2-Isopropenyl-2-oxazoline: A Versatile Monomer for Functionalization of Polymers Obtained via RAFT

Christine Weber,†,‡,§ Toni Neuwirth,† Kristian Kempe,†,‡ Bengi Ozkahraman,⊥ Emel Tamahkar,⊥ Humeyra Mert,⊥ C. Remzi Becer,†,‡,§∥ and Ulrich S. Schubert†

†Laboratory of Organic and Macromolecular Chemistry (IOMC), Friedrich-Schiller-University Jena, Humboldtstrasse 10, 07743, Jena, Germany
‡Jena Center for Soft Matter (JCSM), Friedrich-Schiller-University Jena, Humboldtstrasse 10, 07743, Jena, Germany
§Department of Chemical Engineering, Hitit University, 19030, Corum, Turkey
⊥Department of Chemistry, University of Warwick, CV4 7AL, Coventry, U.K.

Supporting Information

ABSTRACT: 2-Isopropenyl-2-oxazoline (iPOx) was polymerized for the first time via a controlled radical polymerization technique. Reversible addition–fragmentation chain transfer (RAFT) polymerization utilizing a dithiobenzoate-based chain transfer agent was employed to form a backbone that is highly reactive toward thiols and acids. Moreover, the statistical copolymerization of iPOx with methyl methacrylate (MMA) and N-iso-propylacrylamide (NiPam) was investigated resulting in two copolymer series with iPOx content varying from 100% to 13% (PDI = 1.37 to 1.21). The P(iPOx-stat-NiPam) copolymers displayed thermo-responsive behavior in water as well as phosphate buffered saline at higher temperatures in comparison to homopolymers of NiPam due to the hydrophilicity of the introduced iPOx moieties (Tc = 25 to 75 °C). Furthermore, iPOx-based (co)polymers were functionalized by polymer analogous addition reactions with thiophenol, benzoic acid and 4-azidobenzoic acid in high conversions (74−100%). The latter adduct represented a suitable building block for the synthesis of a graft copolymer consisting of a PMMA backbone and poly(2-ethyl-2-oxazoline) (PEtOx) side chains via copper-catalyzed azide–alkyne cycloaddition (CuAAC) of PEtOx with alkylene terminus.

INTRODUCTION

2-Oxazolines are well-known in polymer chemistry for their ability to undergo a living cationic ring-opening polymerization to yield well-defined polymers for use in biomedical applications.1−8 However, one might be less aware of the fact that the 2-oxazoline ring is also capable of addition reactions with a wide range of nucleophiles, such as carboxylic acids or thiols.9 These reactions have been exploited for polyaddition reactions of bis-oxazolines and dicarboxylic acids yielding polyesteramides.10−13 In addition, the 2-oxazoline ring provides a versatile tool for postpolymerization functionalization when it is connected in a pendant fashion to a polymer backbone. Such a structure can be obtained by the polymerization of 2-isopropenyl-2-oxazoline (iPOx), a commercially available monomer, via its vinyl moity. This polymerization can be performed under either anionic14 or free radical15 polymerization conditions. On the other hand, attempts to polymerize iPOx cationically via its oxazoline moiety resulted only in ill-defined oligomeric products.16 It was already demonstrated that the pendant oxazoline ring can be readily used for further modification of the free radically polymerized P/iPOx by attack of acids or thiols, even in aqueous solution.16 More recently, Jerca et al. reported the functionalization of statistical copolymers of iPOx and methyl methacrylate (MMA) with a carbosylic acid functionalized azo dye.17,18 In addition, MMA/iPOx copolymers are commercially available as water-soluble cross-linking agents for carboxylic acid containing polymers.

Nowadays, controlled radical polymerization (CRP) techniques,19−21 such as atom transfer polymerization,22 nitroxide mediated polymerization23 or reversible addition−fragmentation chain transfer (RAFT) polymerization24,25 are widely applied for the synthesis of well-defined polymers from a large number of vinylic monomers, such as acrylates, acrylamides, methacrylamides, methacrylates or vinylesters. One major advantage of these polymerization techniques is the utilization of monomers and solvents without extensive purification procedures as well as the good tolerance against other functional moieties, compared to ionic polymerizations. In addition, the utilization of CRP and various click reactions26−29 enables the engineering of advanced polymer structures, such as...
block or graft copolymers, or the copolymerization with other monomers providing further interesting properties, such as thermostresponsivenes. However, to the best of our knowledge, the CRP of iPox has not been reported up to now, even though the oxazoline moiety should enable access to a range of interesting polymers via polymer analogous reactions when using a well-defined PiPox as a backbone.

In this contribution, we present the homo- and statistical copolymerization of iPox utilizing the RAFT polymerization technique (Scheme 1). To the best of our knowledge, this is the first report on a statistical copolymerization of N-isopropylacrylamide (NiPam) and iPox. Moreover, we have investigated the thermostresponsive behavior of the obtained polymers. Furthermore, selected polymers were subsequently functionalized with benzoic acid and thiophenol as model compounds to present the versatility of the addition reaction. Last but not least, 4-azidobenzoic acid was reacted as precursor material for the synthesis of graft copolymers via “click” chemistry.

**EXPERIMENTAL SECTION**

**Materials.** The monomers iPox (99%), methyl methacrylate (MMA, 99%) and N-isopropylacrylamide (NiPam, 97%) were purchased from Aldrich. MMA was destabilized with inhibitor remover (Aldrich) prior to use. 2,2’-Azobis(2-methylpropionitrile) (98%, Acros, AIBN) was recrystallized from hexane and the chain transfer agent 2-cyanopropyl dithiobenzoate (CPDB, 97%) was obtained from Aldrich. Benzoic acid (99.5%) was purchased from Sigma-Aldrich, 4-azidobenzoic acid (99%) from ABCR, and thiophenol (98%), DMF (99.5%), as well as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 99%) from Fluka. Copper(I) iodide (Cul, 99.5%) was purchased from Aldrich. Poly(2-ethyl-2-oxazoline) (PEtOx-TB) was prepared according to a previously published procedure. Preparative size exclusion chromatography was performed using BioBeads-SX1 from BioRad with THF as eluent. For the cloud point measurements, deionized water and phosphate buffered saline 10X concentrate (Aldrich) were used. All other chemicals and solvents were obtained from common commercial sources and used without further purification, unless otherwise noted.

**Instrumentation.** $^1$H NMR spectra were recorded in CDCl$_3$ or CD$_3$OD on a Bruker Avance 300 MHz using the residual solvent resonance as an internal standard. Size exclusion chromatography (SEC) was measured on a Shimadzu system equipped with a SCL-10A system controller, a LC-10AD pump, a RID-10A refractive index detector using a solvent mixture containing chloroform, triethylamine, and isopropanol (94:4:2) at a flow rate of 1 mL min$^{-1}$ on a PSS-SDV-linear M $\times$ 5 $\mu$m column at 40 °C. The system was calibrated with PMMA (2–88 kDa) standards. For polymers containing secondary amides, a different SEC system was used. This system is equipped with a SCL-10A system controller, a LC-10AD pump, a RID-10A refractive index detector, and both a PSS Gran30 and a PSS Gran1000 column in series, whereby N,N-dimethylacetamide with 2.1 g L$^{-1}$ of LiCl was applied as an eluent at 1 mL min$^{-1}$ flow rate and the column oven was set to 60 °C. GC measurements were performed on a Shimadzu GC-2010 equipped with a Restek Rtx-5 column, a FID detector and a PAL autosampler. IR spectra were recorded on an Affinity-1 Fourier transform infrared spectrophotometer from Shimadzu.

For the measurement of the matrix-assisted laser desorption/ ionization (MALDI) mass spectra an UltixfleIII TOF/TOF (Bruker Daltonics, Bremen, Germany) was used. The instrument was equipped with a Nd:YAG laser and a collision cell. All spectra were measured in the positive reflector or linear mode. The instrument was calibrated prior to each measurement with an external PMMA standard from PSS Polymer Standards Services GmbH (Mainz, Germany). Electrospray ionization time-of-flight mass spectrometry (ESI TOF MS) measurements were performed with a micrOTOF (Bruker Daltonics) mass spectrometer equipped with an automatic syringe pump, which is supplied from KD Scientific for sample injection. The mass spectrometer was operating in the positive ion mode. The standard electrospray ion source was used to generate the ions. The ESI TOF MS instrument was calibrated in the m/z range from 50 to 3000 g mol$^{-1}$ using an internal calibration standard (Tunemix solution), which was supplied from Agilent. Data were processed via Bruker Data Analysis software version 4.0. Cloud point temperatures ($T_{cp}$) were determined using a Crystal 16 from Avantium Technologies being connected to a chiller (Julabo FP 40) at a wavelength of 500 nm and a heating ramp of 1 K min$^{-1}$. The concentration of the polymer was kept constant at 5 mg mL$^{-1}$, and $T_{cp}$ values are reported from 50% transmittance in the second heating cycle.

**Synthesis.** Kinetic Studies RAFT Polymerization. iPox (1.5 g, 13.5 mmol) was dissolved in 5.2 mL toluene and a solution of 11.1 mg (0.067 mmol) AIBN in toluene as well as a solution of 59.7 mg (0.27 mmol) CPDB in toluene were added. The concentration of the monomer was 2 mol L$^{-1}$ and the ratio of [iPox]:[CPDB]:[AIBN] was 50:1:0.25. Subsequently, the mixture was degassed with a gentle flow of nitrogen for 30 min and divided over 7 separate vials that were

<table>
<thead>
<tr>
<th>Table 1. Characterization Data of Statistical Copolymers of iPox with MMA and NiPam</th>
</tr>
</thead>
<tbody>
<tr>
<td>comonomer type (M)</td>
</tr>
<tr>
<td>-------------------</td>
</tr>
<tr>
<td>P1</td>
</tr>
<tr>
<td>P2</td>
</tr>
<tr>
<td>P3</td>
</tr>
<tr>
<td>P4</td>
</tr>
<tr>
<td>P5</td>
</tr>
<tr>
<td>P6</td>
</tr>
<tr>
<td>P7</td>
</tr>
<tr>
<td>P8</td>
</tr>
<tr>
<td>P9</td>
</tr>
<tr>
<td>P10</td>
</tr>
<tr>
<td>P11</td>
</tr>
<tr>
<td>P12</td>
</tr>
</tbody>
</table>

$^a$Determined via SEC (CHCl$_3$) using PMMA calibration. $^b$Determined via SEC (DMA) using PMMA calibration. $^c$Degree of polymerization estimated from the integral ratio of the aromatic signals of the dithiobenzoate end group and signals of both repeating units in the $^1$H NMR spectra.

Scheme 1. Schematic Representation of the RAFT Polymerization of 2-Isopropenyl-2-oxazoline

![Scheme 1](image-url)
capped and shortly degassed with nitrogen one more time. All vials were placed simultaneously in an oil bath at 70 °C and taken out after varying reaction times between 4 and 56 h. Subsequent to cooling with tap water, the vials were opened and samples were taken for SEC (CHCl₃) and SEC (CHCl₃). The conversions were determined via GC using the reaction solvent as an internal standard. The polymerization conditions of iPOx using CPDB as CTA. SEC traces can be found in ESI (Figure SI-2, Supporting Information).

**RESULTS AND DISCUSSION**

**Homopolymerization of iPOx.** In an initial screening, varying classes of chain transfer agents (CTAs), such as dithio benzoate, trithiocarbonate, and dithiocarbamate, were applied in order to gain first insights into the RAFT polymerization conditions of iPOx. All polymerizations were performed in 2 M solution in toluene for 18 h at 70 °C using AIBN as initiator, whereby the ratio of [iPOx]: [CTA]: [AIBN] was set to 50: 1: 0.25. As depicted in Figure S1-1, Supporting Information, utilization of dithiocarbamate as well as trithiocarbonate-based CTAs resulted in broad molar mass distributions, whereas the RAFT polymerization with the dithiobenzoate-based CTA (CPDB) yielded polymers with a more narrow molar mass distribution (PDI = 1.38). In addition, the lower molar mass of the resulting polymer indicated that the polymerization could be controlled by CPDB to a certain extent. As a result, CPDB was selected for the performance of further experiments, such as kinetic studies and the synthesis of statistical copolymers of iPOx with other monomers.

The kinetic studies of the RAFT polymerization of iPOx utilizing CPBD as CTA were performed under similar reaction conditions as described above. The resulting kinetic plots are depicted in Figure 1. Even though the molar mass of the polymer increases in a linear fashion with monomer conversion and the PDI values remain well below 1.4, the semilogarithmic plot reveals that the polymerization slows down significantly at monomer conversions of around 30%. Since the kinetic studies were accomplished in separate vials this fact cannot simply be a result of contamination of the reaction mixture during sampling. Instead, after initiation by AIBN, the intermediate structure during the RAFT process might be too stable to reinitiate the polymerization once it has been formed. This assumption is supported by the fact that CPDB is frequently reinitiated.
applied for RAFT polymerization of more activated monomers as well as by the observation that free CTA was still present in the reaction solution, even at later stages of the polymerization, as confirmed by preparative SEC on a BioBeads column showing two pink fractions (i.e., PiPOx and free CPDB) that eluted separately from each other.

Matrix-assisted laser desorption/ionization time-of-flight (MALDI TOF) mass spectrometry analysis of the obtained PiPOx revealed a single distribution with a m/z difference of 111.1 between two neighboring peaks, which corresponds to the molar mass of the iPOx repeating unit (Figure 2). Because of the rather harsh ionization during the MALDI process, the dithiobenzoate end group is cleaved and polymer chains with both saturated as well as unsaturated end groups are formed. The m/z difference of 2 between those end groups results in an overlapping of the isotopic patterns of the assigned structures.

In contrast, the softer ionization taking place during electro spray ionization (ESI) partially preserved the dithiobenzoate end group, although also polymer chains with saturated and unsaturated end groups could be assigned. The peak assignment of the resulting ESI mass spectrum of PiPOx is shown in Figure 3.

**Statistical Copolymerization of iPOx with MMA and NiPAm.** Encouraged by the rather successful homopolymerization that delivered PiPOx with much narrower molar mass distributions compared to the results obtained by free radical polymerization, two series of statistical copolymers of iPOx with other monomers, i.e., MMA and NiPAm, were prepared. In order to evaluate the amount of iPOx that can be incorporated into a copolymer without suppressing reversible chain transfer, the iPOx content was varied systematically from 100 to 10% for both series. Except for a ratio of [monomer]:[CTA] of 100:1 for the copolymer series with MMA as reactive monomer, all polymerizations were carried out under similar conditions as described above. The results of the characterization of the obtained copolymers by means of SEC and 1H NMR spectroscopy are summarized in Table 1.

SEC analysis of the statistical copolymers consisting of iPOx and MMA P1–P6 (Figure 4, top) revealed that, with increasing amount of the more activated MMA in the feed, the molar mass distribution becomes much more narrow with PDI values...
between 1.37 for the PiPOx homopolymer and 1.21 for the statistical copolymer containing only 13 mol % iPOx. In addition, the molar mass of the copolymer increases with the MMA content. In order to evaluate if the latter is simply an effect of a variation in hydrodynamic volume of the polymers with altered composition, the degree of polymerization (DP) of each comonomer was roughly estimated from appropriate signals in the $^1$H NMR spectra, assuming full end functionalization with the dithiobenzoate moiety. Indeed, keeping in mind the accuracy of the applied method, at least the two copolymers with the largest mole fraction of MMA (P5 and P6) have significantly higher DP values than the copolymers with lower MMA content (see Table 1). In addition, as depicted in Figure 5, the copolymer composition, which was calculated from the ratio of the peak integrals of the methylene protons of the 2-oxazoline ring of the iPOx and the methyl protons of MMA, was found to be close to the feed ratio of both monomers. All these results indicate that the low ability of the intermediate species that is formed during RAFT polymerization of iPOx to undergo reversible chain transfer can be overcome by utilization of MMA as more activated comonomer.

As next step, iPOx functionalities were incorporated into a polymer displaying thermo-responsive properties, namely PNiPAm. For this second series of statistical copolymers P7–12, SEC analysis (Figure 4, bottom) revealed a significant increase of the molar mass and a satisfying peak shape only for P12, the copolymer with the highest mole fraction of NiPAm (83%), even though the PDI values for all copolymers remained well below 1.3, except for P9. In addition, the conversion of iPOx was found to be higher than that of NiPAm, which is reflected in an increased mole fraction of iPOx in the polymers with respect to the feed ratios. However, it was possible to obtain polymers with varying iPOx content from roughly 17 to 88% (as determined by $^1$H NMR spectroscopy, Figure 5), that could be used for an investigation of the effect of the iPOx moieties upon the lower critical solution temperature (LCST) behavior of PNiPAm.

**Aqueous Solution Behavior of (P(iPOx-stat-NiPAm)) Copolymers.** The thermo-responsive properties of P7–12 in aqueous solution were investigated by means of turbidimetry at a polymer concentration of 5 mg mL$^{-1}$ in water as well as phosphate buffered saline (PBS). In order to determine the reversibility of the coil to globule transition two heating cooling cycles were conducted for each sample with a heating rate of 1 K min$^{-1}$. Turbidity curves from the second heating run are displayed in Figure 6 (left). The PiPOx homopolymer P7 remained water-soluble during the whole investigated temperature range up to 100 $^\circ$C indicative of its high hydrophilicity. The latter also caused complete solubility of the copolymer with the highest iPOx content P8. Consequently, an increasing mole fraction of iPOx in the statistical copolymers P9–12 was expected to result in elevated cloud point temperatures ($T_{cp}$) of the aqueous solutions. Surprisingly, as shown in Figure 6 (right), this holds true only for copolymers with mole fractions of iPOx above 50%. Below that value, $T_{cp}$ remained rather unaffected by the copolymer composition around 25 to 26 $^\circ$C in PBS and around 33 to 35 $^\circ$C in water. As a result of the hydrophilic iPOx moieties, the latter value is slightly higher than the $T_{cp}$ of a comparable PNiPAm solution at 30 $^\circ$C under similar measurement conditions. In addition, the transition becomes less sharp with increasing iPOx/NiPAm ratio in the copolymer. Possible explanations for this unexpected behavior...
A process (as indicated by the whitish instead of pink color of dithiobenzoate end group) is cleaved during the reaction with thiophenol reactions and, especially for the addition product with hydrodynamic volume of the polymers after the addition. Supporting Information) revealed a significant increase of the in Table 2.

The formation of ester functionalities after the polymer analogous reactions with carboxylic acids could be confirmed by means of FT-IR spectroscopy (Figure 8). The IR spectra of addition of thiophenol proceeded quantitatively as demonstrated by the disappearance of the oxazoline derived signals. The formation of ester functionalities after the polymer analogous reactions with carboxylic acids could be confirmed by means of FT-IR spectroscopy (Figure 8). The IR spectra of both A2 and A3 clearly show a characteristic band at 1720 cm\(^{-1}\) that can be assigned to the carbonyl stretching vibration of the formed ester. In addition, the IR spectrum of A3 provides evidence of the presence of azide moieties due to the characteristic \(\nu_N=\nu_N\) band at 2120 cm\(^{-1}\). It should be noted that might either be a gradient composition of the copolymers facilitating the solubilization of already collapsed NiPAm rich parts by iPPO rich parts below \(T_{cpr}\) or the rather small overall DP of the copolymers P9–12 that exhibit LCST behavior (in the range of 12 to 16). Because of the latter small variations of the composition of individual polymer chains directly result in a mixture of thermoresponsive polymers with varying \(T_{cpr}\). In this case, polymer chains containing a similar mole fraction of NiPAm might be present in both copolymers (P9 and P10) and would collapse prior to chains with smaller NiPAm content.

**Functionalization of iPPO-Containing Polymers with Carboxylic Acids and Thiols.** In order to evaluate the possibility to synthesize functionalized polymers from the iPPO containing copolymers, polymer analogous addition reactions with benzoic acid and thiophenol as model substances were performed under mild conditions (at 60 °C) using iPPO homopolymers as starting material. In addition, 4-azidobenzoic acid was applied as reactant in order to obtain a polymer that is functionalized with multiple azide moieties. The poly-(methacrylamide) structure of the resulting addition products functionalized with multiple azide moieties. The polyacid was applied as reactant in order to obtain a polymer that is mixture of thermoresponsive polymers with varying the composition of individual polymer chains directly result in a

### Table 2. Characterization Data of Addition Products Obtained after Reaction of iPPO with Thiophenol and Carboxylic Acids

<table>
<thead>
<tr>
<th>code</th>
<th>reactant</th>
<th>premodification</th>
<th>postmodification</th>
<th>theoretical</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(M_n^q) [g mol(^{-1})]</td>
<td>PDI</td>
<td>(M_n^q) [g mol(^{-1})]</td>
</tr>
<tr>
<td>A1</td>
<td>thiophenol</td>
<td>2130</td>
<td>1.45</td>
<td>11 200</td>
</tr>
<tr>
<td>A2</td>
<td>benzoic acid</td>
<td>2930</td>
<td>1.45</td>
<td>6200</td>
</tr>
<tr>
<td>A3</td>
<td>4-azidobenzoic acid</td>
<td>2130</td>
<td>1.45</td>
<td>8070</td>
</tr>
</tbody>
</table>

\(^a\)Determined via SEC (DMA) using PMMA calibration. \(^b\)Calculated from the DP of the used iPPOs and the degree of functionalization. \(^c\)Degree of functionalization determined from \(^1\)H NMR.

Figure 7. \(^1\)H NMR spectra (300 MHz, CD\(_2\)Cl\(_2\) or CDCl\(_3\)) of a iPPO homopolymer (top) and of the addition products with thiophenol (A1), benzoic acid (A2) as well as 4-azidobenzoic acid (A3).
the carbonyl stretching vibration of the amide moiety at 1655 cm$^{-1}$ in the IR spectra of all addition products A1–3 is overlapping with the $-C\equiv N$ vibration of the oxazoline ring in PiPOx.

The fact that the copper-catalyzed azide–alkyne cycloaddition (CuAAC) has become a common and versatile method in polymer chemistry led to the availability of a wide range of interesting building blocks for this type of “click” reaction. In this context, addition products of PiPOx-based copolymers with 4-azidobenzoic acid could serve as starting material for further functionalization, or the synthesis of graft copolymers if the utilized alkyne represents an end functionalized polymer. As depicted in Scheme 3, the latter route was applied in order to obtain a graft copolymer having a PMMA-based backbone and poly(2-ethyl-2-oxazoline) (PEtOx) side chains.

A first hint toward a successful grafting of alkyne-terminated PEtOx onto the azide functionalized PMMA-based copolymer A4 is provided by SEC analysis of the graft copolymer A5 (Figure 9). The SEC trace of A5 is shifted to smaller elution volume when compared to A4 indicative of its larger hydrodynamic volume due to the grafting process. In addition, the complete removal of the excess of PEtOx after preparative size exclusion chromatography is confirmed by the monomodal peak shape.

With this knowledge it is possible to gain further insights regarding the copolymer composition by interpretation of the $^1$H NMR spectrum of A5. As depicted in Figure SI-5, Supporting Information, the signals of the PEtOx side chains are clearly visible, and the formation of the triazole ring is manifested by a change of the signals in the aromatic region. Most likely due to steric hindrance by already grafted PEtOx, around 20% of the attached azide functionalities underwent no 1,3-dipolar cycloaddition, as could be roughly estimated from the peak integrals of residual 4-azidobenzoate moieties.

**CONCLUSION**

PiPOx homopolymers bearing a dithiobenzoate end group could be obtained with PDI values below 1.4 utilizing CPDB as CTA. The irreversible chain transfer taking place during RAFT homopolymerization of iPOx could be overcome by statistical copolymerization with MMA as well as with NiPAm resulting in two copolymer series with varying iPOx content. The copolymers of NiPAm with iPOx revealed thermoresponsive properties in aqueous media at elevated temperatures compared to PNiPAm due to the hydrophilicity of the incorporated iPOx moieties. In addition, the iPOx functionalities provided a versatile tool for post polymerization modification of the synthesized homo- and copolymers via addition reactions with nucleophiles, such as carboxylic acids and, in particular, thiophenol. The polymer analogous reaction with 4-azidobenzoic acid supplied polymers carrying multiple azide functionalities that represent suitable building blocks for the subsequent grafting of alkyne-terminated PEtOx onto PMMA by copper-catalyzed 1,3-dipolar cycloaddition. Future work will focus on the full exploitation of the potential to functionalize the well-defined copolymers with biologically active thiolis, such as sugars or proteins, and on the development of more challenging copolymer architectures.

**ASSOCIATED CONTENT**

Supporting Information
SEC traces obtained with varying CTA’s and during kinetic studies, full MALDI TOF mass spectrum of PiPOx, SEC traces of A1–3, and $^1$H NMR spectra of A4 and A5. This material is available free of charge via the Internet at http://pubs.acs.org.

**AUTHOR INFORMATION**

Corresponding Author
*E-mail: c.r.becer@warwick.ac.uk. Fax: +44 2476 151795.

**ACKNOWLEDGMENTS**

Anja Baumgaertel and Esra Altuntas are acknowledged for MALDI and ESI MS measurements. This work forms part of...
the research program of the Dutch Polymer Institute (DPI), Project Number 612 (technology area HTE) and Project Number 686 (technology area BIO-inspired). The authors thank the Thüringer Ministerium für Wissenschaft, Bildung und Kultur for the financial support of this study (Grant No. B514-09051, NanoConSens). K.K. is grateful to the Landesgraduiertenförderung for financial support.

**REFERENCES**