Well-defined novel fluorene-containing polymers

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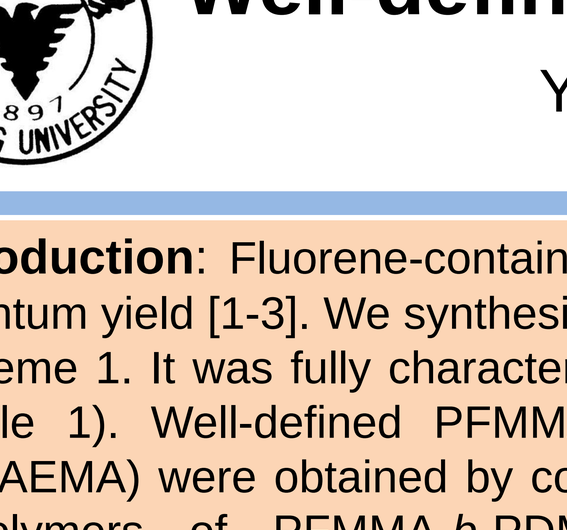
Introduction: Fluorene-containing vinyl monomers and their polymers have strong fluorescent emission with high quantum yield [1-3]. We synthesized a new monomer, 9,9-diethylfluoren-2-yl methyl methacrylate (FMMA) as shown in Scheme 1. It was fully characterized by means of NMR, FT-IR (Fig. 1 and 2), Mass spectra and elemental analysis (Table 1). Well-defined PFMMA, block and random copolymers with 2-(N,N-dimethylamino)ethyl methacrylate (DMAEMA) were obtained by controlled RAFT polymerizations (Scheme 2 and Table 2). Spherical micelles of block copolymers of PFMMA-*b*-PDMAEMA were obtained in water. The PFMMA core of micelles showed photoluminescence when carrying dichloromethane "guest" molecules and the emission was quenched after the release of the guest (Fig. 10) [4].

Synthesis of monomer



Scheme 1. Synthesis of 9,9-diethylfluoren-2-yl methyl methacrylate.

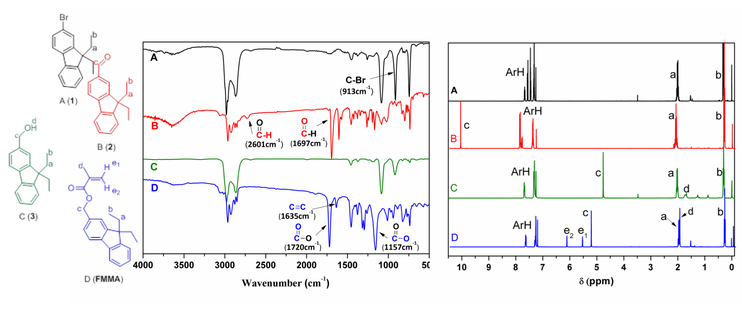


Fig. 1. ^{1}H NMR and FT-IR spectra of **1** (A), **2** (B), **3** (C) and FMMA (D).

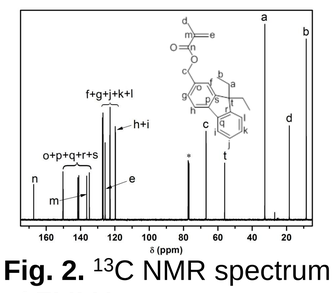


Fig. 2. ^{13}C NMR spectrum of FMMA.

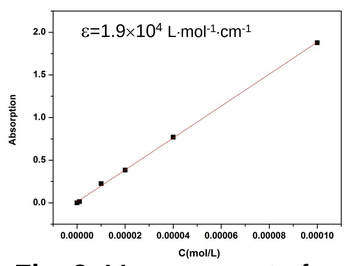
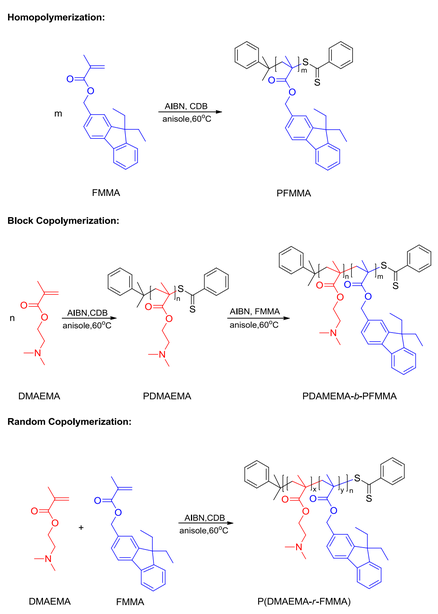


Fig. 3. Measurement of molar absorptivity of FMMA by UV-Vis spectra at 306 nm.

Table 1. The Mass Spectra and element analysis results and theoretical values of **1**,**2**,**3** and FMMA.

Run	Mn(Exp.)	Mn(Theo.)	C(%)Expe.	C(%)Theo.	H(%)Expe.	H(%)Theo.
1($C_{17}H_{17}Br$)	301.22	301.22	67.56	67.78	5.65	5.69
2($C_{18}H_{18}O$)	250.33	250.14	86.36	86.13	7.82	7.25
3($C_{18}H_{20}O$)	251.10	252.35	86.78	85.67	8.22	7.99
FMMA($C_{22}H_{24}O_2$)	320.42	320.42	82.09	82.46	7.68	7.55

Polymerizations



Scheme 2. Synthesis of PFMMA, PDMAEMA-*b*-PFMMA and P(DMAEMA-*r*-FMMA).

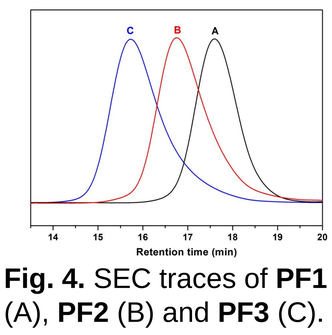


Fig. 4. SEC traces of **PF1** (A), **PF2** (B) and **PF3** (C).

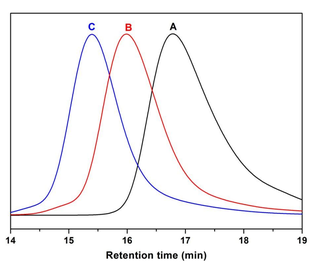
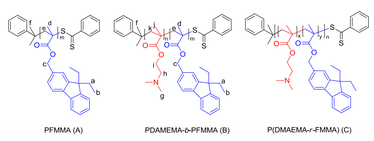


Fig. 5. SEC traces of **PD** (A), **PDF1** (B) and **PDF2** (C).

Table 2. Polymerizations of FMMA, DMAEMA at 60 °C in anisole.

Sample	Monomer	$[M]_0$/ $[CTA]_0$	Time (h)	Yield (%)	[DMAEMA]/ [FMMA] in polymer	$M_{n,thero.}$ (kDa)	$M_{n,SEC}$ (kDa)	PDI
PF1	FMMA	6.7/1	20	85.3	-	2.1	3.8	1.06
PF2	FMMA	20/1	20	82.8	-	5.6	5.8	1.14
PF3	FMMA	63/1	20	65.6	-	13.5	10.6	1.14
PD	DMAEMA	35/1	20	65.1	-	3.9	5.4	1.14
PDF1	FMMA	18/1	16	74.7	100/50	9.7	8.8	1.12
PDF2	FMMA	34/1	16	70.5	100/91	13.1	11.9	1.14
PDrF	FMMA+ DMAEMA	30/30/1[d]	12	60.9	100/86	9.0	7.0	1.17



Thermal properties

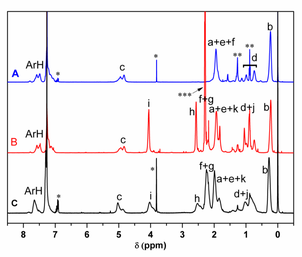


Fig. 6. ^{1}H NMR spectra of **PF3** (A), **PDF1** (B) and **PDrF** (C) in $CDCl_3$

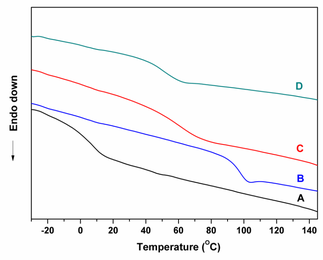


Fig. 7. DSC profiles of **PD** (A), **PF2** (B), **PDF2** (C) and **PDrF** (D).

Photoluminescence

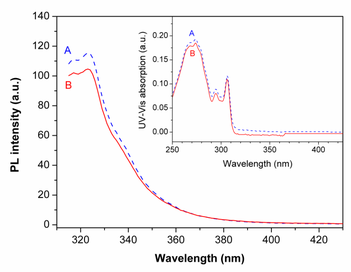


Fig. 8. UV-Vis and PL at the excitation wavelength of 306 nm of **PF2** (A) and **PDF1** (B) with the concentrations of FMMA unit of at 10^{-5} mol/L in THF.

Micellization

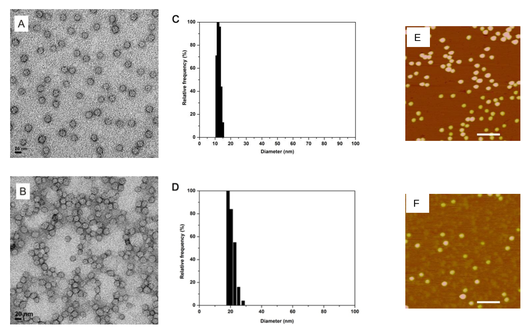


Fig. 9. TEM, DLS and AFM measurements of **PDF1** (A, C, E) and **PDF2** (B, D, F) in aqueous media at 25 °C.

The critical micelle concentration values of **PDF1** and **PDF2** are 2.75×10^{-3} g/L and 1.02×10^{-3} g/L, respectively. The sizes of spherical micelles are about 20 nm.

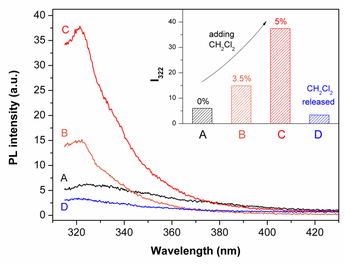


Fig. 10. Emission spectra of **PDF1** in H_2O (A), CH_2Cl_2/H_2O (v/v)=3.5% (B), CH_2Cl_2/H_2O (v/v)=5% (C), and after the release of CH_2Cl_2 (D), respectively.

The micelle is able to accommodate guest molecules in its hydrophobic PFMMA core hence decreasing the aggregation-induced quenching effect. Upon release of the guest molecules, re-aggregation of the PFMMA blocks follows resulting in fluorescence quenching.

Conclusions: A novel fluorene-containing methacrylate monomer has been synthesized and used in controlled RAFT free radical polymerizations. The micellization of the PDMAEMA-*b*-PFMMA were studied by DLS, TEM and AFM. Their hydrophobic FMMA cores are potentially capable to carry guest molecules with their release being monitored by fluorescence.

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References: [1] R. Chen, X. Zhang, T.E. Hogen-Esch, Macromolecules 36 (2003) 7477.
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