Supporting Information For

Direct Functionalization of Poly(vinyl chloride) by Photo-Mediated ATRP without Deoxygenation Procedure

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Figure S1. Representative configuration comprising reaction vial surrounded by LED strips (10 W, 460-470 nm).

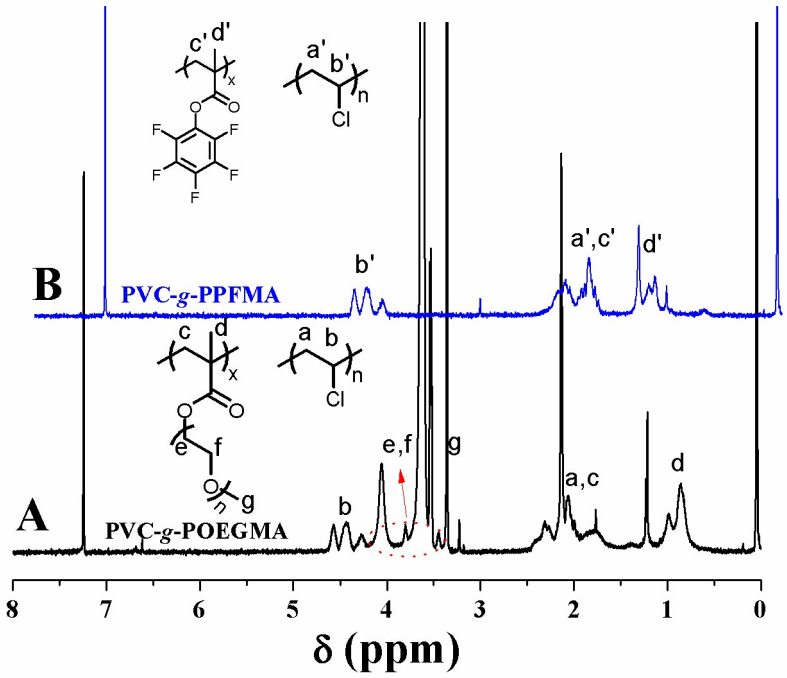

Figure S2. ^{1}H NMR spectra of (A) PVC-*g*-POEGMA and (B) PVC-*g*-PPFMA in $CDCl_3$.

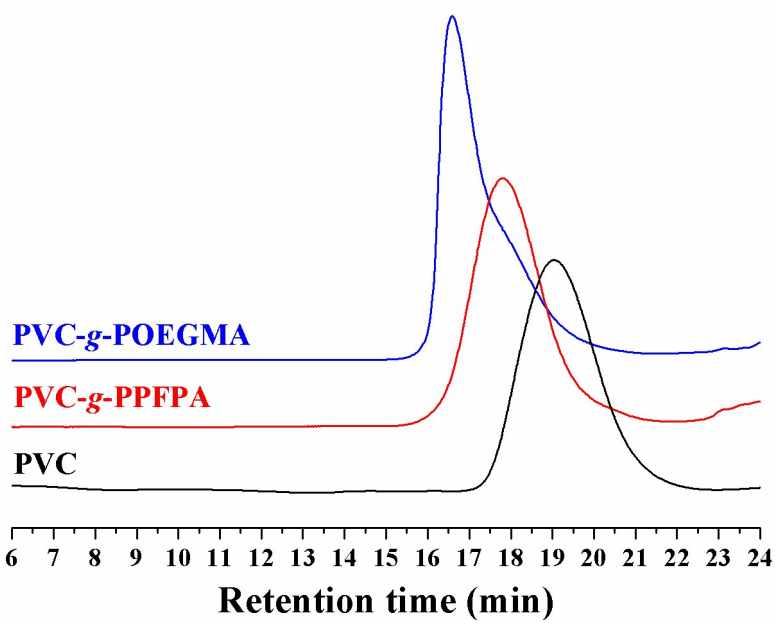

Figure S3. Typical GPC curves of pristine PVC, PVC-*g*-POEGMA and PVC-*g*-PPFMA prepared with deoxygenation procedures.

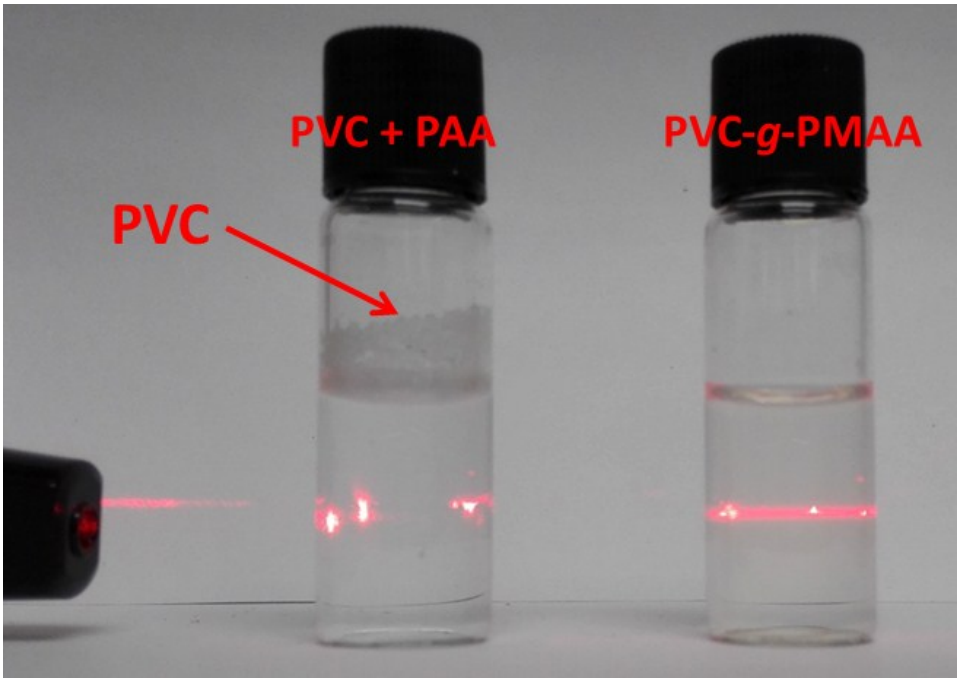

Figure S4. Photograph of aqueous solutions of PVC-*g*-PMAA (right) and blends of PVC and PAA homopolymer (left).

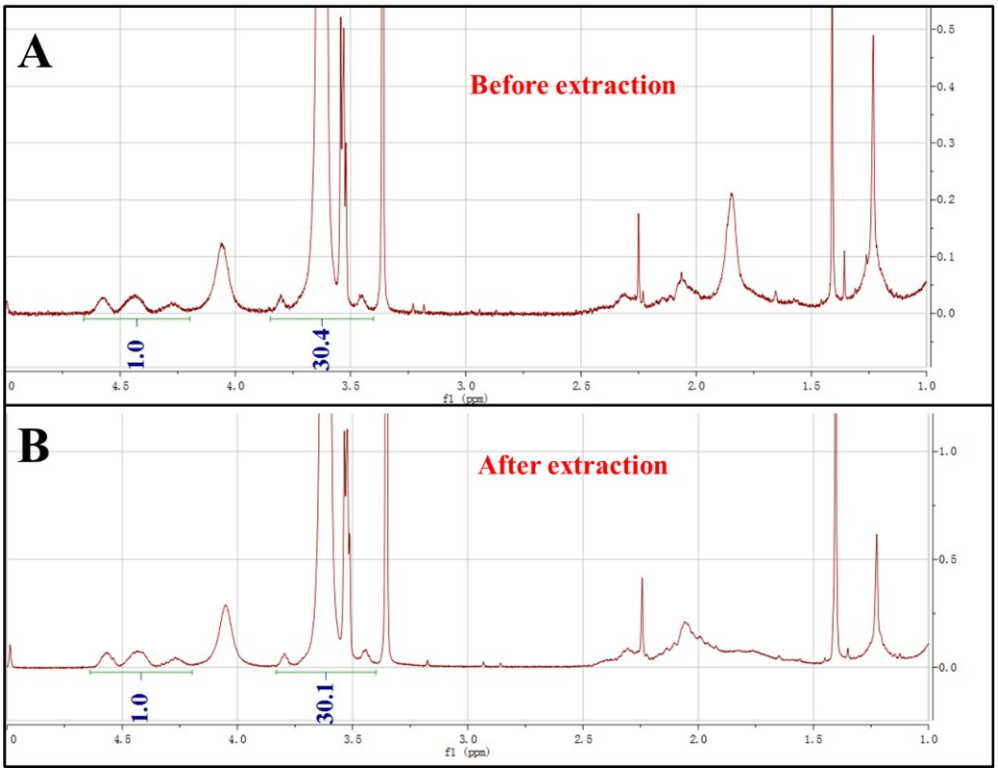

Figure S5. ^{1}H NMR spectra of (A) sample before extraction and (B) organic phase after extraction. The procedures are as follows: The obtained product (50 mg) was firstly dissolved in THF (5 mL) and then the solution was added slowly into water (5 mL). Emulsion-like solution was obtained. Subsequently, CH_2Cl_2 (5 mL) was added and extraction was conducted. The compositions of extracted product (organic phase) and sample before extraction were checked by ^{1}H NMR. The peaks at 4.45 ppm and 3.63 ppm were attributed to characteristic protons of PVC and POEGMA segments, respectively. The ratio of integration areas of the peak at 4.45 ppm to the peak at 3.63 ppm reflected the relative content of PVC to POEGMA. The ratio just changed from 30.4 to 30.1, which indicated that the ratio almost kept constant before and after the extraction by CH_2Cl_2. If the obtained product consisted of PVC homopolymer, the ratio after extraction would be higher than that before the extraction due to high hydrophobicity of PVC and hydrophicility of POEGMA. In other words, the almost consistency in the ratio before and after the extraction might demonstrate that there was no PVC and POEGMA homopolymer in obtained product after copolymerization, which is consistent with above-mentioned results in surface coating and solubility test on PMAA-functionalized PVC.

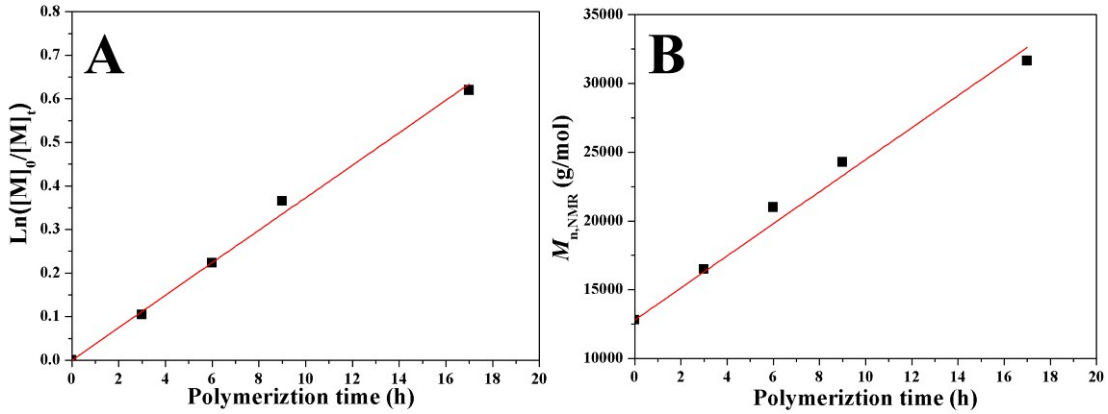

Figure S6. Photomediated ATRP of MMA using PVC as initiator and $Ir(ppy)_3$ as photocatylyst: (A) $\ln([M]_0/[M]_t)$ versus exposure time and (B) M_n versus conversion at different exposure time. [MMA]:[$Ir(ppy)_3$] = 100:0.0005, [PVC] = 0.07 g/mL, [MMA] = 2.67 mol/L, room temperature, blue LED light strips (10 W, 460-470 nm), deoxygenation by three cycles of freezing-pump-thaw.

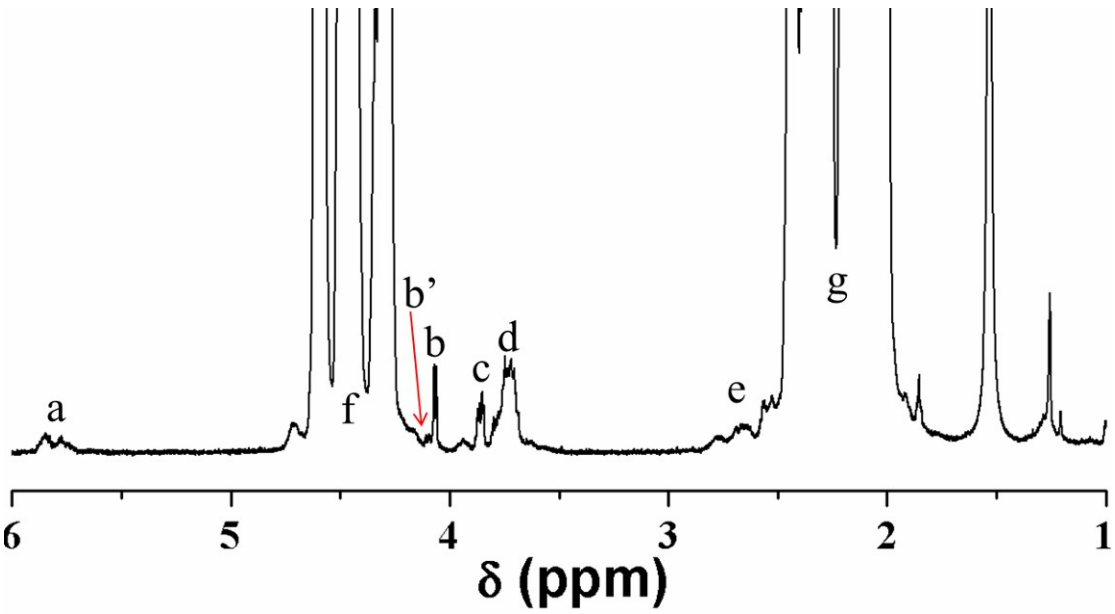

Figure S7. ^1H NMR spectrum of pristine PVC in $CDCl_3$ (a: -C*H*=C*H*CH_2Cl and -CH=CH-CHCl-; b: *trans*- –CH=CHC*H*$_2$Cl; b': *cis*- –CH=CHC*H*$_2$Cl; c: -CHClC*H*$_2$Cl; d: -C*H*$_2$Cl branch and -C*H*$_2$Cl; e: -C*H*$_2$CH=CHC*H*$_2$Cl; f: -C*H*Cl-; g: -C*H*$_2$CHCl-), the assignment of signals can be found in previous literatures.[1,2]

Table S1. Polymerization of MMA Initiated by Model Compounds[a]

Initiator	Time (h)	M_n[b] (g/mol)	M_w/M_n[b]	Conv.[c] (%)	Initiation Efficiency[d] (%)
3-chloride-propene	24	66,700	1.38	9.1	3.4
tert-butyl chloride	24	76,250	1.49	9.9	3.2
isopropyl chloride	24	60,580	1.46	5.1	2.1

[a] General polymerization conditions: methacrylate monomer (160 mmol), $Ir(ppy)_3$ (4.0×10^{-5} mmol), and initiator (0.64 mmol) in DMF (10 mL) at room temperature after deoxygenation with irradiation from blue LED light strips (10 W, 460-470 nm). [b] Measured by GPC in THF using PMMA as standards. [c] Determined by ^{1}H NMR. [d] Calculated from the ratio of theoretical M_n to measured M_n of obtained product.

References

1. Heuvel, C. J. M.; Weber, A. J. M. *Makromol. Chem.* **1983**, *184*, 2261.
2. Benedikt, G. M.; Cozens, R. J.; Goodall, B. L. Rhodes, L. F.; Bell, M. N.; Kemball, A. C.; Starnes, W. H. *Macromolecules* **1997**, *30*, 10.