Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information for

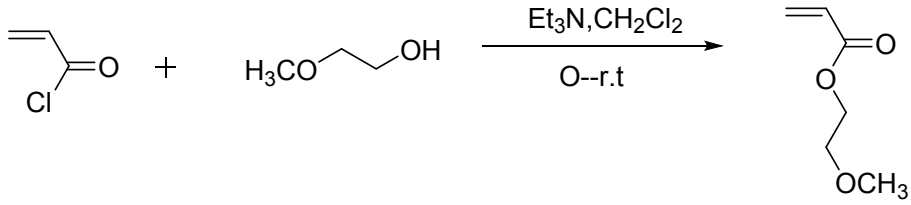
New Difluoromethoxyl-Containing Acrylate Monomer for PEG-*b*-PDFMOEA Amphiphilic Diblock Copolymer

Liu Haoyu, *Guolin Lu*,* *Chun Feng*, *Xiaoyu Huang**

Key Laboratory of Synthetic and Self-Assembly Chemistry for Organic Functional Molecules, Center for Excellence in Molecular Synthesis, Shanghai Institute of Organic Chemistry, University of Chinese Academy of Sciences, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, People's Republic of China.

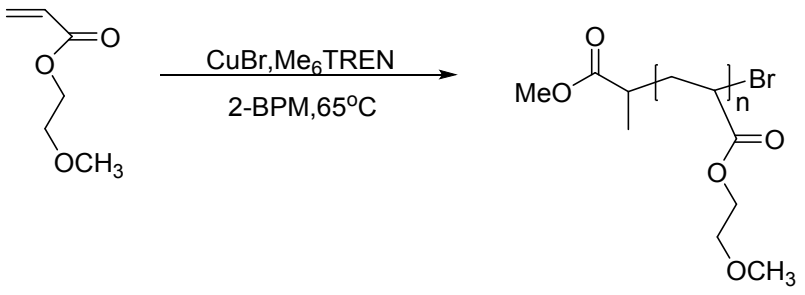
* To whom correspondence should be addressed, E-mail: luguolin@sioc.ac.cn (Tel: +86-21-54925546, Fax: +86-21-64166128); xyhuang@mail.sioc.ac.cn (Tel: +86-21-54925310, Fax: +86-21-64166128).

Synthesis of 2-methoxyethyl acrylate



Ethylene glycol monomethylether (19.32 g, 253 mmol) and Et_3N (52.8 mL, 381 mmol) were dissolved in 300 mL of anhydrous dichloromethane. The solution was cooled to 0°C followed by adding acryloyl chloride (24.8 mL, 304 mmol) dropwise within 30 min. The mixture was slowly warmed up to room temperature and stirred at room temperature for 12 h. The precipitated salt was removed by filtration and the filtrate was washed with brine three times. The volatiles were rotary evaporated and the residue was distilled at 68°C under reduced pressure to give 24.6 g (75% yield) of colorless liquid. ^{1}H NMR: δ (ppm): 3.37 (s, 3H, $CO_2CH_2CH_2OCH_3$), 3.61 (t, 2H, $3J$ = 4.0 Hz, $CO_2CH_2CH_2OCH_3$), 4.29 (t, 2H, $3J$ = 4.0 Hz, $CO_2CH_2CH_2OCH_3$), 5.82 (d, 1H, $2J$ = 8.0 Hz, CH=CH_2), 6.14 (dd, 1H, $2J$ = 8.0 Hz, $3J$ = 16.0 Hz, CH=CH_2), 6.40 (d, 1H, $3J$ = 16.0 Hz, CH=CH_2).

ATRP Homopolymerization of 2-methoxyethyl acrylate



CuBr (22.7 mg, 0.17 mmol), Me_6TREN (0.064 mL, 0.24 mmol), 2-MBP (0.018 mL, 0.16 mmol) and 2-methoxyethyl acrylate (1.65 g, 12.6 mmol) were first added to

a 25 mL Schlenk flask (flame-dried under vacuum prior to use) sealed with a rubber septum for degassing and kept under N_2. The flask was degassed by three cycles of freezing-pumping-thawing followed by immersing the flask into an oil bath set at 65°C. The polymerization was terminated after 1 h by immersing the flask into liquid N_2. The reaction mixture was dissolved by THF and was purified by flash chromatography on neutral alumina. THF was rotary evaporated and the crude product was precipitated in hexane/diethyl ether (v:v = 5:1) three times followed by drying *in vacuo* overnight to give a colorless oil of poly(2-methoxyethyl acrylate) (PMOEA) homopolymer (739 mg). GPC: M_n = 14,000 g/mol, M_w/M_n = 1.31. ^{1}H NMR: δ (ppm): 0.87, 1.14, 1.25 (3H, C*H*$_3$CHCO$_2$CH$_3$), 1.53, 1.68, 1.94 (2H, C*H*$_2$CH), 2.38 (1H, CH$_2$C*H*), 3.35 (3H, CO$_2$CH$_2$CH$_2$OC*H*$_3$ and CH$_3$CHCO$_2$C*H*$_3$), 3.56 (2H, CO$_2$CH$_2$C*H*$_2$OCH$_3$), 4.20 (2H, CO$_2$C*H*$_2$CH$_2$OCH$_3$).

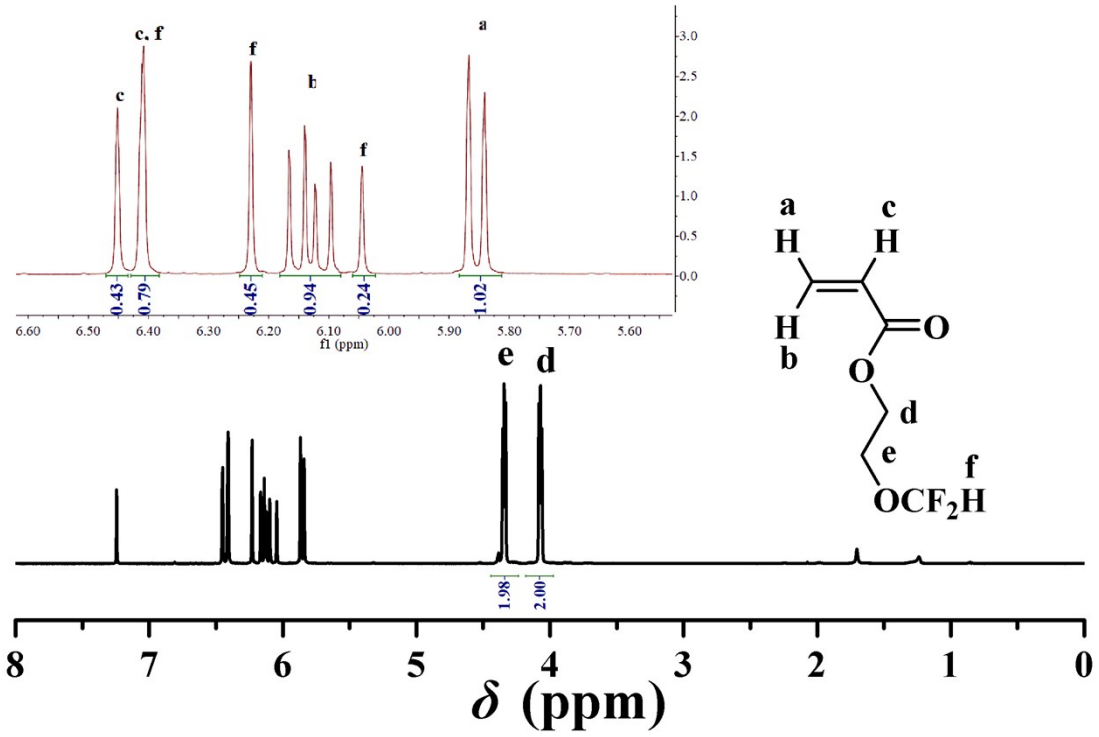


Figure S1. ^{1}H NMR spectrum of DFMOEA in $CDCl_3$ (inset: the expansion between 5.60 ppm and 6.60 ppm).

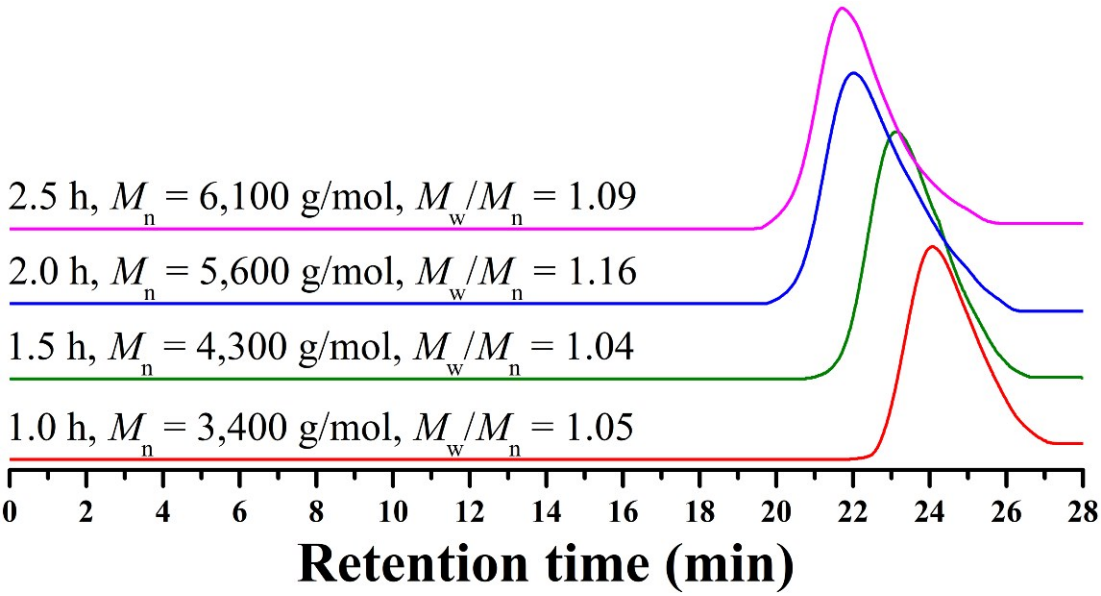


Figure S2. GPC curves (in THF) of PDFMOEA homopolymers prepared by solution ATRP of DFMOEA.

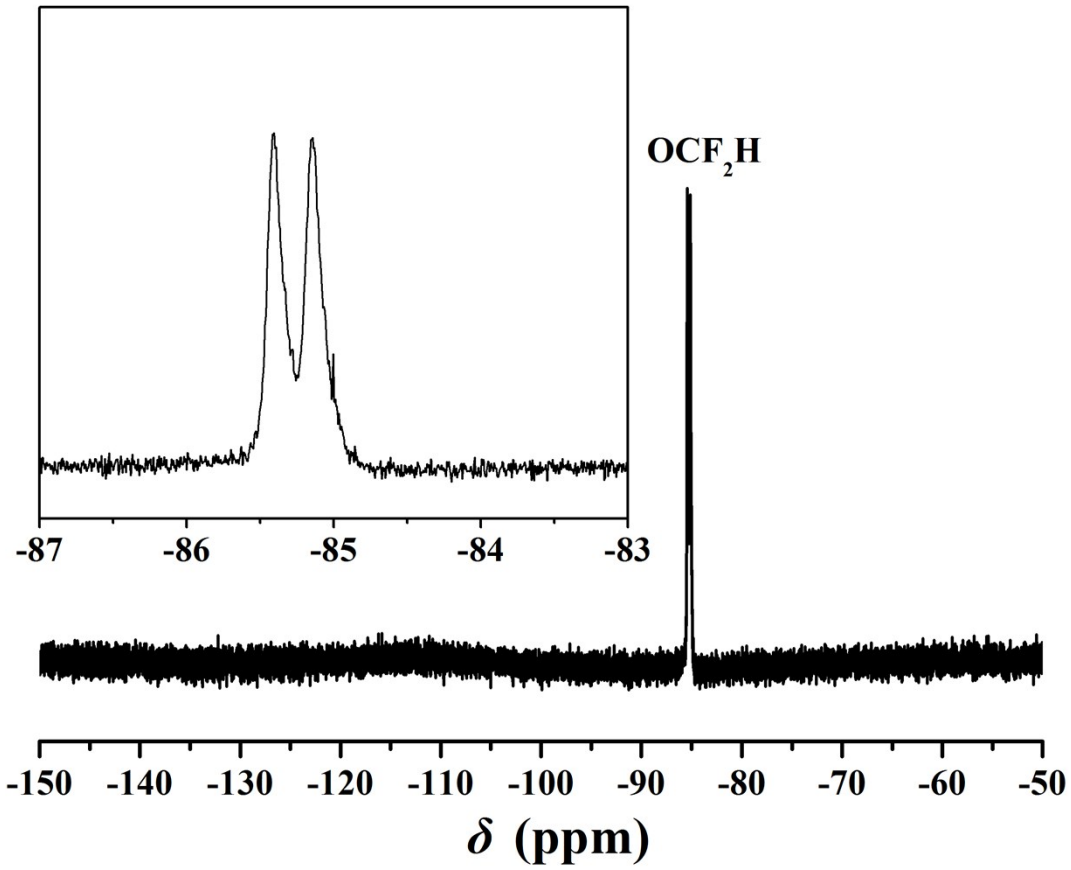


Figure S3. ^{19}F NMR spectrum of PDFMOEA in $CDCl_3$.

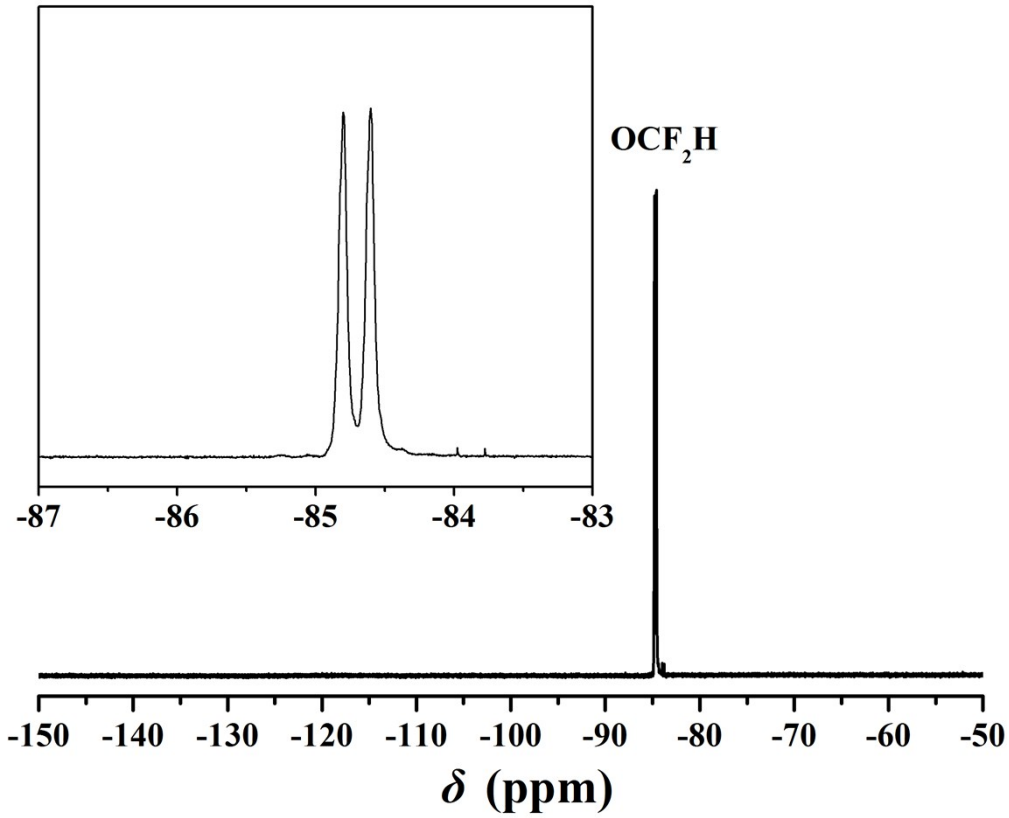


Figure S4. ^{19}F NMR spectrum of PEG-*b*-PDFMOEA in $CDCl_3$.

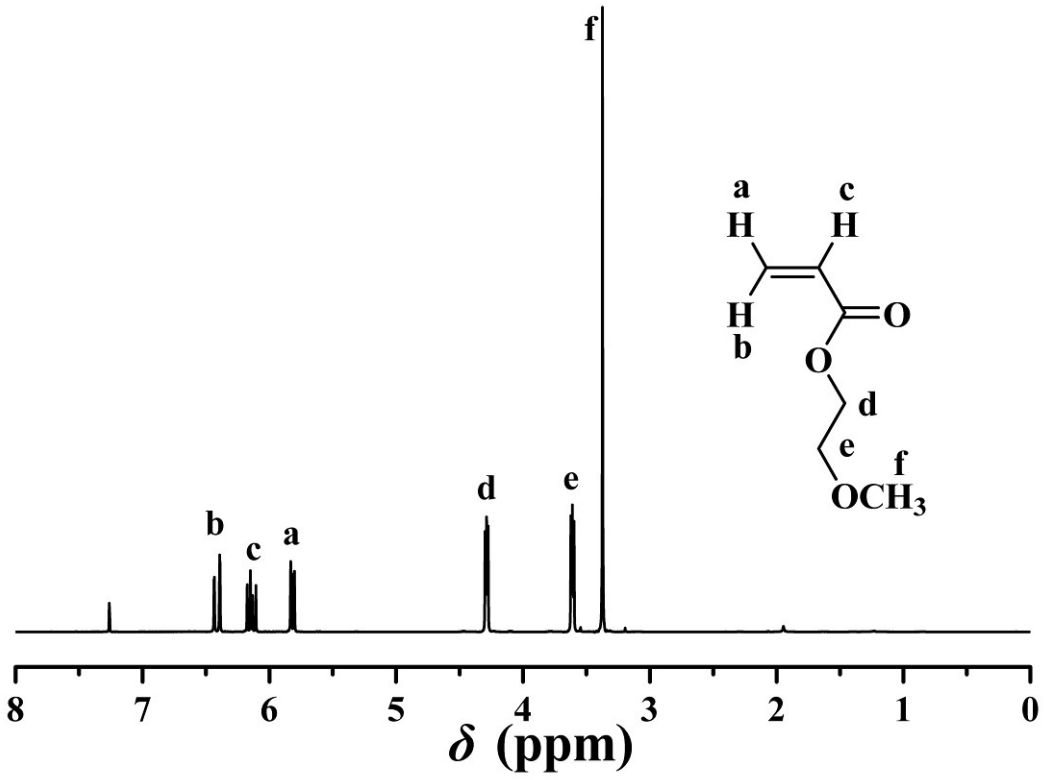


Figure S5. ^{1}H NMR spectrum of MOEA in $CDCl_3$.

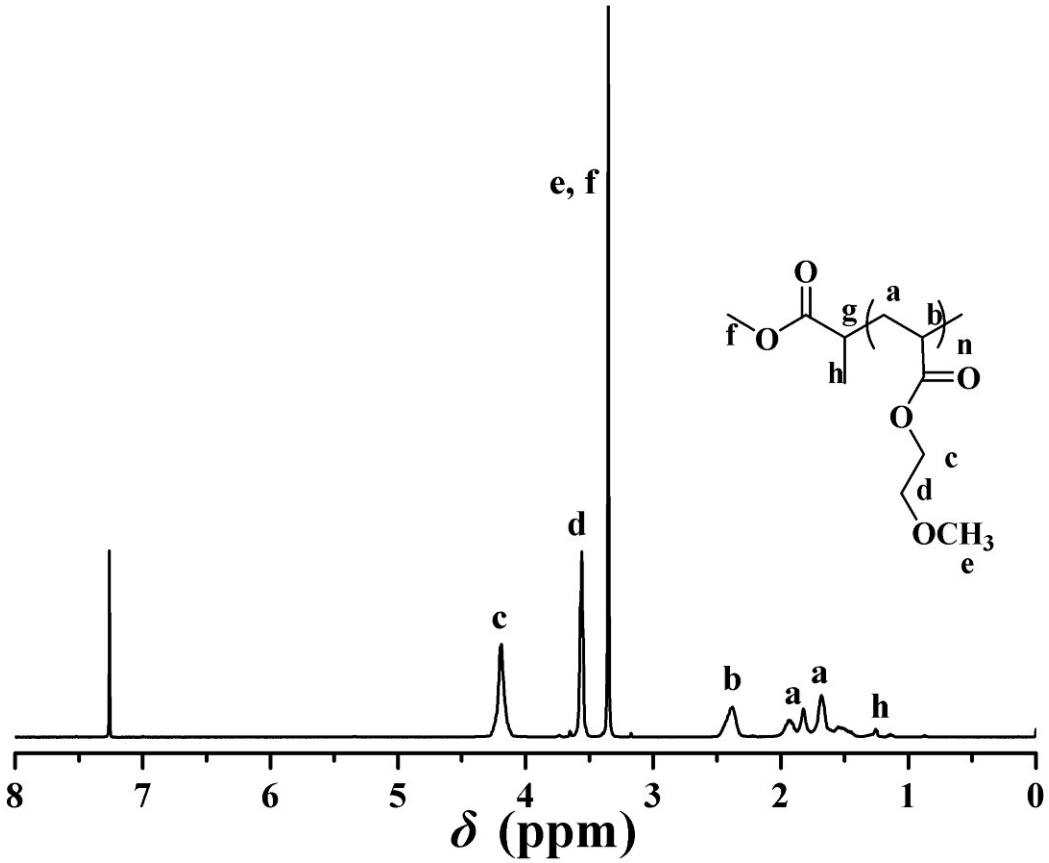


Figure S6. ^{1}H NMR spectrum of PMOEA in $CDCl_3$.