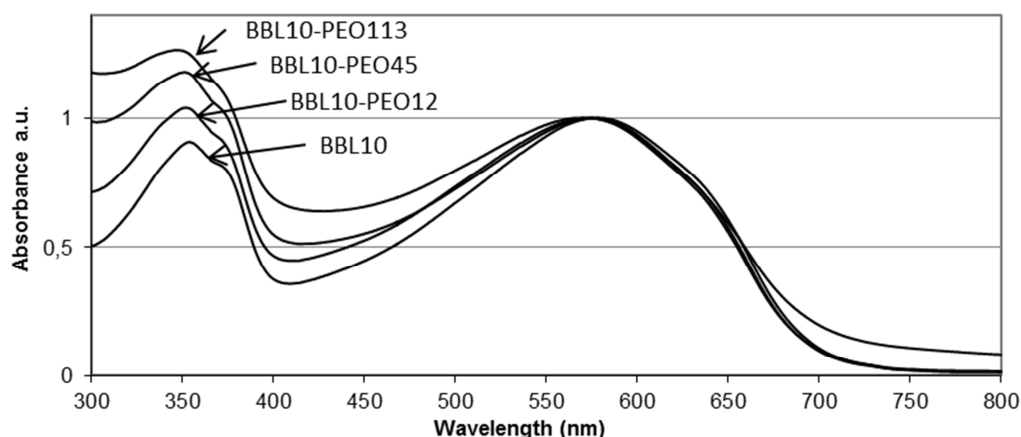


Figure 20. UV-vis-spectra of BBL and BBL-PEOs in aqueous dispersion. The numbers indicate the DP of different polymer blocks.

The relative intensities of the two absorption maxima varies and the $n-\pi^*$ -absorption is clearly more intense for the BBLs modified with PEO and the relative intensity of $\pi-\pi^*$ -absorption is more intense with unmodified BBL dispersions. This can be explained with a change in the packing of the individual chains to less ordered structure when the BBL chain ends become more crowded. When the spectra of BBLs differing only in M_w are recorded the curves overlap practically completely so it is unlikely that the changes in the spectra would be a result of slight differences in the BBL molecular weight. As the BBL block is formed prior to the attachment of the second polymer, it is highly unlikely that the chemical structure of BBL would be changed. BBL-PNIPAMs that have low PNIPAM fraction and do not form stable dispersions have UV-vis-spectra very similar to that of unmodified BBL with only a slight increase in the relative intensity of the absorption at 350 nm. The well dispersible BBL-PNIPAMs show more complicated spectra and there is a clear hypsochromic shift of the $\pi-\pi^*$ -transition maximum from 575 nm to 550 nm as the proportion of PNIPAM increases, figure 21. Also, a new shoulder on the $n-\pi^*$ -transition maximum starts to form at around 400 nm. These changes in the absorbance coincide with the changes in dispersibility and indicate changes in the packing of BBL in the particles.

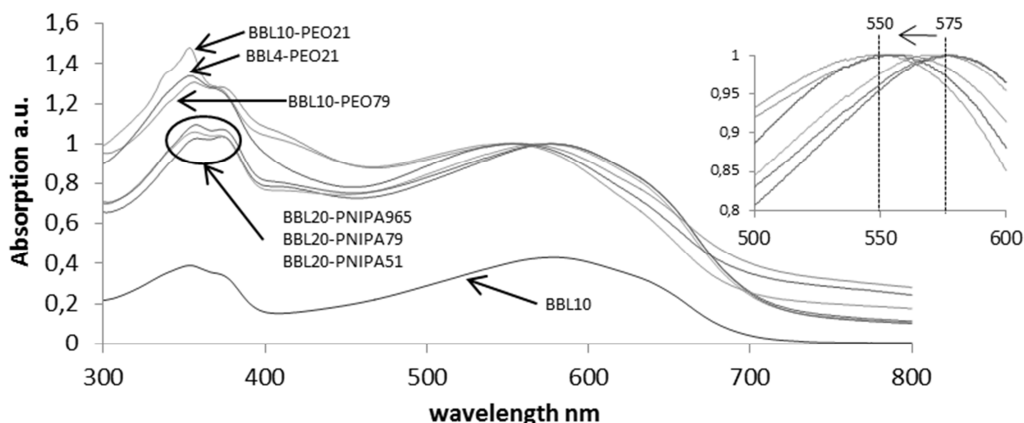


Figure 21. UV-vis-spectra of aqueous BBL and BBL-PNIPAM dispersions. The inset shows the shift in the π - π^* -absorption as enlargement. The numbers indicate the DP of different polymer blocks.

Of the main chain modified BBLs, BBL-Br and BBL-CN could be dispersed in water and their UV-Vis-spectra were recorded. BBL-Br does not have the deep-blue color but is graphite gray. The π - π^* -absorption maximum is hypsochromically shifted at 527 nm and its relative intensity to n - π^* -absorption is greatly reduced. The onset of absorption could not be reliably determined as it shows a steady increase in intensity from 1100 nm, which is the upper limit of the instrument, to 527 nm. BBL-CN dispersion has brown-yellow color and a clear π - π^* -absorption maximum cannot be clearly determined while the n - π^* -absorption maximum is blue-shifted to 323 nm.

4.6.2 UV-Vis-spectrometry of BBL-1HE-Click and BBL-2EHA in DMSO (paper III)

BBL-1HE-Click shows π - π^* -absorption maximum at 421 nm which is significantly blue-shifted in comparison to BBLs which are either unmodified or substituted at the chain ends. The onset of absorption is shifted to 537 nm. Also, the n - π^* -absorption maximum is shifted below 300 nm. BBL-2EHA shows less changes, the n - π^* -absorption maximum is hypsochromically shifted to 470 nm but the onset of absorption is still at rather long wavelengths at 781 nm. The π - π^* -absorption maximum is shifted below 300 nm as with BBL-1HE-Click.

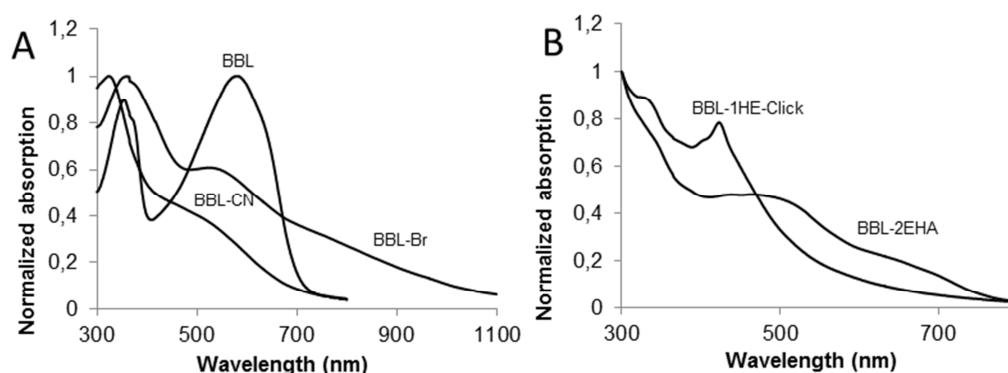


Figure 22. UV-Vis-spectra of A) BBL, BBL-CN and BBL-Br recorded in aqueous dispersion B) BBL-1HE-Click and BBL-2EHA recorded in DMSO

4.6.3 UV-Vis-spectrometry of BBL and BBL-derivatives in MeSO₃H

Dissolving BBLs in MeSO₃H changes the electronic structure of the material as the carboxylic oxygens and imine nitrogens are protonated by the acid and this is immediately observed as a color change to red. The π - π^* -absorption maximum of pristine BBL is shifted to 543 nm and a new absorption is observed at 379 nm along absorptions at 335 and 315 nm. BBL-Br and BBL-CN both show hypsochromic shifts of the π - π^* -absorption maximum to 468 and 475 nm, respectively. For both of these polymers the n- π^* -absorption maximum is shifted below 300 nm. BBL-1HE-Click shows slightly smaller blue-shift as the π - π^* -absorption maximum is shifted to 510 nm. BBL-2EHA shows strong absorption throughout the scanned range of wavelengths 300-800 nm and the absorption grows in intensity towards shorter wavelengths. The π - π^* -absorption maximum can be observed at 500 nm. For both, BBL-1HE-Click and BBL-2EHA the intensity of absorption is very high below 500 nm growing in intensity toward 300 nm.

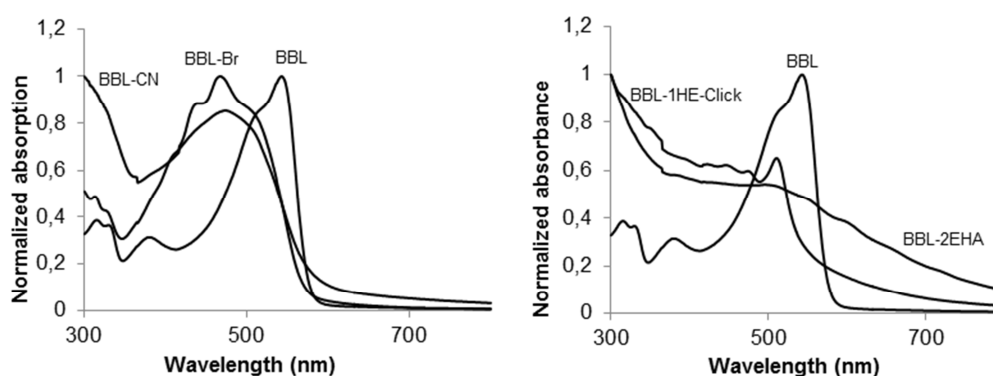


Figure 23. UV-Vis-spectra recorded in MeSO₃H. A) BBL, BBL-Br and BBL-CN. B) BBL, BBL-1HE-Click and BBL-2EHA.

5 CONCLUSIONS

The solution processability of poly(benzimidazobenzophenanthroline) has been improved using two approaches: i) preparation of block-copolymers by substituting the chain ends of BBL with another polymer ii) attaching alkyl side chains on one of the monomers. The modification of the monomer was shown to have an effect to the band gap of the polymer.

Short or oligomeric BBL has been prepared and the stoichiometry of the starting materials used in such a way that the BBL has desired functional groups, either carboxylic acid or an amine, at the chain ends. Addition of either monofunctional PEO or PNIPAM into the reaction mixture then leads to a partial substitution of the BBL chain ends with the respective polymer. PEO did not show any indication of degradation when exposed to the harsh conditions in the coupling reaction but the side groups of PNIPAM degraded significantly. BBL-PEO and BBL-PNIPAM could be processed into aqueous dispersions using ultrasonication and the dispersions have good colloidal stability. Also pristine BBL could be processed into an aqueous dispersion but it has poor colloidal stability and the dispersed material was shown to precipitate in a matter of days. BBL and BBL-PEOs were found to form gels when sonicated at higher concentrations and the origin for this was shown to be the packing of the polymers into nanowires which then form a physical network. BBL-PNIPAMs form gels upon sonication in higher concentrations if the fraction of PNIPAM is low but as the PNIPAM content is increased the gelling behavior is lost. The origin of the colloidal stability of BBL-PEO and BBL-PNIPAM was shown to be mainly the electrostatic stabilization. With BBL-PEOs this can be easily disrupted by increasing the ionic strength as the electrostatic stabilization is caused by the non-reacted BBL chain ends. However, due to the charges introduced into PNIPAM upon hydrolysis of some of the isopropylamide side groups, BBL-PNIPAMs are colloiddally much more tolerant to the increase in the ionic strength as there are significantly more of charged groups. The thermal responsiveness of the PNIPAM was lost in neutral media but could be regained upon increasing the ionic strength or adjusting the pH.

Bromination of NTCA, which is one of the monomers used to prepare BBL, provided a good starting point for its modification through various aromatic substitution reactions. Bromine was successfully replaced with 2-ethyl-1-hexylamine yielding alkyl modified NTCA in a 2-step reaction. Substitution of bromine was also achieved with azide which was then used in an azide-alkyne cycloaddition reaction to introduce an alkyl side group. These monomers were then used to prepare modified BBLs. Both of the BBLs bearing the bulky side groups were found to be slightly soluble in NMP and

conclusions

DMSO, the BBL having the 2-ethyl-1-hexylamine groups exhibiting higher solubility of the two. A benefit of the main chain derivatization approach is the possibility to change the electronic levels of the polymer and the UV-vis-spectra of the prepared polymers confirm this. Furthermore, it was found possible to use monobrominated NTCA and NTCA where the bromine was replaced with cyano group as monomers which give wider future possibilities for BBL derivatization.

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