

## **Synthesis and Characterization of Poly(NIPAM-co-AA) Polymers Possessing Perfluorinated Side Chains and Chemically Linked Pyrene Labels**

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### **Abstract**

*The synthesis of Poly(*n*-isopropylacrylamide-co-acrylic acid)/-Poly(NIPAM-co-AA) polymers featuring perfluorinated side chains as well as chemically linked pyrene fluorescence labels has been reported. The resulting polymers have been characterized with the aid of UV/VIS, FTIR spectroscopy and Gel permeation chromatography.*

**Keywords:** *Polymers, Poly(*n*-isopropylacrylamide-co-acrylic acid)/-Poly(NIPAM-co-AA), Pyrene, photochemical sensor, gel permeation chromatography*

### **Introduction**

The synthesis and characterization of high molecular weight, water soluble polymers containing hydrophobic side chains are of high interest for the following reasons: Water soluble polymers which feature chemically linked hydrophobic units are simple models for the interaction of proteins with the solvent water as well as with other polymeric functions. The influence of the hydrophobic centers on the conformation and dynamics of the macromolecules can be elucidated in model system with higher precision<sup>1, 2</sup>. Consequently, the physical properties of these model systems permit their straight-forward applications in systems of technical importance in a straight forward manner. In the work reported here, we introduced chemically linked perfluorinated side chains as a profound example of a hydrophobic function in the water soluble Poly (NIPAM –co-AA) polymer<sup>3</sup>.

The development and application of photochemical sensors which rely on changes of the dynamics and conformation of polymers offers new opportunities for the production of inexpensive and long term stable sensors for gases and ions of environmental importance<sup>4</sup>. The detection of these changes as a function of the environment impact can be achieved using chemically attached fluorescence labels<sup>5</sup>. We report here the synthesis and characterization of hydrophobically modified poly(NIPAM-co-AA) polymers which feature chemically linked 1-aminomethyl-pyrene as fluorescence labels. The application of the well-established pyrene fluorophore permits the detection of the polymer dynamics by means of the separate

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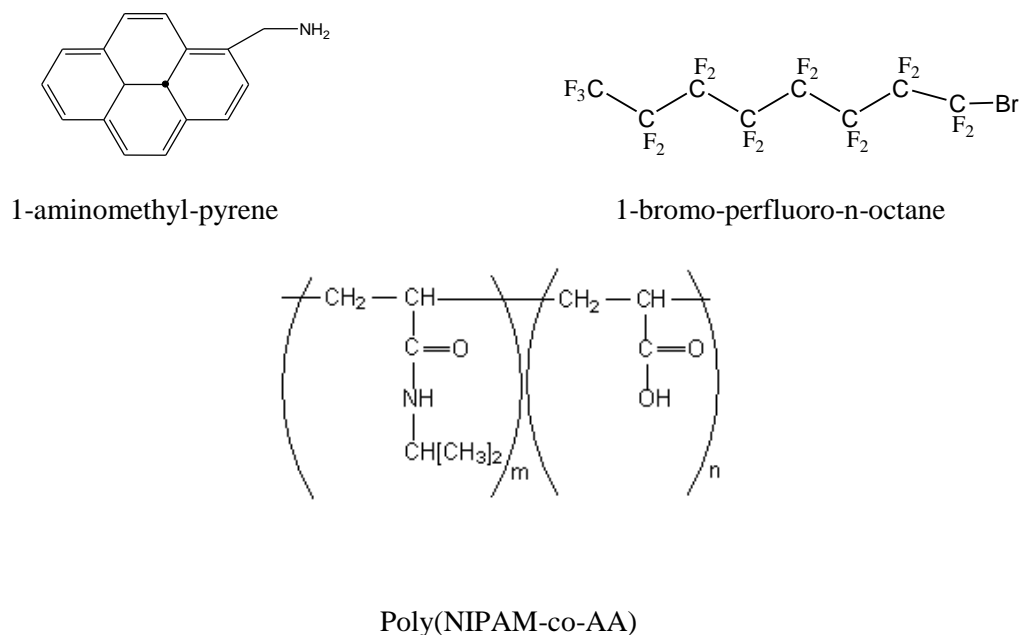
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measurement of the monomer and excimer emission. Whereas monomer emission arises from isolated pyrene units in the photochemically excited singlet state, excimer emission occurs from an excited dimer, formed by an excited and ground state pyrene molecule<sup>6</sup>.

## Experimental Methods

### Materials

All commercial chemicals (i.e. N-isopropylacrylamide, acrylic acid, 2,2'-azoisobutyronitrile, tert-butyl alcohol, tetrahydrofuran, n-hexane, diethyl ether, 1-aminomethyl-pyrene, 1-bromo-perfluoro-n-octane, sodium carbonate, dimethylformamide) were from Aldrich Chemical Co. unless otherwise mentioned, and were used without purification. Figure 1 shows the structure of the employed polymer and other compounds.



**Figure 1:** Structure of employed polymer and other compounds

### Synthesis procedures and characterization techniques

The starting material Poly(NIPAM-co-AA) was synthesized according to our previous published report.<sup>3</sup>

### Synthesis of Poly(NIPAM-co-AA) featuring perfluorinated side chains

An amount (3.0 g) of Poly(NIPAM-co-AA) was dissolved in 50 mL anhydrous DMF and the solution stirred for an hour. An amount of 0.068 g (0.001 mol) and 1.38 g (0.002 mol) of 1-bromo-perfluoro-n-octane (C<sub>8</sub>F<sub>17</sub>Br, m = 498.9 g mol<sup>-1</sup>) and 2.0 g of Na<sub>2</sub>CO<sub>3</sub> were added and the reaction mixture was allowed to react for 15 h at 120 °C. The resulting polymer solution was filtered warm in order to remove the inorganic salts. After being cooled to 10 °C, 80 mL of

diethyl ether was added dropwise and the polymer precipitated slowly. After being stirred for 1 h, the polymer was filtered off and dissolved again in 30 mL of DMF. Then again, 80 mL of diethyl ether was added and the polymer was collected. This procedure was repeated one additional time. Copolymers, Poly(NIPAM-co-AA)-C<sub>8</sub>F<sub>17</sub> having mol % 95.3 and 90.8 of NIPAM, 2.2 and 4.2 of acrylic acid and 2.5 and 5 mol % of C<sub>8</sub>F<sub>17</sub> were synthesized using this procedure. The yield was about 2.4-2.5 g

*Synthesis of Poly(NIPAM-co-AA) featuring perfluorinated side chains and chemically linked pyrene*

An amount 0.010 g ( $3.73 \times 10^{-5}$  mol) 1-aminomethyl-pyrene hydrochloride (C<sub>17</sub>H<sub>14</sub>NCl,  $m = 267.7$  g/mol) was dissolved in 10 mL bidistilled water. The pH of the solution was adjusted to 10.0 using sodium hydroxide solution (0.01M). 1-aminomethyl-pyrene was extracted employing 20 mL of diethyl ether.

An amount (3.0 g) of Poly(NIPAM-co-AA) was dissolved in 50 mL anhydrous DMF and the solution stirred for an hour. An amount 0.03 g ( $1.15 \times 10^{-4}$  mol) of dicyclohexylcarbodiimide (DCC, C<sub>13</sub>H<sub>22</sub>N<sub>2</sub>,  $m = 206.3$  g/mol) and the 20 mL of diethyl ether containing 1 aminomethyl-pyrene were added and the mixture, which was constantly purged with nitrogen and allowed to react for 2 h at 60°C. Then 0.68 g (0.001 mol) and 1.38 g (0.002 mol) of 1-bromo-perfluoro-n-octane (C<sub>8</sub>F<sub>17</sub>Br,  $m = 498.9$  g mol<sup>-1</sup>) and 2.0 g of Na<sub>2</sub>CO<sub>3</sub> were added and the reaction mixture was allowed to react for 15 h at 120 °C. The resulting polymer solution was filtered warm in order to remove the inorganic salts. After being cooled to 10 °C, 80 mL of diethyl ether was added dropwise and the polymer precipitated slowly. After being stirred for 1 h, the polymer was filtered off and dissolved again in 30 mL of DMF. Then again, 80 mL of diethyl ether was added and the polymer was collected. This procedure was repeated one additional time. The Yield was about 2.4-2.6 g

The characterization of the polymers was performed using the following techniques:

The pyrene content of the novel polymer material was determined using UV/VIS spectroscopy (Hewlett-Packard 8452A diode array spectrometer with HP8452 Win system software based on Windows 3.1). The infrared spectra were measured with solid samples on a Hartmann and Braun FTIR spectrometer using Bomem Grams/32 software (version 4.04) for data processing. Samples were prepared by mixing the pulverized polymer with spectrograde potassium bromide in a ratio of approximately 1:5 and pressing a tablet using a hydraulic press at approximately 200 bar. Polymers that could not be pulverized because of their plastic nature were dissolved in spectrograde chloroform. The saturated solution was applied on a KBr tablet and the solvent was evaporated leaving a polymer film on the tablet. IR spectra were recorded in a wavenumber range from 3600 to 500 cm<sup>-1</sup>.

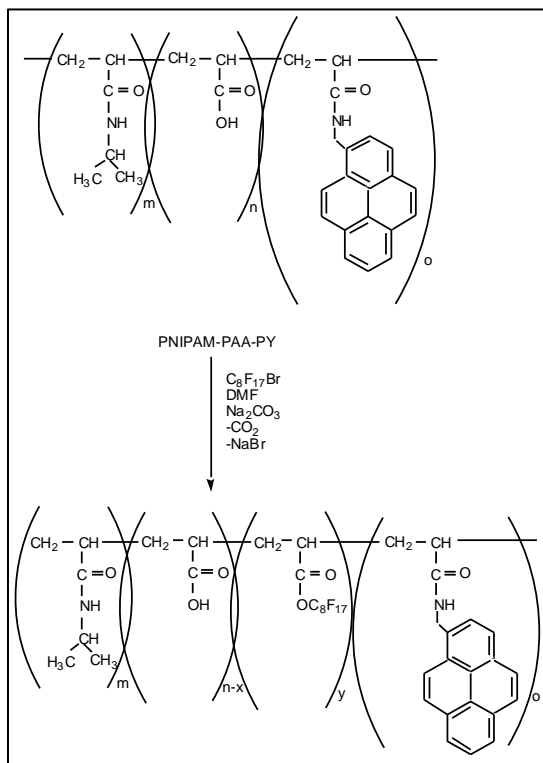
*Gel permeation chromatography*

The gel permeation chromatography (GPC) experiments were carried out employing an HP TSK-AC/4000 SW; 7.5 x 300 mm column. An aqueous solution of Na<sub>2</sub>SO<sub>4</sub> (0.10 M<sup>-1</sup>) and Na<sub>2</sub>HPO<sub>4</sub> (0.10 M<sup>-1</sup>) was used as eluent. The pH of 7 was adjusted using diluted H<sub>3</sub>PO<sub>4</sub>. The polymers were detected at a wavelength of 220 nm. Commercially available polyacrylic acid standards (Aldrich) were used for GPC calibration.

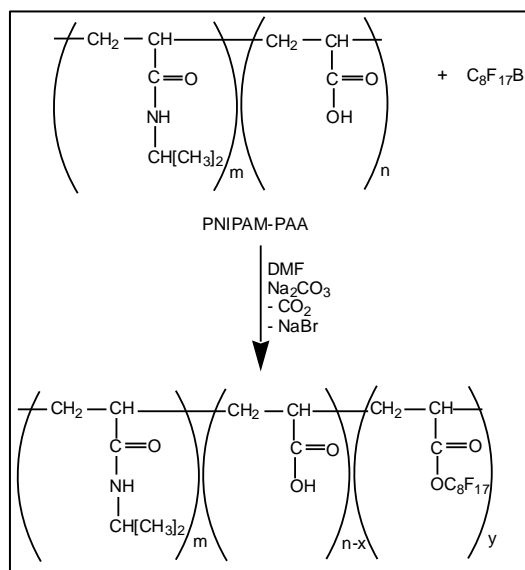
## Results and Discussion

*Synthesis of Poly(NIPAM-co-AA) possessing hydrophobic side chains as well as chemically linked pyrene, (Poly(NIPAM-co-AA)-C<sub>8</sub>F<sub>17</sub>-PY)*

Poly(NIPAM-co-AA) was used as starting material for the synthesis of both Poly (NIPAM-co-AA)-C<sub>8</sub>F<sub>17</sub> and Poly(NIPAM-co-AA)-C<sub>8</sub>F<sub>17</sub>-PY polymers. The labeled copolymers were prepared by the reaction of 1-aminomethylpyrene and 1-bromoperfluoro-n-octane with a copolymer of N-isopropylacrylamide and acrylic acid, Poly(NIPAM-co-AA). 1-Aminomethyl-



**Figure 2:** Labeling of copolymer of the Poly(NIPAM-co-AA) with 1-aminomethyl pyrene and 1-bromo-perfluoro-n-octane by the formation of an amide bond and ester linkage respectively with carboxylic acid function of the copolymer.



**Figure 3:** Labeling of Poly(NIPAM-co-AA) with C<sub>8</sub>F<sub>17</sub>

pyrene has been attached to the carboxylic acid functions of the copolymer by the formation of an amide bond<sup>7</sup>. Figure 2 and 3 show the synthesis of Poly(NIPAM-co-AA)-C<sub>8</sub>F<sub>17</sub>-PY.

The formation of an amide bond between carboxylic acid group of the copolymer and 1-aminomethyl-pyrene was accomplished using dicyclohexylcarbodiimide (DCC) as agent for the removal of water in dimethylformamide (DMF) as solvent<sup>8</sup>. The hydrophobic side chains were

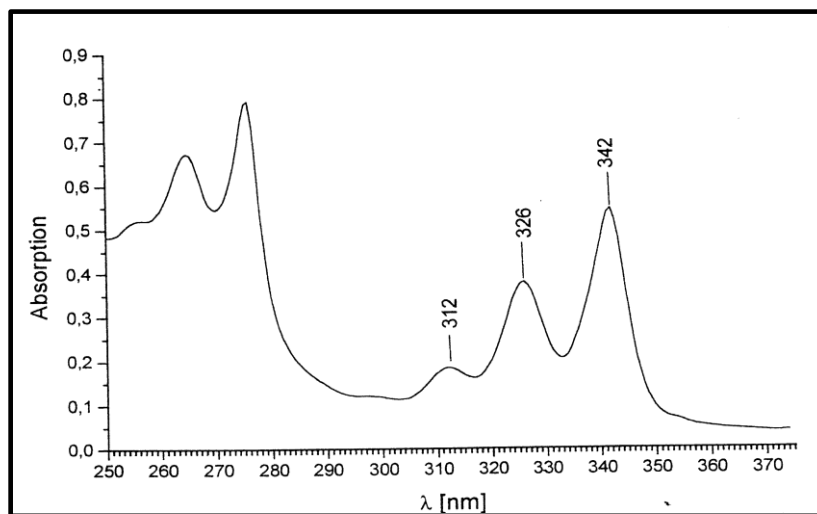
introduced by the reaction of carboxylic acid group of the copolymer and 1-bromo-perfluorooctane in DMF. Sodium carbonate was added in order to trap the HBr formed during synthesis. The copolymers were purified by repeated precipitations of DMF solutions into diethyl ether, a non-solvent for copolymers but a good solvent of all the monomers.

#### *Determination of pyrene content*

The pyrene content of the novel polymers has been determined by using UV/VIS-spectroscopy ( $\epsilon$  (334 nm) = 42500 [mol cm L<sup>-1</sup>]<sup>9</sup>) and it was found to be in between 0.20 and 0.47 mol % of pyrene. The UV absorption spectra of pyrene labeled Poly(NIPAM-co-AA) is shown in Figure 4. The three characteristics absorption bands of aminomethyl-pyrene are located at 312, 326 and 342 nm.

#### *FTIR- Spectroscopy*

Infra-red spectra of fluorinated and non-fluorinated polymers (the samples without pyrene) were recorded in order to determine the differences in the spectra due to the hydrophobic -C<sub>8</sub>F<sub>17</sub> side chains. The spectra were normalized in order to adjust the intensities and the spectrum of the fluorinated polymer was superimposed to the non-fluorinated one.



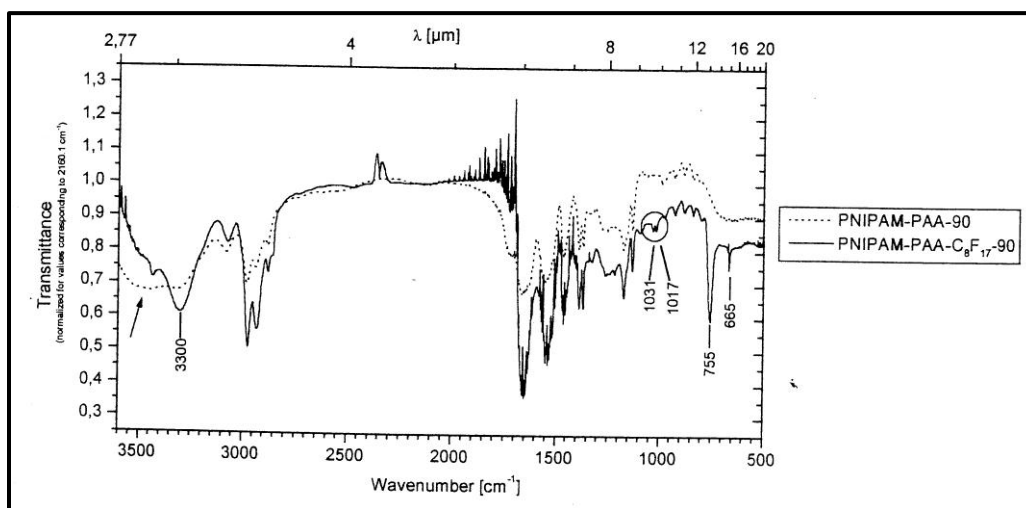
**Figure 4:** *UV absorption spectrum of pyrene labeled Poly(NIPAM-co-AA)*

Figure 5 shows the superimposed spectra of the respective polymers for comparison. Apart from little differences in the intensity, the spectra are very similar. However, the fluorinated polymer has some absorption peaks that do not appear in the spectrum of the corresponding non-fluorinated polymer. The fluorinated polymer spectrum shows a weak peak at 665 cm<sup>-1</sup> and a strong one around 752 cm<sup>-1</sup>. They belong to the -CF<sub>3</sub> group of the per-fluorinated chains. The bands of -CF<sub>2</sub> should appear between 1250 cm<sup>-1</sup> and 1050 cm<sup>-1</sup> but they may be shifted to lower wavenumbers due to the C=O group of the ester.

**Table 1:** Molecular weight and polydispersities of polymers

Polymers	$M_N$	$M_W$	$P_D$
Poly(NIPAM-co-AA)	90,800	131,700	<b>1.45</b>
Poly(NIPAM-co-AA)-C <sub>8</sub> F <sub>17</sub>	103,000	156,500	<b>1.52</b>
<b>Poly(NIPAM-co-AA)-C<sub>8</sub>F<sub>17</sub>-PY</b>	<b>103,500</b>	<b>156,500</b>	<b>1.52</b>

This would be a possible reason for the two little peaks appearing at 1031 cm<sup>-1</sup> and 1017 cm<sup>-1</sup> in the spectrum of the Poly(NIPAM-co-AA)-C<sub>8</sub>F<sub>17</sub> (marked with a circle in the Figure 5). Three bands of carboxylic acid appear between 3000 cm<sup>-1</sup> and 2750 cm<sup>-1</sup> for both, the fluorinated and non-fluorinated polymer. The band around 2350 cm<sup>-1</sup> belongs to atmospheric CO<sub>2</sub>. The broad peak at 3300 cm<sup>-1</sup> in the spectra of the fluorinated polymers belongs to the secondary amide of NIPAM. In the same spectral region (3250 cm<sup>-1</sup> - 3550 cm<sup>-1</sup>) a very broad band can be seen in the spectra of non-fluorinated polymer which overlaps the NIPAM band. It is due to residual water in the polymer without fluorine. In fact, the fluorinated polymer obviously contains less water because of its hydrophobic per-fluorinated alkyl chains<sup>10</sup>. This is the reason for which the amide peak of NIPAM can only be seen in the fluorinated polymer.



**Figure 5:** FTIR spectrum of Poly(NIPAM-co-AA) and Poly(NIPAM-co-AA)-C<sub>8</sub>F<sub>17</sub>

*Gel permeation chromatography(GPC)*

The weight averaged [Mw] and number average [MN] and polydispersities of the synthesized polymers that were determined by means of GPC are summarized in Table 1. It is

apparent that the fluorinated polymer shows a higher molecular weight in comparison to the non-fluorinated polymer. It means that the –COOH groups of the polymer have been reacted with perfluorinated groups to form the hydrophobically modified copolymers.

## **Conclusion**

The synthesis of Poly(NIPAM-co-AA) polymers featuring per-fluorinated side chains and chemically linked pyrene labels has been reported. 1-Aminomethyl-pyrene has been attached to the copolymer by the formation of an amide bond and the hydrophobic units by means of an ester linkage employing 1-bromo-perfluoro-n-octane. The labeling of the copolymers with 1-aminomethyl-pyrene has been confirmed with the help of UV/VIS spectroscopy. Infrared spectroscopy has indicated the presence of fluorinated alkyl chains in the polymer. The pyrene content of the labeled polymer was determined by UV/VIS spectroscopy and the values were found to be in between 0.20 and 0.47 mol-% of pyrene.

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