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Yanjie Pang<sup>a</sup>; Mahesh Kumar Sarvothaman<sup>a</sup>; Helmut Ritter<sup>a</sup>

<sup>a</sup> Institute of Organic Chemistry and Macromolecular Chemistry II, Heinrich-Heine-University of Duesseldorf, Duesseldorf, Germany

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# Novel Synthetic Routes to Synthesis of 5-(Methacryloylamino)-fluorescein and Fluorescent Polymers using 5-MAF as Fluorescent Marker

YANJIE PANG, MAHESH KUMAR SARVOTHAMAN,  
AND HELMUT RITTER

Institute of Organic Chemistry and Macromolecular Chemistry II,  
Heinrich-Heine-University of Duesseldorf, Duesseldorf, Germany

*5-(Methacryloylamino)-fluorescein (5-MAF), a water-soluble fluorescence monomer, was synthesized in high yield via a new synthetic approach. Fluorescent polymers containing 5-MAF as fluorophore were synthesized by copolymerization with other hydrophilic monomers. The fluorescence behavior of these polymers were recorded which revealed interesting effects in diverse conditions. Hydrophobic fluorescent polymers with 5-MAF again as the fluorophore was also prepared via complexation with methylated  $\beta$ -cyclodextrin (Me- $\beta$  CD). N-(tert-butyl)acrylamide, a insoluble monomer, was complexed with Me- $\beta$  CD in varying stoichiometries in water and copolymerized with 5-MAF at 0°C to obtain polymers with strong fluorescence ability.*

**Keywords** fluorescent polymers, synthesis of 5-MAF, high-yield, cyclodextrin

## Introduction

The past decade has witnessed enormous research being performed in the field of fluorescent monomers and polymers primarily owing to their interesting and versatile applications. Fluorescein and its derivatives are members of phenyl xanthene dyes and are widely recognized fluorescent markers in biological and medical researches due to its brilliant fluorescence capability (1–3). Water-soluble fluorescent polymers find potential application as sensors in studying the mechanism of thickeners and as tracers or monitors for understanding the behaviors of biological macromolecules (4). Typical fluorescent polymer synthesis involves two approaches—either a chemical modification of polymers by fluorescent molecules (5–7) or by polymerization of fluorescent monomers (8–10). In this work, we used 5-(methacryloylamino)-fluorescein (5-MAF) as a fluorescent monomer to synthesize fluorescent polymers. 5-MAF is an efficient member among fluorescent monomers, which is water-soluble and effectively fluoresces

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Address correspondence to Helmut Ritter, Institute of Organic Chemistry and Macromolecular Chemistry II, Heinrich-Heine-University of Duesseldorf, Universitätsstr. 1, 40225 Duesseldorf, Germany. Fax: (+49) 211 81 15840; E-mail: H.Ritter@uni-duesseldorf.de

in alkaline media. Its fluorescence changes sensitively with the basicity of the aqueous solution, the more alkaline solution exhibiting stronger fluorescence within a pH range of 6 to 12. In addition, the presence of a salt in solution has a diverse influence on the fluorescence of 5-MAF.

The synthesis of 5-MAF was reported earlier where the yield was either below 10% or hardly mentioned (11–13); this prompted us to achieve high yields through a new synthetic approach. We also report the synthesis of water-soluble fluorescent polymers through a one-step radical polymerization of 5-MAF with other water-soluble monomers. 5-MAF copolymerizes with hydrophobic comonomers forming corresponding hydrophobic fluorescent polymers as well. Copolymerization of 5-MAF with a hydrophobic monomer like *N*-(*tert*-butyl)acrylamide in water mediated through inclusion complexation into a methylated  $\beta$ -cyclodextrin ring to obtain hydrophobic fluorescent polymers is a further part of this work.

## Experimental

### Materials

5-aminofluorescein (5-AF) was purchased from Fluka and used as received. Methylated  $\beta$ -cyclodextrin (Me- $\beta$  CD) was obtained from Wacker-Chemie GmbH, Germany. Me- $\beta$  CD had an average degree of methylation of 1.8 per anhydro glucose unit. *N*-(*tert*-butyl)acrylamide was prepared by a general organic synthetic method (14). All the other reagents were of commercial standards, obtained either from Fluka or from Merck and used without any further purification. The solvents were extra dry and stored over molecular sieves of 3 or 4 Å. The technical solvents for flash column chromatography and polymerizations were distilled before use.

### Measurements

200 MHz  $^1\text{H}$ -NMR spectra were measured on a Bruker Avance DRX 200, and 500 MHz  $^{13}\text{C}$ -NMR spectra on a Bruker Avance DRX 500. IR spectra were recorded with a Nicolet 5SXB FTIR spectrometer, and MALDI-TOF spectra were measured with a Micromass TofSpec-MS spectrometer. DSC measurements were carried out with a Mettler DSC 30. The ESI-TOF Mass spectra measurements were accomplished on a Bruker Esquire 3000, and the dynamic Light Scattering measurements were carried out with a Malvern HPPS-ET equips with a Non-Invasive Back-Scatter technology. SEC were recorded with THF as eluent. The fluorescence spectra were recorded when not mentioned with a JASCO FP-6200.

### Synthesis of 5-MAF

5.4 g (14.5 mmol) of trimethylsilyl chloride was added dropwise under cooling in an ice-bath to a solution of 5.0 g (14.5 mmol) of 5-AF and 6.4 g (63.1 mmol) of *N,N,N*-triethylamine in 200 mL of dichloromethane. The mixture was stirred at room temperature (RT) for 20 h. 2.0 g (18.8 mmol) of methacrylic acid chloride was dropped into this solution under cooling. The mixture was stirred for 20 h at RT and the resulting precipitate was subsequently removed and the solution was hydrolyzed by stirring with water. After 4 h, the crude product precipitated as a yellow solid. The collected crude product was separated and reprecipitated with 1 N NaOH and con. HCl. The product was further purified by flash column chromatography using ethanol/ $\text{CHCl}_3$  (1 : 4 v/v) to give 5.0 g of 5-MAF.

Yield (in comparison with 5-AF) 82%, orange amorphous solid  $R_f$ : 0,71 (Ethanol: Chloroform 1 : 4 v/v).  $^1\text{H NMR}$  (500 MHz,  $\text{DMSO-d}_6$ ):  $\delta$  2,06 (s, 3H); 5,67 (s, 1H), 5,96 (s, 1H), 6,64 (d, 2H), 6,66 (d, 2H); 6,77 (s, 2H); 7,30 (d, 1H), 8,09 (d, 1H); 8,46 (s, 1H) 10,35 (s,  $-\text{NH}-$ , 1H) FT-IR (ATR): 3330, 2921, 1703, 1680, 1634 (amide I), 1520 (amide II), 849, 798  $\text{cm}^{-1}$  ESI-TOF MS:  $m/z$ : 414,2 FAB MS:  $m/z$ : 416 (+H)

### Synthesis of Water-Soluble Fluorescent Polymers

Details of each polymerizations are listed in Table 1. The syntheses of P1, P3, and P4 were performed in an ampoule after feeding it with the desired amount of 5-MAF, comonomers, initiator, and water. The resulting solution was thoroughly degassed and the ampoule was sealed under vacuum. It was then placed in a drying oven at a temperature of  $65^\circ\text{C}$  for 20 h. The resulting polymer solutions were diluted in methanol and the polymer precipitated by adding the same volume of diethylether. The polymers were recovered by centrifugation, dried and purified after reprecipitation twice in methanol/ether/n-hexan (1 : 0.2 : 1 v/v/v).

### Synthesis of Water-Insoluble Fluorescent Polymers

Copolymerization of 5-MAF with the hydrophobic monomer *N*-(*tert*-butyl)acrylamide was performed in the presence of Me- $\beta$  CD. To a 50 wt% aqueous solution of Me- $\beta$  CD (11 mL), equimolar amounts of *N*-(*tert*-butyl)acrylamide was added, after flushing the solution with a strong stream of nitrogen gas. The solution mixture was stirred continuously under nitrogen for nearly 2 h to obtain a homogenous, colorless solution of the complexed monomer in water. 5-MAF (0.5 wt%) is added to this complexed solution, and stirred again for 30 mins. Polymerization is then carried out under ice using redox initiators  $\text{Na}_2\text{S}_2\text{O}_5$  and  $\text{K}_2\text{S}_2\text{O}_8$  (2 mol equivalents each) (15). The resulting polymer gets precipitated in about 2 h reaction time, and was recovered by centrifugation. The fluorescent polymer in about 85% yield was washed repeatedly with water to remove the residual Me- $\beta$  CD. A polymer corresponding to a stoichiometric 1 : 2 monomer/Me- $\beta$  CD complex was also prepared likewise.

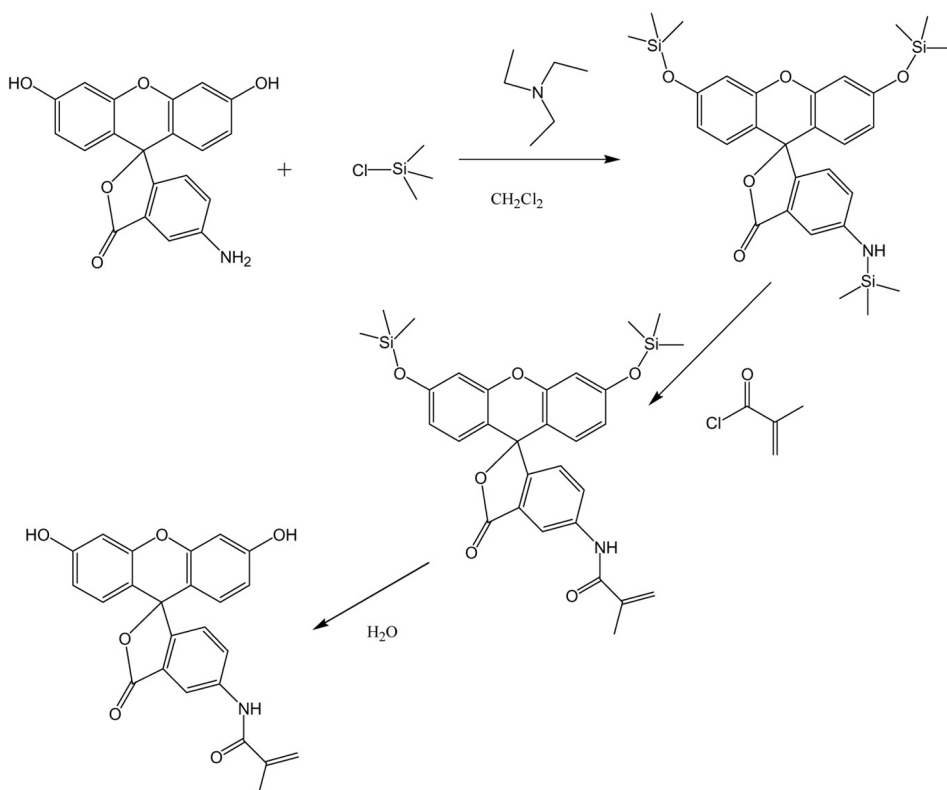
## Results and Discussion

### Preparation of 5-MAF

5-MAF was prepared from 5-aminofluorescein (5-AF), which holds two aromatic hydroxy groups and an aromatic amine group (Figure 1). The two functional groups have similar

**Table 1**  
Recipes for the syntheses of water-soluble fluorescent polymers

Reagenzien	P1	P2	P3	P4
AMPS	2903.1 mg	2900 mg	2900.8 mg	687.9 mg
5-MAF	7.0 mg	7.3 mg	14.5 mg	76.4 mg
AAPH	127.0 mg	127.8 mg	126.9 mg	31.7 mg
$\text{H}_2\text{O}$	16 ml	16 ml	16 ml	5 ml



**Figure 1.** Synthesis of 5-MAF via a new method.

activity and both react favorably with methacrylic acid chloride. A selective reaction at the amine group was achieved by modifying 5-AF to the silylated intermediate (1), by reacting with trimethylsilyl chloride. Both the hydroxy groups were thus protected owing to the large affinity of oxygen to silicon and in turn, the amino group will be activated through the trimethylsilyl group. Without any further separation of 2 involved, methacrylic acid chloride was added which preferentially condenses with the amino group. After a further hydrolysis of the formed 2, the main product 5-MAF is recovered in high yield up to 85%. 5-MAF was found to be soluble in general solvents in addition to water, such as THF, DMF, DMSO methanol and ethanol. It was characterized by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, ESI-TOF Mass, FTIR, UV-VIS, and fluorescence spectroscopy.

Silylation is known in general to be a suitable method for activating aromatic amine groups. A good example is shown by synthesis of all-para-polyamide through polycondensation of trimethylsilyl-substituted 2-chloro-1,4-phenylenediamine with terephthaloyl dichloride (16). Furthermore, silylation is also a very suitable method for simultaneous protection and activation of compounds holding both hydroxy and amino groups, ultimately leading to selective amide formation of the parent compound. In an earlier paper (17), we have reported the selective synthesis of amide derivatives of 4-amino-phenol with the same method. The synthesis was likewise successful.

The  $^1\text{H}$  NMR-spectrum of the synthesized 5-MAF is shown in Figure 2. Proton signals corresponding to all the H-Atom of 5-MAF are clearly visible in the spectrum and the integrals of the signals agree well with the structure. FTIR-spectrum also shows characteristic

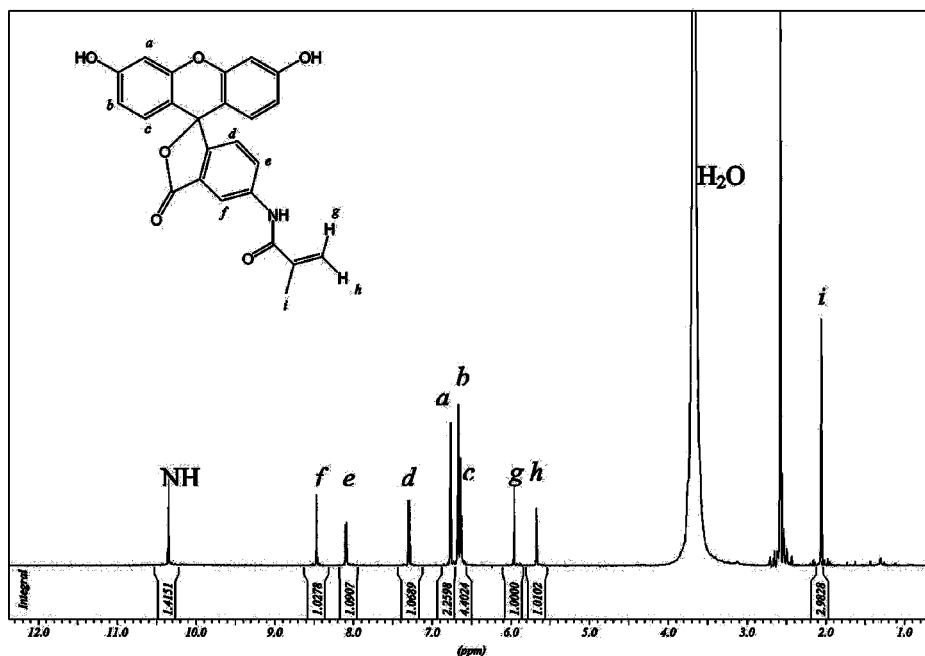


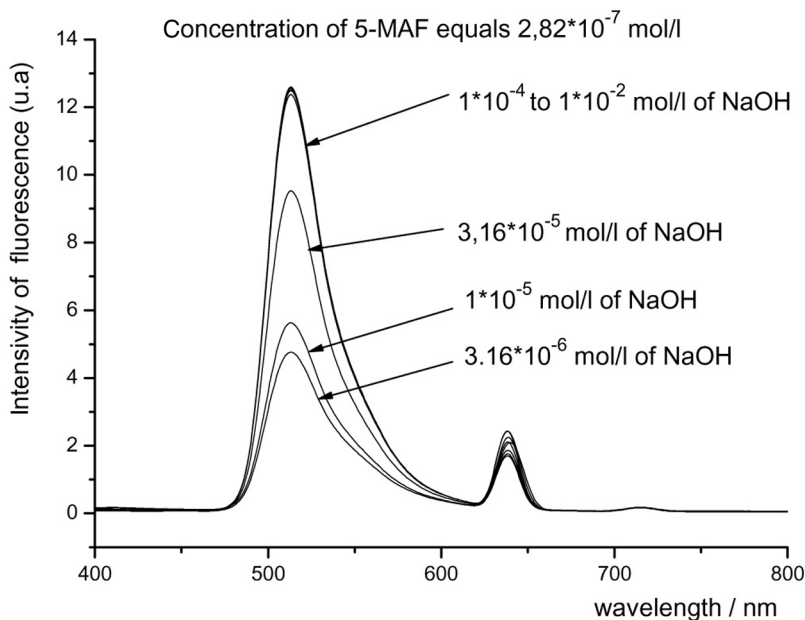
Figure 2. <sup>1</sup>H NMR Spectrum of 5-MAF (500 MHz, DMSO-d<sub>6</sub>).

spectral frequencies due to the formed amide groups, thereby establishing the successful synthesis of 5-MAF. 5-MAF is an orange amorphous solid that dissolves in common organic solvents besides water. An aqueous solution of 5-MAF with a concentration of  $10^{-5}$  mol/L fluoresces very effectively. Under daylight, it gives a green fluorescence, which becomes much stronger under UV-irradiation.

Figure 3 shows the fluorescence spectrums of the aqueous solution of 5-MAF with a concentration of  $2.82 \times 10^{-7}$  mol/L and in varying amounts of NaOH. It is clearly observed that the fluorescence changes very sensitively with the concentration of NaOH to the range of  $10^{-6}$  to  $10^{-4}$  mol/L. However, the  $\lambda_{\max}$  of the fluorescent bands always remain a constant at 513 nm, irrespective of basicity of solutions though their intensities largely differs with basicity. The fluorescence of 5-MAF changes sensitively with the polarity of the solvent, the more polar solvent giving a stronger fluorescence. To add to these specifications, 5-MAF is highly stable and has a long storage life.

### ***Synthesis of Water-Soluble Fluorescent Polymers Through Radical Polymerization of 5-MAF with Water-Soluble Monomers***

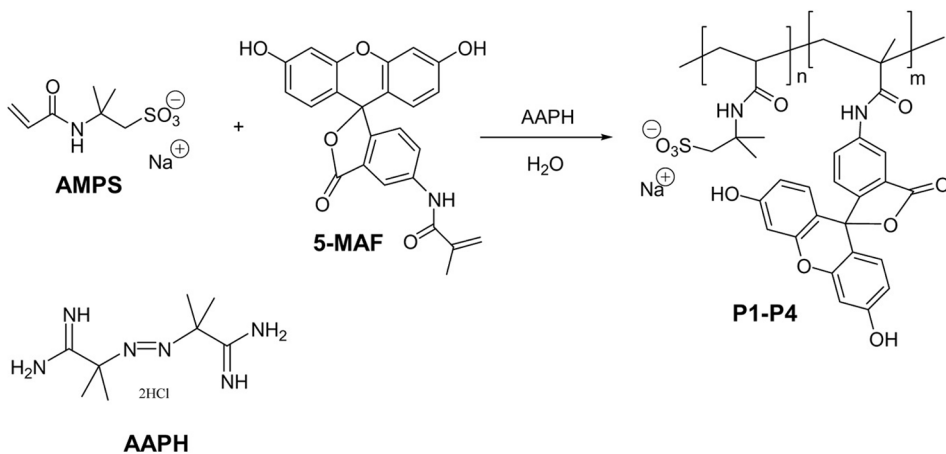
Water-soluble fluorescent copolymers were synthesized using hydrophilic sodium-2-acrylamido-2-methyl-propanesulfonate (AMPS) as comonomers and the water-soluble 2,2'-azobis-(2-methyl-propionamidin)-dihydrochloride (AAPH) as initiator. The polymerizations were carried out in water (Figure 4). The conditions and results are summarized in Table 2. After polymerization the polymers were purified by re-precipitation simultaneously removing unreacted monomers and low-molecular weight oligomers. The polymers obtained were soluble in methanol apart from water. The color of polymers varied from pale yellow to red with increasing content of 5-MAF. The polymers except



**Figure 3.** Fluorescence spectra of aqueous solution of 5-MAF in the presence of different amount of NaOH.

P4 displayed very strong fluorescence behaviors both in solid state and in aqueous solutions under UV-irradiation. In P4, the relatively high amount of 5-MAF reduces the distance between two adjacent 5-MAF molecules and the fluorescence is quenched resulting in a weak fluorescence by P4.

The chemical structure of the polymers was confirmed by IR and  $^1\text{H}$  NMR spectra. The photo-physical behavior was confirmed by UV-VIS and fluorescence spectroscopy. Figure 5 shows the  $^1\text{H}$  NMR spectrum of the polymer P4, which evidently supports the



**Figure 4.** Synthesis of water-soluble fluorescent copolymers via radical polymerization.

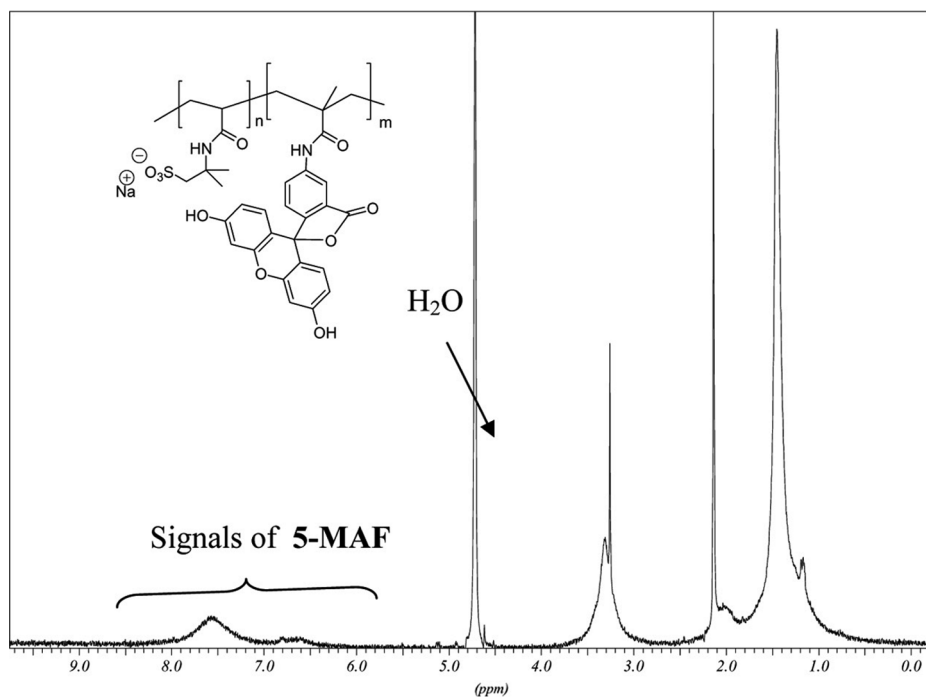
**Table 2**  
Synthesis of water-soluble fluorescent polymers via radical polymerizations

Polymer no.	Content of 5-MAF wt%	Conc. of monomer wt%	Temp. °C	Initiator mol%	Yield	$M_w^a$	$D^a$	$T_g$ °C
P 1	0.24	15.4	65	3.7	92%	378000	1.28	160.2
P 2	0.25	15.4	65	3.7	89%	491000	1.29	159.3
P 3	0.50	15.4	65	3.7	92%	366000	1.27	121.5
P 4	10.00	13.5	65	3.9	78%	198000	1.48	156.0

<sup>a</sup> $M_w$  and  $D$  were estimated by dynamic light scattering.

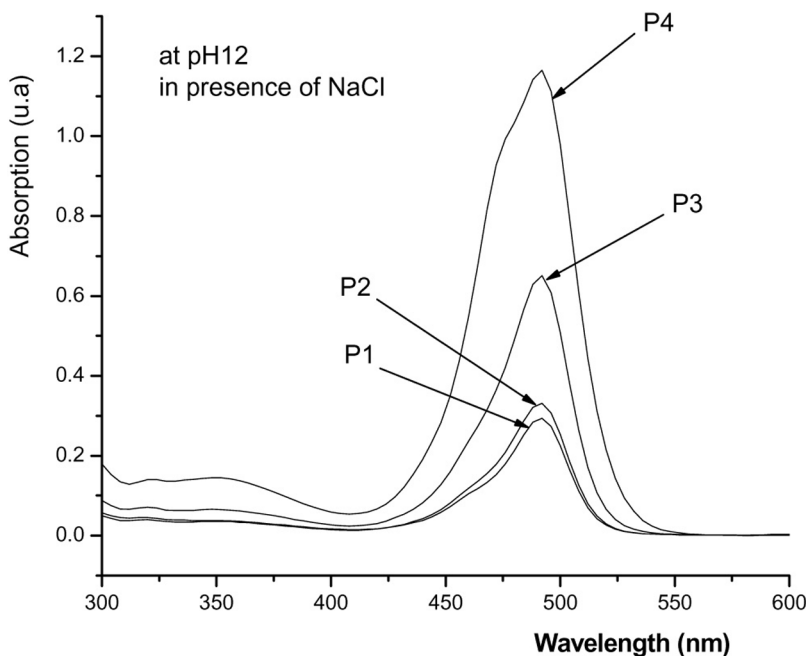
copolymerization of 5-MAF with AMPS/DMAA. The proton signals from 5-MAF can be observed between 6.0 and 9.0 ppm, which, due to the copolymerization, are strongly spread. Likewise, strongly spread signals between 1.0 and 4.0 ppm belong to polymerized AMPS.

A statistical evaluation to determine 5-MAF content in the synthesized polymers was performed using UV-VIS spectroscopy. Figure 6 shows the UV-VIS-spectra of the fluorescent polymers measured at a constant concentration of 0.1 wt%. The absorption band for P1 and P3 at 492 nm is clearly visible just as the monomeric 5-MAF, which indicates that the conformation of 5-MAF is unchanged even after the polymerization.



**Figure 5.** <sup>1</sup>H NMR-spectrum (500 MHz, D<sub>2</sub>O) of the synthesized P4.





**Figure 6.** UV-VIS spectra of synthesized water-soluble fluorescent polymers. The spectra were recorded at pH12 in the presence of salt.

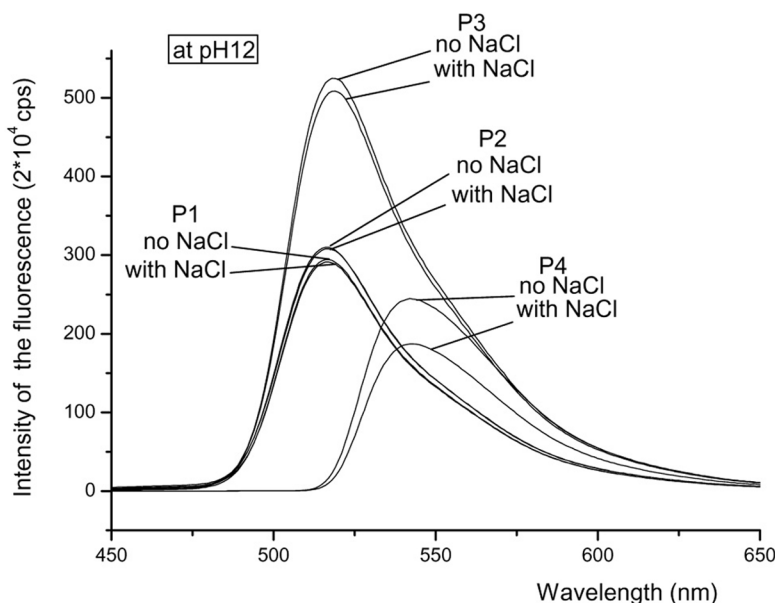
The intensity of the absorptions at 492 nm correlates to the amount of 5-MAF present in the polymers. Exceptional behavior is noticeable in P4 in which the thick UV-VIS-absorption bands consists of two bands that are different from the monomeric 5-MAF, indicating a possible conformation change due to the high density of the voluminous 5-MAF in the polymer.

The fluorescence spectra of synthesized fluorescent polymers at pH12 in presence and absence of NaCl are shown in Figure 7. The presence of salt has diverse influence on the fluorescence intensity, yet does not change the  $\lambda_{\max}$  of the fluorescence band.

Nevertheless, P4 shows a fluorescence band at about  $\lambda_{\max}$  542 nm indicating a possible formation of aggregation of 5-MAF in the polymer. There must be considerable stress induced in the polymer chain of P4 because of the presence of the more voluminous groups in the polymer chain. Additionally, the fluorescence of the polymers at pH 7 in the presence and absence of NaCl were also measured. The results are summarized in Table 3.

#### ***Synthesis of Hydrophobic Fluorescent Polymers Through Radical Polymerization of 5-MAF with *N*-(*tert*-butyl)acrylamide***

Hydrophobic polymers exhibiting fluorescence property were obtained successfully in aqueous medium (Figure 8). The property of methylated  $\beta$ -cyclodextrin to form highly water soluble inclusion complexes with hydrophobic molecules was utilized to dissolve a completely insoluble monomer like *N*-(*tert*-butyl)acrylamide in water (18, 19). The fluorescing monomer 5-MAF in a relatively low proportion (only 0.5 wt%) was added to the *N*-(*tert*-butyl)acrylamide-Me- $\beta$  CD complex and copolymerized at 0°C yielding the polymer in a considerable yield. The obtained yellow solid



**Figure 7.** Fluorescence spectra of synthesized fluorescent polymers. The concentration of the polymer solutions remains constant for all measurements at 0.1 wt%. (The spectra were recorded using a FloroMax-3 of Jobin.)

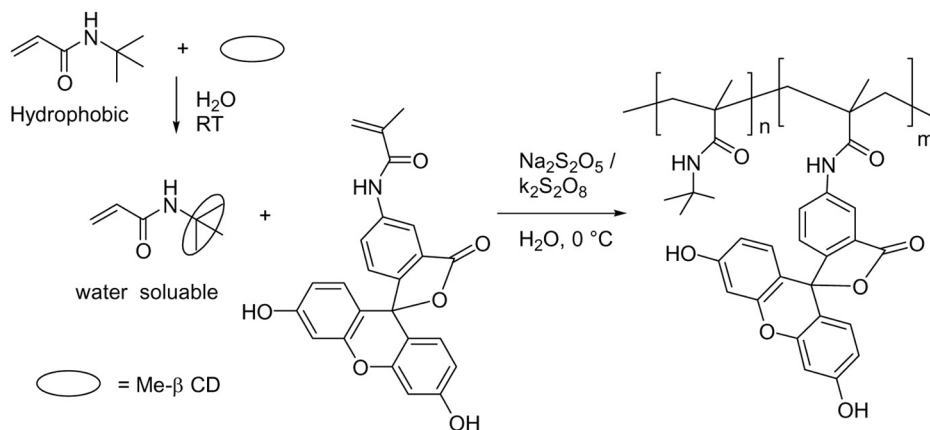
polymer has a glass transition temperature of 147.3°C. The measurement of SEC shows an average number molecular weight of 4600 with a polydispersity of 2.22. The polymer exhibited strong fluorescence in solid state and also in organic solvents. The fluorescence ability changes just as the monomeric 5-MAF with the polarity of the solvent, showing a intense fluorescence band at  $\lambda_{\max}$  515 nm in methanol and a comparatively weak fluorescence band at  $\lambda_{\max}$  408 nm in DMF. The relative fluorescence spectra for these two solvents are shown in Figure 9. A similar polymer obtained from a stoichiometric 1 : 2 *N*-(*tert*-butyl)acrylamide-Me- $\beta$  CD complex using the same amount of the fluoro-

**Table 3**

Fluorescence of synthesized water-soluble fluorescent polymers. Concentration of the polymer solutions remain the same for all of measurements at 0.1 wt%<sup>a</sup>

Polymer no.	$\lambda_{\max}$ of the fluorescence band (nm)				Intensity of fluorescence ( $2 \times 10^4$ cps)			
	pH 7		pH 12		pH 7		pH 12	
	no salt	with salt	no salt	with salt	no salt	with salt	no salt	with salt
P1	518	516	517	517	35.2	182.6	294.1	291.4
P2	517	516	517	517	39.1	171.6	309.8	308.0
P3	518	516	518	519	56.4	206.8	525.0	508.5
P4	542	538	542	543	143.6	121.0	244.7	187.0

<sup>a</sup>The fluorescence spectra were recorded with a FloroMax-3 of Jobin Yvon.

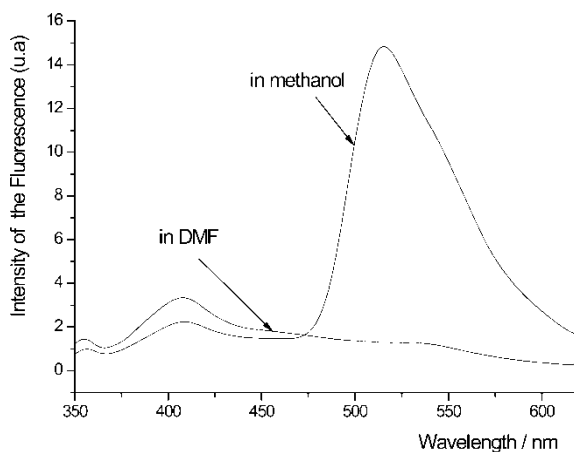


**Figure 8.** Synthesis of hydrophobic fluorescent polymers in water in the presence of cyclodextrin via radical polymerization.

phore exhibited the same property suggesting a zero-effect on the fluorescence property of the polymer with increasing amounts of Me- $\beta$  CD used for complexation.

## Conclusions

Water-soluble fluorescent monomer 5-MAF was synthesized via a new method with high yield. The behavior of 5-MAF was studied. 5-MAF was radically polymerized with other hydrophilic comonomers yielding highly effective water-soluble fluorescent polymers. The fluorescence behaviors of these polymers were recorded under varying conditions. Additionally, hydrophobic fluorescent polymers based on *N*-(*tert*-butyl)acrylamide and 5-MAF were synthesized via inclusion complexation with methylated  $\beta$ -cyclodextrin in water. The fluorescent capability of these polymers were studied as well. The exceptional



**Figure 9.** Fluorescence spectra of hydrophobic polymer in methanol and DMF. The concentration of the polymer amounts to 1 g/L.

emission characteristics shown by the polymers enable their convincing use as sensor for understanding the nature and efficiency of thickeners in alkaline media and in the presence of salt.

## Acknowledgements

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