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SYNTHESIS AND CHARACTERIZATION OF WATER-SOLUBLE BLOCK COPOLYMERS WITH AN END-TAGGED NAPHTHALENE PROBE

Ralf Weberskirch[a]; Oskar Nuyken[b]
[a] Technische Universität München, Garching, Germany [b] Technische Universitüt München, Garching, Germany

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SYNTHESIS AND CHARACTERIZATION OF WATER-SOLUBLE BLOCK COPOLYMERS WITH AN END-TAGGED NAPHTHALENE PROBE

RALF WEBERSKIRCH and OSKAR NUYKEN*

Lehrstuhl für Makromolekulare Stoffe
Technische Universität München
D-85748 Garching, Germany

Key Words: Amphiphilic Block Copolymers, Oxazoline Polymers, Naphthalene Label, Micelle Formation

ABSTRACT

Water-soluble A-B block copolymers of 2-perfluoroethyl-2-oxazoline or 2-pentyl-2-oxazoline as hydrophobic monomers and 2-methyl-2-oxazoline as hydrophilic monomer were prepared by means of the living cationic ring-opening polymerization. The polymerization was initiated with N-methyl-2-(1-naphthyl)-2-oxazolinium trifluoromethanesulfonate as fluorescence label followed by sequential addition of the hydrophobic and the hydrophilic monomer. The polymerization was monitored by ^{1}H NMR spectroscopy and gel permeation chromatography (GPC) measurements. The results revealed that fluorophilic block copolymers can be prepared by this method while lipohilic block copolymers are not accessible by this monomer sequence. Micelle formation of the fluorophilic block copolymers in aqueous solution was studied by means of steady-state fluorescence spectroscopy which confirmed strong intermolecular excimer

* Author to whom correspondence should be addressed.

Phone: +49 89 289 13571; Fax: +49 89 289 13584; E-mail: nuyken@makroserv.tech.chemie.tu-muenchen.de.

formation of the terminal bounded naphthalene moiety. In chloroform as a good solvent for both blocks, only monomer fluorescence could be observed.

INTRODUCTION

The synthesis of tailored block copolymer systems has been the subject of increasing attention in recent years due to their unique properties in solution and in the solid state as a consequence of molecular structure [1-3]. When dissolved in a selective solvent that is a good solvent for one block but a precipitant for the other, block copolymers behave like typical amphiphiles and associate reversibly to form micelles with higher stability and wider variation in size compared to the more familiar detergent micelles [4, 5].

One interesting property of micelles is their ability to incorporate or release organic molecules in aqueous media which makes them suitable to concentrate and transport molecules that show only limited solubility in the solvent (6, 7]. However, there is an increasing interest to introduce functional groups into amphiphilic block copolymers and to enhance the scope of polymeric micelles from pure delivery vehicles to microreactors with special application in micellar catalysis [8, 9] and drug delivery [10].

It was demonstrated that naphthalene labeled copolymers are suitable systems to study polymer dynamics [11] and compatibility [12]. Recently, steady-state fluorescence spectroscopy was also applied for the micelle formation of naphthalene-labeled polystyrene-*block*-poly(methacrylic acid) copolymers. The naphthalene group was introduced by vinyl-2-naphthalene at the beginning of the polymerization [13]. In good solvents (unimers only), pendant fluorophores were mobile and upon excitation excimers were formed within the life-time of the excited state of the monomeric fluorescence [14]. In micelle forming solvents, the pendant 2-naphthalene groups were immobilized in the core enviroment. Mutual orientation of neighboring 2-naphthyl groups was random and only a low fraction of fluorophores was suitable for excimer formation that originates from contact pairs. Block copolymers with one naphthalene unit on average indicated no excimer formation [15, 16].

Here we report on a new synthesis for the selective introduction of naphthalene as a fluorescence label into amphiphilic block copolymers by the initiator method [17]. The choice of the initiator salt reflects two considerations: a) exactly one fluorescence unit is selectively introduced into each polymer and, b)

upon micellization in selective solvents possible excimer formation must be due to *intermolecular* dimer formation. Therefore, we focused our primary attention on the synthesis of the naphthalene containing initiator salt. We investigated its ability to initiate the cationic polymerization of fluorophilic or lipophilic 2-oxazolines followed by 2-methyl-2-oxazoline to prepare amphiphilic block copolymers [18, 19]. Finally, we studied micelle formation in aqueous solution by steady-state fluorescence spectroscopy.

EXPERIMENTAL

Materials

Acetonitrile and 2-methyl-2-oxazoline were dried by calcium hydride, distilled and stored over molecular sieve (4Å). Diethyl ether was dried by sodium, distilled and stored under a dry nitrogen atmosphere. All other reagents were of commercial grade and used as received. All operations were carried out under a dry nitrogen atmosphere.

Methods

^{1}H NMR (300.13 MHz), ^{13}C NMR (75.45 MHz) and ^{19}F NMR (282.5 MHz) spectra were recorded on a Brüker ARX 300 spectrometer. FT-IR spectra were measured on a Brüker IFS 55 in KBr or neat. Gel permeation chromatography (GPC) was performed using a Waters Liquid Chromatograph with refractive index and UV detector (254 nm); columns: Waters Ultrastyragel (pore size 10^3, 10^4, 10^5 Å); solvent chloroform with polystyrene calibration. Steady-state fluorescence spectra of the polymer solutions were recorded at room temperature on a Spex Fluorolog-2 fluorescence spectrometer.

Synthesis

2-Pentyl-2-oxazoline **1**, 2-(1-Naphthyl)-2-oxazoline **2,** 2-(n-Penta-fluoroethyl)-2-oxazoline **3** and 2-(n-Heptafluoropropyl)-2-oxazoline **4** were prepared according to the literature [21, 25, 26].

*N-Methyl-2-(1-naphthyl)-2-oxazolinium Trifluoromethansulfonate **5***

2.0 g (10.14 mmol) of **2** dissolved in 20 ml of dry ether were added dropwise to a solution of methyl triflate (8.32 g, 0.0507 mmol) in 20 ml of dry ether under ice cooling. The mixture was stirred for 2 hours at 0-5°C. A white solid

precipitated during the reaction that was filtered and washed with cooled ether and dried *in vacuo* to give 3.37 g of **5**. Yield: 92% of a white solid. ^{1}H NMR ($CDCl_3$): 3.26 (s, CH_3-, 3 H); 4.69 (t, -CH_2-O-, 2 H); 5.32 (t, -CH_2-N-, 2 H); 7.26-8.10 (CH_{aromat}, 7 H). ^{13}C NMR (δ in ppm, $CDCl_3$): 31.26 ($\underline{C}H_3$-), 53.28 ($\underline{C}H_2$-O-); 72.50 ($\underline{C}H_2$-N); 117.12-135.3 (C_{aromat}); 173.94 (O-C-N). Anal. Calcd. for $C_{15}H_{14}NO_4F_3S$: C: 49,8; H: 3,9; N: 3,9 ; found: C: 50.1 H: 4.0 N: 4.0.

N-(2-hydroxyethyl)-N-methyl-1-naphthylamid ***6*** *[27]*

0.928 g (16.6 mmol) KOH in 10 ml methanol was added to 0.2 g (5.54 mmol) of **5** and the solution was stirred for 2 hours at room temperature. The solvent was completely removed *in vacuo*. The residue was dissolved in 20 ml diethyl ether and extracted three times with water. The organic fraction was separated and dried over $MgSO_4$. After evaporation of the solvent and drying in vacuo at 40°C a colorless oil was obtained in 70% yield (0.1 g).

^{1}H NMR ($CDCl_3$): (δ ppm) = 2.82 and 2.95 (2s, CH_3-N- *syn* and *anti*, 3H); 2.96 and 3.13 (2t, -OH, 1H); 3.25-3.40 (m, -CH_2-N-; 2H); 3.45-3.62 (m, -$C\underline{H}_2$-OH, 2H), 7.29-7.78 (m, C-H_{aromat}, 7H).

^{13}C NMR ($CDCl_3$): (δ ppm) = 33.6; 38.3 ($\underline{C}H_3$-N-); 50.7; 53.2 (-N-$\underline{C}H_2$-); 60.2; 61.3 (-$\underline{C}H_2$-O-); 124.5; 124.6; 125.2; 125.2; 125.5; 126.7; 127.3; 127.6; 128.7; 129.3; 130.0; 133.8; 134.7 (C_{aromat}); 171.9; 172.9 (-N-C=O). FT-IR (film): 3450 (-OH); 3050 (CH_{aromat}); 2927, 2851 (C-H_{aliph}); 1625 (C=O).

Anal. Calcd. for $C_{14}H_{15}NO_2$ (229,27): C: 73.3; H: 6.6; N: 6.1; found: C: 73.2 H: 6.7 N: 6.0. According to the literature [28] the signals shifted to higher field correspond to the syn-conformer.

Lipophilic Block Copolymers LAB

A typical procedure for **LAB 2** was as follows. In a glass tube 0,1 g (0,3037 mmol) of **5** was dissolved in 10 ml acetonitrile. 780 mg (5.537 mmol) of **1** was added under nitrogen at 0°C. The tube was sealed and kept at 80°C for 72 hours. After the first block was completed, about 1 ml of the solution was poured into an excess amount of diethyl ether. The polymeric material was collected and dried under reduced pressure to give a pale yellow powdery material. Afterwards, 2-methyl-2-oxazoline was added to the reaction mixture. The tube was sealed and kept at 80°C for 24 hours (second stage). The polymerization was terminated with an excess of dry piperidine for 30 minutes at 60°C and precipitated into a large excess of diethyl ether. The polymeric material was collected, dried *in vacuo* for two days. Purification was performed by dissolving the polymer in methanol with Amberlyst A-26 for 12 hours. The solution was filtered and

precipitated (diethyl ether). The lipophilic block polymer **LAB 2** was collected and additionally dried *in vacuo* for two days.

^{1}H NMR (δ in ppm, $CDCl_3$): 0.87 (t, C$\underline{H}_3$-$(CH_2)_4$-, 3 H); 1.25 (m, CH_3(C$\underline{H}_2$)-H, 4 H); 1.56 (m, C_3H_7(C$\underline{H}_2$), 2H); 2.09-2.14 (m, (C=O)-CH_3, (C=O)-CH_2-, 5H); 2.89 (s, CH_3-N, 3H), 3.48 (m, -N-(CH_2), 4H); 7.35-7.88 (m, C_{arom}-H, 7H). ^{13}C NMR (δ in ppm, $CDCl_3$): 14.41 ($\underline{C}H_3$-$(CH_2)_4$-); 21.51 (C_4H_9-$\underline{C}H_2$-, $\underline{C}H_3$-C=O); 22.98-32.07 (CH_3($\underline{C}H_2$)$_3$-); 43.94 - 47.90 ($\underline{C}H_2$-$\underline{C}H_2$-N); 171.13; 171.79 (-N-$\underline{C}$=O). FT-IR (KBr) $\tilde{\nu}$ in cm^{-1}:3152 w (ν C-H_{arom}); 2956, 2926 m (ν C-$H_{aliph.}$); 1636 s (ν C=O_{Amid}); 1505, 1493 w (ν C=C_{arom}); 1236; 764.

Fluorophilic Block Copolymers FAB

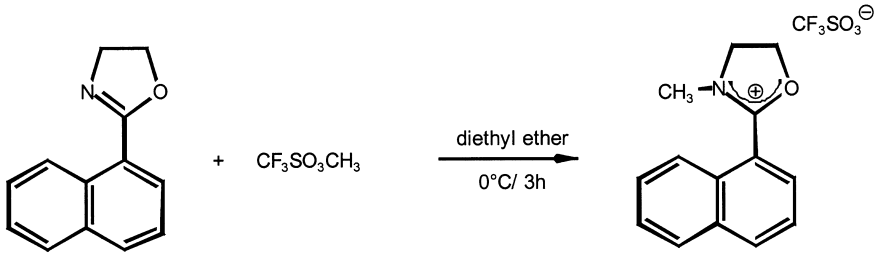
The synthesis and work up procedure for FAB 2 was performed similar as described for the lipophilic block copolymers LAB. The polymerization time for the first block was 72 hours at 110°C, for the second block 24 hours at 80°C.

^{1}H NMR (δ in ppm, $CDCl_3$): 1.44 (m, -N$(CH_2)_4$-(C$\underline{H}_2$), 2H), 1.56 (m, -N$(CH_2)_2$-(C$\underline{H}_2$)$_2$-(CH_2), 4H); 2.08-2.14 (m, CH_3-C=O, 3H); 2.46 (m, $(CH_2)_3$N, 6H), 2.91 (s, CH_3-, 3H), 3.46 (m, -N-(C$\underline{H}_2$)$_2$-, 4H); 7.36 -7.88 (m, C_{aroma}^{t}H, 7H). ^{13}C NMR (δ in ppm, $CDCl_3$): 15.62 (C^8); 21.54 ($\underline{C}H_3$-C=O); 45.68-47.94 (-N-$\underline{C}H_2$-$\underline{C}H_2$); 66.20 ($\underline{C}H_3$-N); 171.03; 171.68 (O=C-N). ^{13}F NMR (δ in ppm, $CDCl_3$): -81.25 (CF_3), -120.60 (CF_2). FT-IR $\tilde{\nu}$ in cm^{-1} (KBr): 3150 w (ν C-H_{arom}); 2955, 2928 m (ν C-$H_{aliph.}$); 1635 s (ν C=O_{Amide}); 1505, 1493 w (ν C=C_{arom}); 1236.

RESULTS AND DISCUSSION

Depending on the nature of the initiator, the ring-opening polymerization of 2-perfluoroalkyl-2-oxazolines with sulfonates proceeds via two different propagation mechanisms [21, 22]. With methyl tosylate, the propagation of 2-perfluoroalkyl-2-oxazolines proceeds via covalent species leading to low polymer yield even at high polymerization temperature, while the use of methyl triflate gives rise to the very reactive oxazolinium cation as propagation species. Following the fast initiator method of Kobayashi *et al.* [17] we used the ability of 2-oxazoline monomers to form stable 1:1 adducts with a sulfonate initiator. We prepared 2-(1-naphthalene)-2-oxazoline that was reacted with methyl triflate to give the desired oxazolinium salt (Scheme 1).

The salt was isolated and used to induce the polymerization of the lipophilic and fluorophilic 2-oxazoline monomers.



2-(1-naphthyl)-2-oxazoline **2** initiator salt **5**

Scheme 1.

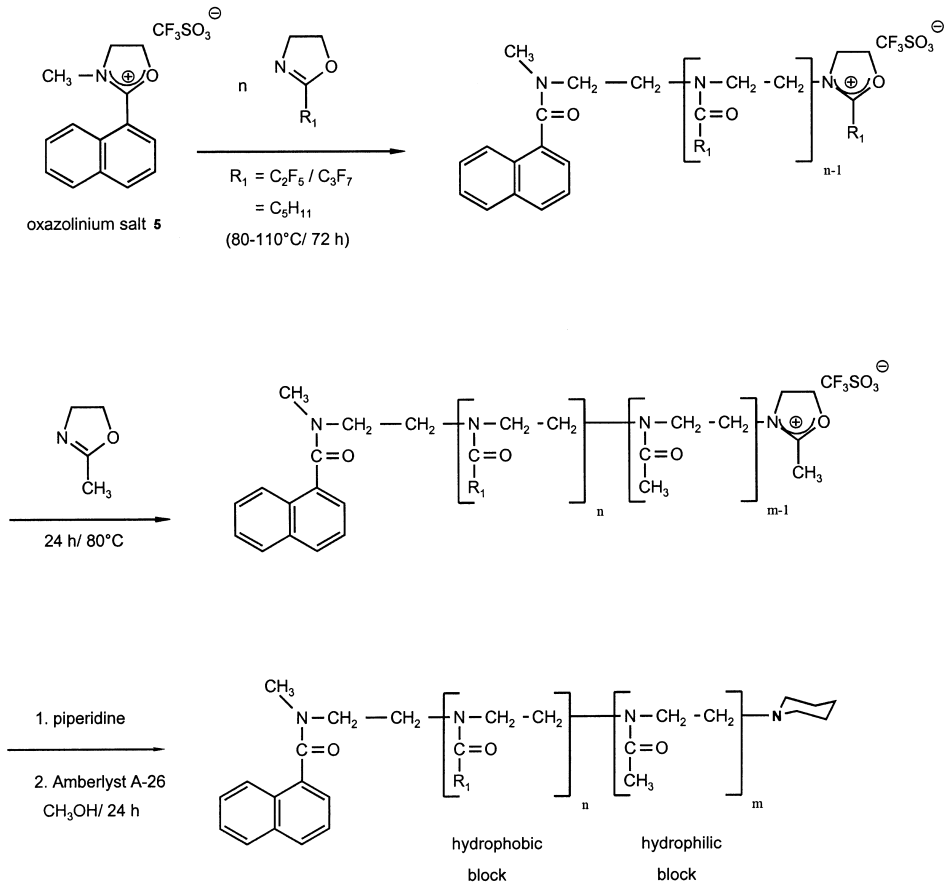
Polymerization of the Block Copolymers by the Fast 'Initiator Method'

The synthesis of the block copolymers is shown in Scheme 2. This route allowed to bound the functional group directly to the corona forming hydrophobic polymer block. The block copolymers were prepared by a 'one pot-two stage method' [22, 23] of two different monomer types of cyclic imino ethers initiated by the oxazolinium salt **5**. After complete conversion of the first monomer, as confirmed by ^{1}H-NMR spectroscopy, the reaction mixture was divided into two portions. One fraction was directly subjected to the work-up procedure in order to determine the structure and length of the homopolymer with the naphthalene containing oxazoline initiator by ^{1}H NMR end group analysis. 2-Methyl-2-oxazoline was added to the second portion to build the hydrophilic segment. After termination with piperidine the resulting copolymer was isolated by precipitation in diethyl ether. The degree of polymerization for each block was determined by the integral ratio of the ^{1}H NMR signals due to the naphthalene end group and the -CH_2- groups to the polymer main chain. From earlier studies, we know that ^{1}H NMR analysis is a valuable method for the determination of molar masses of polyoxazolines [24].

Figure 1 shows a spectra of the fluorintaed segment of **FAB 2** (Figure 1a) and of the complete block copolymer (Figure 1b). The signals can be clearly assigned to the naphthalene end group and the main chain methylene units in both cases. In addition, the monomer ratio (n:m) can be determined by the ratio of the intensities of signal **3** and **6**.

Fluorophilic Block Copolymers FAB 1-5

Table 1 summarizes the results obtained by ^{1}H NMR analysis of each block and allowed a good agreement between the calculated and experimental



Scheme 2.

values of $\overline{DP}_n$ of the segments. In this system, the chain length of the hydrophilic block could be successfully controlled by the reactivity of the active species of the fluorine containing monomer. The electron withdrawing perfluoroalkyl group into the 2-oxazolinium ring enhances its ring-opening activity, namely the reactivity of the 2-perfluoroethyl oxazolinium is much higher compared to the 2-methyloxazolinium cation.

Lipophilic Block Copolymers LAB 1-2

Kobayashi *et al.* described the synthesis of ABA and BAB triblock copolymers where A denotes 2-n-octyl-2-oxazoline and B the 2-metyl-2-oxazoline [22]. Based on these results, we prepared two lipophilic block copolymers **LAB 1** and **LAB 2** (from 2-n-pentyl-2-oxazoline and 2-methyl-2-oxazoline) and

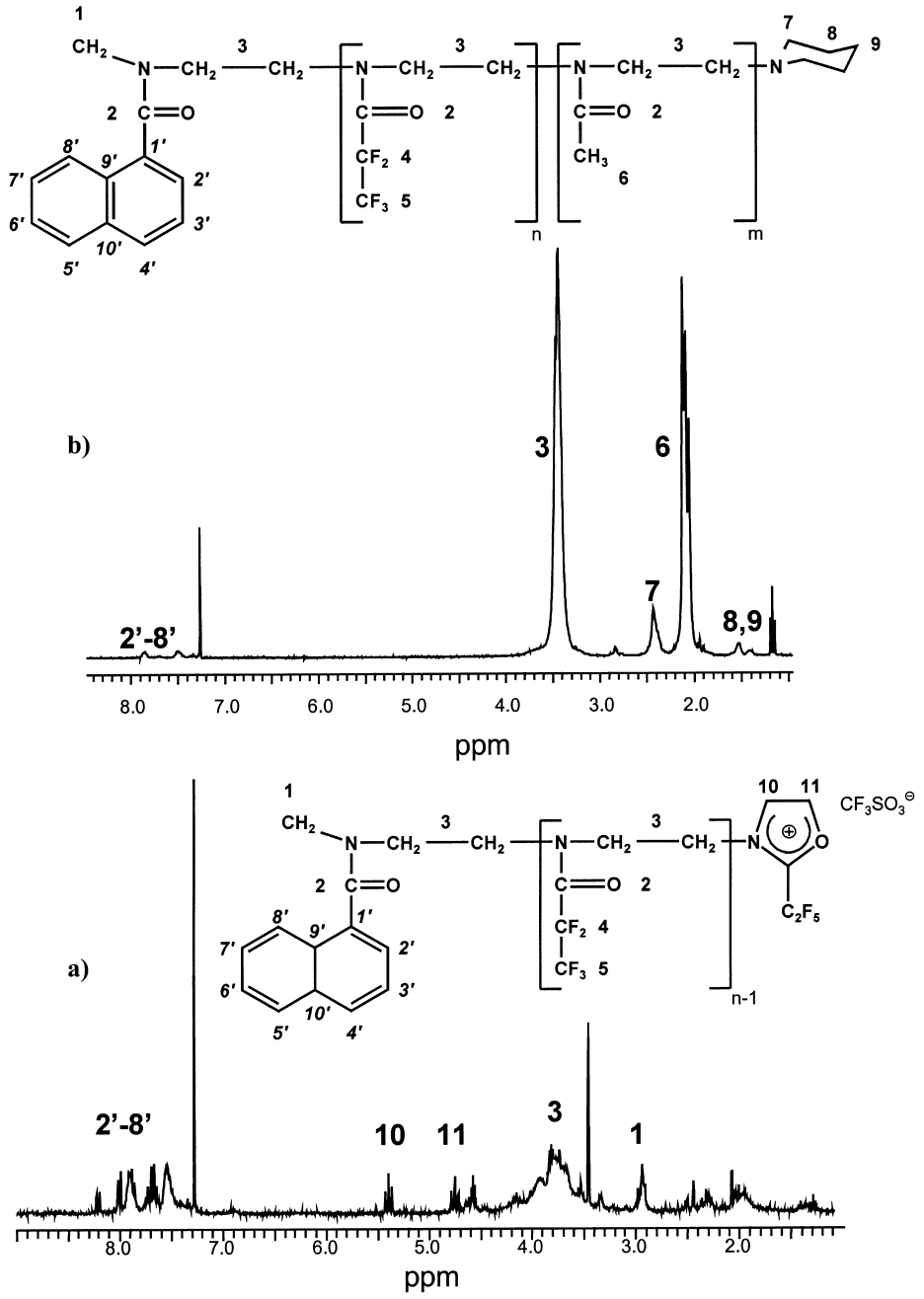


Figure 1. [1]H NMR spectrum of **FAB 2**, a) after the first block copolymerization at 110°C and 72 hours and b) the end product.

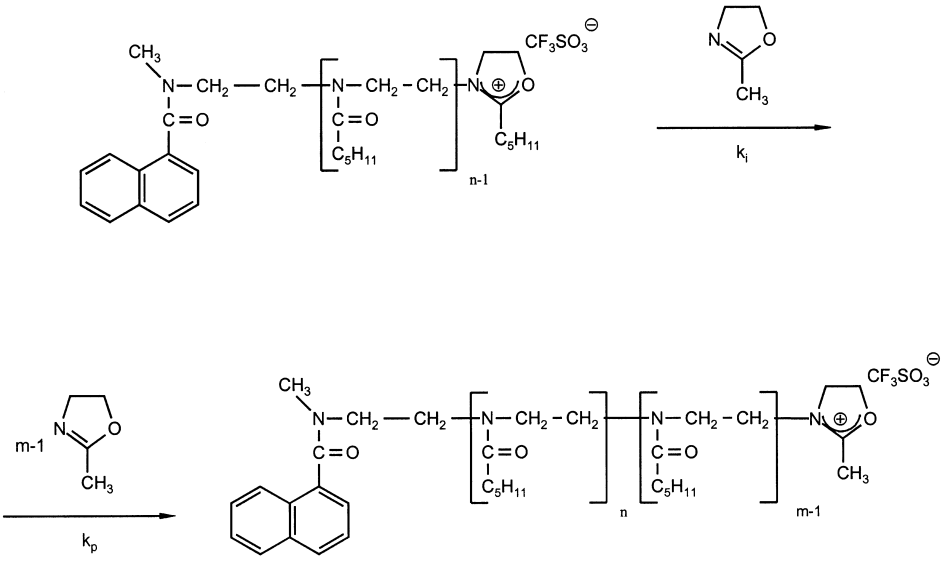
TABLE 1. Results of the Naphthalene-Labeled Block Copolymers; Solvent: CH_3CN, Time of Polymerization: 1st Block: 72 Hours at 80°C (**LAB**) or 110°C (**FAB**); 2nd Block: 2-Methyl-2-oxazoline, 80°C for 24 Hours

Polymer No.	R_1	$\overline{DP_n}$ a) 1. block	$\overline{DP_n}$ b) 1. block	$\overline{DP_n}$ a) 2. block	$\overline{DP_n}$ b) 2. block	$\overline{M_n}$ c)	$\overline{M_w}$ / $\overline{M_n}$ c	Yield [%]
LAB 1	C_5H_{11}	10	11	50	139	2990	1.34	79
LAB 2	C_5H_{11}	20	21	50	132	3120	1.41	81
FAB 1	C_2F_5	5	4	50	52	2260	1.23	97
FAB 2	C_2F_5	10	7	50	53	2070	1.19	93
FAB 3	C_2F_5	15	14	50	51	1820	1.25	98
FAB 4	C_3F_7	10	9	50	56	2110	1.31	97
FAB 5	C_3F_7	20	17	50	53	2130	1.26	98

a) charged $[M]_0:[I]_0$ ratio; b) by ^1H NMR end-group analysis; c) by GPC measurements (polystyrene standards)

studied their polymer composition similar as described before. Table 1 summarizes the results of the polymerization of each block. The agreement of calculated and experimental degree of polymerization is excellent for the first block, however, we observed a significant difference for the second block. GPC analysis gave only one eluation peak of a slightly broader distribution compared to the fluorophilic block copolymers **FAB**. In addition, the total polymer yield decreases to 80% indicating that only the fraction with a sufficient high polymethyloxazoline content was obtained after reprecipitation of the copolymer mixture (diethyl ether/ chloroform). Due to the stronger inductive effect of the pentyl group compared to the methyl substituent pentyl group, the 2-pentyloxazolinium group is less reactive towards 2-methyl-2-oxazoline meaning that slow initiation is followed by fast propagation.

These results can be explained by the fact that the triflate anion is a weaker nucleophile than the tosylate. Therefore, the substituents of the oxazolinium end group is determining factor for the reactivity of the propagating chain end if **5** is used as initiator. In the case of tosylate anions, the differences in reactivity of 2-methyloxazolinium and 2-n-octyloxazolinium can be neglected and block copolymer synthesis published by Kobayashi *et al*. [22] becomes possible.



Scheme 3.

Steady-State Fluorescence Spectroscopy

Fluorometric techniques are excellent tools for studying dynamics and conformations of polymer chains and are particularly suited to monitor micellization processes. Amphiphilic block copolymers with fluorophores specifically attached at the end of the hydrophobic block offer versatile possibilities to study the corona part of the micellar structure. We have studied our block copolymers in two different solvents. In chloroform, as a good solvent for the block copolymer (unimers only), association was not observed and we were able to study the fluorescence behavior of molecular dispersed block copolymers. In aqueous solution, the molecular structure behave like an typical amphiphile forming micellar aggregates. The model compound N-(2-hydroxyethyl)-N-methyl-1-naphthylcarbonamide **6** was synthesized by hydrolysis of the oxazolinium salt **5**. The steady-state fluorescence spectrum (λ_{ex} = 293 nm) of the model compound in chloroform is shown in Figure 2.

The emission profile consists of a structured band with a maximum at (λ_{Em} = 341 nm. Figure 3 shows the emission spectra of the block copolymer **FAB 2** in chloroform. We observed a substantial loss of resolution of the typical naphthalene vibrational structure in comparison to the low molecular weight model compound. The spectra indicated two maxima at (λ_{Em} = 342 nm and 354 nm for all concentration and no excimer formation was found.

Finally, the fluorescence of **FAB 2** in aqueous solution at different concentration was studied. Only a strong and broad fluorescence band with a maxi-

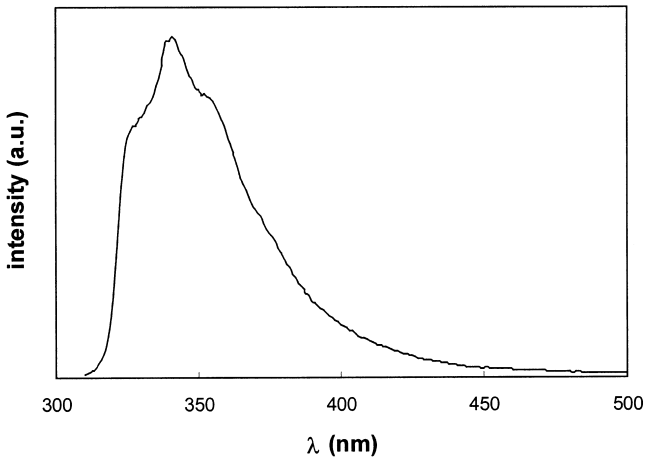


Figure 2. Fluorescence spectrum of N-(2-hydroxyethyl)-N-methyl-1-naphthyl-carbonamide; λ_{ex}=293 nm.

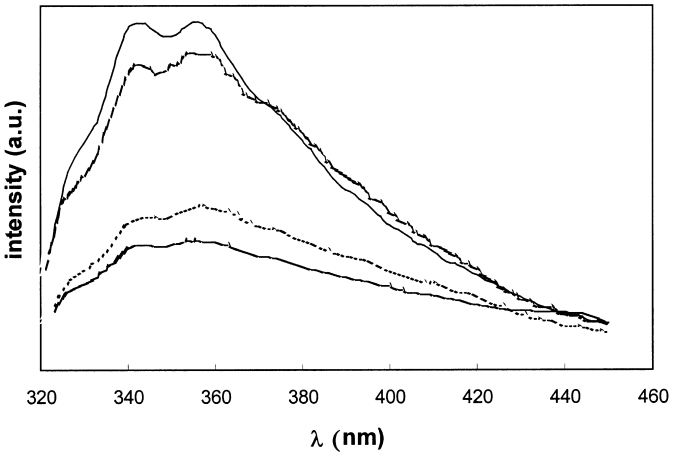


Figure 3. Fluorescence spectra for **FAB 2**; (— 10.0 g/L, — — 5.0 g/L, ---- 1.0 g/L, - — - — 0.5 g/L); λ_{ex}= 293 nm in chloroform.

mum at (λ_{Em}= 393 nm (Figure 4) could be detected. Due to the molecular structure of the block copolymers, this effect can only be explained by intermolecular excimer formation of neighboring block copolymers. It is noteworthy that almost no monomer fluorescence was observed. Excimers can be formed when the naphthalene groups are in a proper distance of about 3 Å. In addition, sufficient rotational freedom of the fluorophores and mobility of the polymer chain so that a cofacial sandwich geometry can be achieved is necessary. In contrast to the results reported by Prochazka *et al.* [14] where excimer formation in the

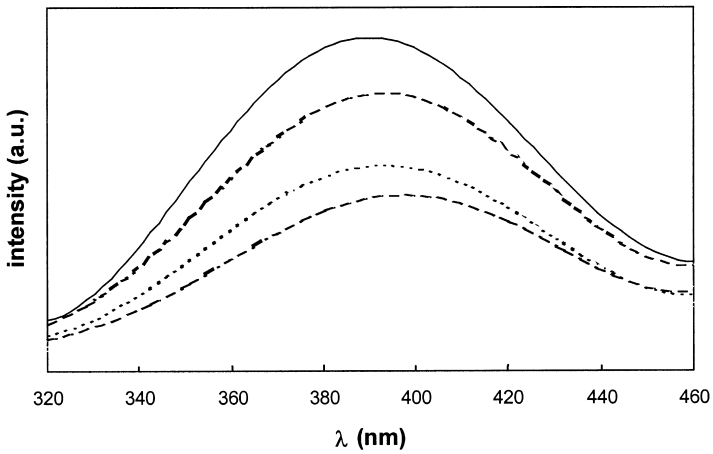


Figure 4. Fluorescence spectra of **FAB 2** in aqueous solution; (— 10.0 g/L; ---- 5.0 g/L, ·····1.0 g/L, -· - · - · - 0.5 g/L); λ_{ex}=293 nm.

micellar core was prevented by the limited rotational freedom of the naphthalene groups, our results demonstrated very clearly that the core enviroment of the **FAB 2** based micelles is not restricted. The naphthalene moieties still have the possibility to orientate in a cofacial sandwich conformation during monomer fluorescence.

From these results, we conclude that our micellar core is not very compact. The naphthalene labels were able to move and can form the sandwich geometry for excimer formation. The relatively short hydrophobic part of the block copolymer (5 to 20 repeating units) might be of advantage for the intermolecular excimer formation compared to the systems used by Ramireddy *et al* [13] (200 to 320 polystyrene units). Moreover, the hydrophobic (N-acyl-ethylenimines) units are still of amphiphilic character due to the amide function.

CONCLUSION

A novel method for the introduction of a fluorescence probe into block copolymers by the use of naphthalene labeled oxazolinium salts was demonstrated. We were able to synthesize fluorophilic block copolymers of precise structure however the synthesis of lipophilic block copolymers with a controlled composition were not possible within the same parameters. Steady state fluorescence spectroscopy of the micelles in aqueous solution of **FAB 2** showed strong intermolecular excimer formation and demonstrated the utility of the end-capped block copolymers to study micelle formation.

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