

Supporting Information

Facile synthesis of V-shaped copolymer brushes grafted onto the surface of graphene oxide via coupling reactions

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Experimental

Materials. All solvents, monomers, and other chemicals were purchased from Alfa Aesar unless otherwise stated. Graphene oxide (GO) was synthesized from natural graphite powder (40 μm in size, Qingdao Henglide Graphite Co., Ltd.) using a modified Hummers method.¹ (4-Cyanopentanoic acid)-4-dithio benzoate (CPDB) was synthesized and purified according to literature method.² Methyl acrylate (MA, 99%), *tert*-butyl acrylate (*t*BA, 98%), methyl methacrylate (MMA, 99%), glycidyl methacrylate (GMA, 95%, TCI), *N,N*-dimethylacrylamide (DMA, 99%), poly(ethylene glycol) methyl ether methacrylate (PEGMA, $M_n = 300$, Sigma-Aldrich) and styrene (St, 99%) were passed through a basic alumina (Brockmann I) column to remove the inhibitor before use. γ -Methacryloxypropyltrimethoxy silane (MPS, 98%, Diamond Advanced Material of Chemical Inc). *N*-Isopropylacrylamide (NIPAM, 97%) was recrystallized twice from mixtures of hexane and toluene. Poly(ethylene glycol) methyl ether (MPEG, $M_n = 2000$, Sigma-Aldrich) was used as received. Triethylamine (TEA, 99%) was dried over KOH, refluxed with *p*-toluenesulfonyl chloride and distilled before use. *N,N'*-Dicyclohexylcarbodiimide (DCC, 98%) and 4-(*N,N*-dimethylamino) pyridine (DMAP, 98%) were used as received. 2,2'-Azobis(isobutyronitrile) (AIBN) was recrystallized twice from ethanol. Dichloromethane and toluene were dried and distilled over CaH_2 , and *N,N*-dimethyl formamide (DMF) was dried over anhydrous MgSO_4 and distilled under reduced pressure. Hexane, chloroform, acetone, *N*-methyl-2-pyrrolidinone (NMP), tetrahydrofuran (THF), and other solvents were obtained from Sinopharm Chemical Reagent Co., Ltd. and used as received. Other chemicals were of analytical grade and used as received.

Synthesis of MPEG-CPDB macro CTA. To a three-neck round flask were added anhydrous MPEG (9.74 g, 4.87 mmol), CPDB (1.68 g, 6.02 mmol), DMAP (62.7 mg, 0.503 mmol) and 100 mL of dichloromethane under nitrogen. The solution was stirred for 5 min, cooled with an ice-water bath, and then a solution of DCC (1.25 g, 5.94 mmol) in 20 mL of anhydrous dichloromethane was added dropwise into the mixture under stirring. The contents were gradually warmed to ambient temperature and further stirred for 30 h. After filtration, the filtrate was concentrated and

precipitated into diethyl ether thrice. The precipitate was collected, dried under vacuum overnight, and the macro CTA MPEG-CPDB (10.5 g, 95.4% yield) was obtained as red powder.

MPEG-CPDB: ^1H NMR (CDCl_3): δ 7.92, 7.58, 7.41 (PhH), 4.27 ($\text{CH}_2\text{OCOCH}_2$), 3.65 ($\text{CH}_2\text{CH}_2\text{O}$ of PEG), 3.38 (CH_3O), 2.71 (CH_2COO), 2.60 and 2.45 (CH_2), 1.94 (CH_3). FT-IR (KBr): 2908, 2882, 1737, 1643, 1557, 1469, 1413, 1350, 1292, 1247, 1101, 950, 841, 763 cm^{-1} .

Synthesis of MPEG-*b*-PM₁ diblock copolymers by RAFT polymerization mediated by MPEG-CPDB. RAFT polymerization was conducted in toluene using AIBN as the primary radical source and MPEG-CPDB as a macro chain transfer agent. In a typical polymerization (run 1 of Table 1S), GMA (1.42 g, 10.0 mmol), MPEG-CPDB (2.26 g, 1.0 mmol), and AIBN (32.8 mg, 0.2 mmol) were added to a glass tube with a magnetic stirring bar, and toluene was added until the total volume was 10.0 mL. The tube was sealed with a rubber septum, and the contents were degassed with nitrogen for 10 min. The tube was subsequently immersed into an oil bath preheated to 60 °C. After 5 h, the polymerization was quenched by putting the tube into an ice-water bath. About 0.1 mL of the polymerization solution obtained was diluted with CDCl_3 and subjected to ^1H NMR measurement. The monomer conversions were determined to be 41.2% by comparing the integrated areas of characteristic signals of monomer and polymer, and the number-average molecular weight determined by NMR ($M_n(\text{NMR})$) was 2850. After precipitating into a large amount of diethyl ether thrice, 2.65 g of MPEG-*b*-PGMA diblock copolymer was isolated, and its molecular weight and polydispersity were obtained by gel permeation chromatography (GPC): $M_n = 4000$, PDI = 1.05. Other polymers were synthesized and purified according to a similar approach.

MPEG-*b*-PGMA: ^1H NMR (CDCl_3): δ 7.90, 7.57, 7.41 (PhH), 4.26 ($\text{CH}_2\text{OCOCH}_2$), 4.33 and 3.82 (CH_2OCO of GMA unit), 3.65 ($\text{CH}_2\text{CH}_2\text{O}$ of PEG), 3.38 (CH_3O), 3.24 (CH of GMA unit), 2.84 and 2.64 (CH_2O of GMA unit), 2.53 ($\text{CH}_2\text{C}(\text{CH}_3)\text{S}$), 2.25 (CH_2COO), 0.8-2.4 (CH_2 and CH_3). FT-IR (KBr): 2912, 2882, 1731, 1642, 1561, 1461, 1412, 1351, 1299, 1250, 1101, 950, 843 cm^{-1} .

MPEG-*b*-PtBA: 28.8% conversion, $M_n(\text{NMR}) = 2630$, $M_n(\text{GPC}) = 3900$, PDI = 1.03. ^1H NMR (CDCl_3): δ 7.97, 7.54, 7.39 (PhH), 4.71 (CHS), 4.24 ($\text{CH}_2\text{OCOCH}_2$), 3.65 ($\text{CH}_2\text{CH}_2\text{O}$ of PEG), 3.38 (CH_3O), 2.2-2.8 (CH_2CHS and CHCO of *t*BA unit), 2.16 (CH_2COO), 1.95 ($\text{CH}_2\text{CH}_2\text{COO}$), 1.2-1.9 (CH_2 and CH_3). FT-IR (KBr): 2913, 2882, 1730, 1642, 1561, 1464, 1412, 1352, 1299, 1250, 1101, 950, 843 cm^{-1} .

MPEG-*b*-PMPS: 68.4% conversion, $M_n(\text{NMR}) = 3960$, $M_n(\text{GPC}) = 6200$, PDI = 1.04. ^1H NMR (CDCl_3): δ 7.86, 7.51, 7.35 (PhH), 4.23 ($\text{CH}_2\text{OCOCH}_2$), 3.90 (CH_2O of MPS unit), 3.65 ($\text{CH}_2\text{CH}_2\text{O}$ of PEG), 3.58 (CH_3OSi of MPS unit), 3.38 (CH_3O), 2.52 ($\text{CH}_2\text{C}(\text{CH}_3)\text{S}$), 2.20 (CH_2COO), 0.7-2.4 (CH_2 and CH_3), 0.66 (CH_2Si). FT-IR (KBr): 2912, 2885, 1731, 1643, 1558, 1470, 1413, 1352, 1298, 1249, 1197, 1101, 951, 838 cm^{-1} .

Synthesis of MPEG-*b*-PM₁-*b*-PM₂ triblock copolymers by RAFT polymerization mediated by MPEG-*b*-PM₁ macro CTAs. In a typical polymerization (run 8 of Table 1S), MPEG-*b*-PGMA

($M_n(\text{NMR}) = 2850$, PDI = 1.05, 0.428 mg, 0.15 mmol), St (3.12 g, 30 mmol), and AIBN (4.9 mg, 0.030 mmol) were added to a glass tube, and the tube with a magnetic stirring bar was sealed with a rubber septum. The contents were stirred for 5 min, degassed with nitrogen for 15 min and polymerized at 80 °C for 22 h. The glass tube was removed and cooled to room temperature immediately. The resultant copolymer was recovered by precipitating its solution into cold methanol thrice, and the monomer conversion of 34.2% was determined by gravimetry. The molecular weight and polydispersity of PEG-*b*-PGMA-*b*-PSt triblock copolymer given by GPC were $M_n = 10000$ and PDI = 1.19, and the number-average molecular weight determined by NMR ($M_n(\text{NMR})$) was 9970. Other triblock copolymers were synthesized and recovered according to a similar approach using various macro CTAs.

Triblock copolymers with PAA segment were obtained by hydrolysis of MPEG-*b*-PtBA-*b*-PM₂. In a typical run, 0.50 g of MPEG-*b*-PtBA-*b*-PSt was dissolved in 20 mL of dichloromethane, and then 1.5 mL of trifluoroacetic acid was injected to perform the hydrolysis under nitrogen. The reaction was conducted at ambient temperature for 20 h. The mixture was concentrated and precipitated into cold methanol thrice. After vacuum drying, 0.45 g of MPEG-*b*-PAA-*b*-PSt was obtained.

Synthesis of GO grafted with V-shaped copolymers by coupling reactions. Triblock copolymers comprising carboxyl, epoxy or trimethoxysilane functionalities in the middle block were used for the graft reaction. In a typical run, 50 mg of GO and 5.0 mL of DMF in a round flask was subjected to ultrasonic pulse for 30 min, and then 250 mg of triblock copolymer was added to the solution under nitrogen. The contents were reacted at constant temperature ($T = 80\text{-}110$ °C) for 40 h. For coupling reaction using block copolymers comprising PGMA or PAA segment, 20 μL of triethylamine was typically added to the reaction mixtures to promote the graft reaction. After reaction, the mixtures were subjected to centrifugation and thoroughly washed with toluene and THF for at least five times. The product was carefully collected and dried under vacuum at 60 °C until constant weight. GO grafted with V-shaped copolymers was obtained as black powders.

The weight grafting ratio ($G_r = W_{\text{graft polymer}}/W_{\text{GO}}$, defined as weight ratio of grafted polymer to GO substrate in GO-copolymer nanocomposite) and apparent grafting efficiency ($G_e = W_{\text{graft polymer}}/W_{\text{feed polymer}}$, defined as weight ratio of grafted polymer to feeded polymer) were determined by TGA or elemental analyses using the following equations.

$$G_r = (W_{100,\text{GO-polymer}} \times W_{800,\text{GO}})/(W_{800,\text{GO-polymer}} \times W_{100,\text{GO}}) - 1 \quad (\text{equation 1})$$

$$G_r = N\% \times M_n(\text{NMR})/(14\text{DP} - N\% \times M_n(\text{NMR})) \quad (\text{equation 2})$$

$$G_e = (W_{\text{graft polymer}}/W_{\text{feed polymer}}) \times 100\% \quad (\text{equation 3})$$

Where $W_{100,\text{GO-polymer}}$ and $W_{100,\text{GO}}$ are residual weight of copolymer grafted onto GO and pristine GO at 100 °C, $W_{800,\text{GO-polymer}}$ and $W_{800,\text{GO}}$ are residual weight of copolymer grafted onto GO and pristine GO at 800 °C, $W_{\text{feed polymer}}$, $W_{\text{graft polymer}}$ and W_{GO} are weights of feeded polymer, grafted polymer and pristine GO, N% was the nitrogen content of GO-g-polymer determined by elemental analysis,

M_n (NMR) was molecular weight of grafted copolymer determined by NMR, and DP was degree of polymerization of PDMA or PNIPAM segment of triblock copolymers.

Characterization. The number-average molecular weight (M_n) and polydispersity (PDI) of polymer samples were measured on a Waters 150-C gel permeation chromatography equipped with three Ultrastyrigel columns with 10 μm bead size at 35 °C. Their effective molecular weight ranges were 100-10 000 for Styragel HT2, 500-30 000 for Styragel HT3, and 5000-600 000 for Styragel HT4. The pore sizes are 50, 100, and 1000 nm for Styragels HT2, HT3, and HT4, respectively. THF was used as an eluent at a flow rate of 1.0 mL/min, polystyrene samples were calibrated with PSt standard samples; other samples were calibrated using PMMA standard samples. ^1H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on a Varian spectrometer at 25 °C using CDCl_3 as a solvent. Fourier Transform Infrared (FT-IR) spectra were recorded on a Perkin-Elmer 2000 spectrometer using KBr discs. Raman spectra were recorded on a LabRam confocal micro-Raman system. The exciting wavelength was 632.8 nm from an air-cooled He-Ne laser with a power of 16 mW and a spot of *ca* 3 μm on the surface. X-ray photoelectron spectroscopy (XPS) was recorded on a PHI 5000c ESCA photoelectron spectrometer. Thermal gravimetric analysis (TGA) was carried out using a Perkin-Elmer Pyris 6 TGA instrument with a heating rate of 20 °C/min under a nitrogen flow. Scanning electron microscopy (SEM) images were carried on a Hitachi S-4700 field emission SEM system. Transmission electron microscopy (TEM) images were obtained through a Hitachi H-600 electron microscope. Water contact angles of various films were measured on a SL200C contact angle measuring machine.

References

- (1) Kovtyukhova, N. I.; Ollivier, P. J.; Martin, B. R.; Mallouk, T. E.; Chizhik, S. A.; Buzaneva, E. V.; Gorchinskiy, A. D. *Chem. Mater.* **1999**, *11*, 771–778.
- (2) Mitsukami, Y.; Donovan, M. S.; Lowe, A. B.; McCormick, C. L. *Macromolecules* **2001**, *34*, 2248-2256.

Table S1. Synthesis of functional di- and triblock copolymers by RAFT polymerization mediated by various macro CTAs^a

run	Polymer ^b	M	DP ₀	T (°C)	t (h)	C% ^c	M _n (NMR) ^d	M _n (GPC) ^e	PDI ^e
1	MPEG ₄₅ - <i>b</i> -PGMA ₄	GMA	10	60	5	41.2	2850	4000	1.05
2	MPEG ₄₅ - <i>b</i> -PtBA ₃	<i>t</i> BA	10	80	12	28.8	2630	3900	1.03
3	MPEG ₄₅ - <i>b</i> -PMPS ₇	MPS	10	70	6	68.4	3960	6200	1.04
4	MPEG ₄₅ - <i>b</i> -PGMA ₄ - <i>b</i> -PPEGMA ₅₃	PEGMA	70	80	22	75.4	18700	15500	1.18
5	MPEG ₄₅ - <i>b</i> -PGMA ₄ - <i>b</i> -PSt ₆₈	St	200	80	22	34.2	9970	10000	1.19
6	MPEG ₄₅ - <i>b</i> -PGMA ₄ - <i>b</i> -PNIPAM ₃₂	NIPAM	70	80	22	46.3	6510	7230	1.15
7	MPEG ₄₅ - <i>b</i> -PGMA ₄ - <i>b</i> -PDMA ₈₄	DMA	100	80	22	84.2	11200	11800	1.16
8	MPEG ₄₅ - <i>b</i> -PGMA ₄ - <i>b</i> -PMA ₇₂	MA	150	80	22	47.8	9020	9800	1.18
9	MPEG ₄₅ - <i>b</i> -PtBA ₃ - <i>b</i> -PNIPAM ₄₇	NIPAM	100	80	22	46.9	7930	8410	1.12
10	MPEG ₄₅ - <i>b</i> -PtBA ₃ - <i>b</i> -PDMA ₉₅	DMA	150	80	22	63.4	12100	12600	1.04
11	MPEG ₄₅ - <i>b</i> -PtBA ₃ - <i>b</i> -PSt ₂₃	St	100	70	22	22.5	4970	5600	1.06
12	MPEG ₄₅ - <i>b</i> -PtBA ₃ - <i>b</i> -PSt ₅₄	St	150	80	22	35.7	8210	9280	1.18
13	MPEG ₄₅ - <i>b</i> -PtBA ₃ - <i>b</i> -PSt ₁₀₈	St	300	80	22	36	13900	14700	1.12
14	MPEG ₄₅ - <i>b</i> -PMPS ₇ - <i>b</i> -PSt ₄₃	St	150	80	22	28.9	8470	8800	1.06
15	MPEG ₄₅ - <i>b</i> -PMPS ₇ - <i>b</i> -PSt ₁₀₀	St	300	80	22	33.4	14400	14300	1.15

^a Reaction conditions: [M]₀:[macro CTA]₀: [AIBN]₀ = DP₀:1:0.2, [M]₀ = 1.0 (runs 1-6) or 2.0 (runs 7-10) mol/L, in bulk (for St polymerization), toluene (runs 1 and 2) or dioxane (other runs); macro CTAs were MPEG-CPDB (runs 1-3), MPEG-*b*-PGMA (runs 4-8), MPEG-*b*-PtBA (runs 9-13) and MPEG-*b*-PMPS (runs 14 and 15). ^b Resultant copolymers in which the subscript denotes degree of polymerization of each block. ^c Monomer conversion determined by NMR or gravimetry. ^d Molecular weight determined by NMR analysis. ^e Molecular weight and polydispersity estimated by GPC.

Table S2. Results for graft reaction between GO and middle-functionalized triblock copolymers^a

run	graft copolymer	M_n (NMR)	PDI	G_r^b	G_e (%) ^c	G_p (mmol/g) ^d	CA (°) ^e
1	MPEG ₄₅ - <i>b</i> -PGMA ₄ - <i>b</i> -PPEGMA ₅₃	18700	1.18	1.51	30.2	0.081	42.9 ± 2.0
2	MPEG ₄₅ - <i>b</i> -PGMA ₄ - <i>b</i> -PSt ₆₈	9970	1.19	3.12	62.4	0.313	85.7 ± 3.6
3	MPEG ₄₅ - <i>b</i> -PGMA ₄ - <i>b</i> -PNIPAM ₃₂	6510	1.15	2.08	41.6	0.320	68.8 ± 1.6
4	MPEG ₄₅ - <i>b</i> -PGMA ₄ - <i>b</i> -PDMA ₈₄	11200	1.16	1.71	34.2	0.153	20.3 ± 2.0
5	MPEG ₄₅ - <i>b</i> -PGMA ₄ - <i>b</i> -PMA ₇₂	9020	1.18	2.96	59.2	0.328	75.8 ± 2.5
6	MPEG ₄₅ - <i>b</i> -PAA ₃ - <i>b</i> -PNIPAM ₄₇	7930	1.12	2.18	43.6	0.275	46.3 ± 2.0
7	MPEG ₄₅ - <i>b</i> -PAA ₃ - <i>b</i> -PDMA ₉₅	12100	1.04	1.83	36.6	0.151	19.4 ± 2.2
8	MPEG ₄₅ - <i>b</i> -PAA ₃ - <i>b</i> -PSt ₂₃	4970	1.06	2.64	52.8	0.531	66.8 ± 3.2
9	MPEG ₄₅ - <i>b</i> -PAA ₃ - <i>b</i> -PSt ₅₄	8210	1.18	2.78	55.6	0.339	75.5 ± 3.0
10	MPEG ₄₅ - <i>b</i> -PAA ₃ - <i>b</i> -PSt ₁₀₈	13900	1.12	2.53	50.6	0.182	96.6 ± 2.4
11	MPEG ₄₅ - <i>b</i> -PMPS ₇ - <i>b</i> -PSt ₄₃	8470	1.06	3.63	72.6	0.429	74.3 ± 2.2
12	MPEG ₄₅ - <i>b</i> -PMPS ₇ - <i>b</i> -PSt ₁₀₀	14400	1.15	3.01	60.2	0.209	90.3 ± 3.6

^a Reaction conditions: $W_{\text{polymer}}:W_{\text{GO}} = 5$, $W_{\text{polymer}}:V_{\text{DMF}} = 50$ mg/mL, in DMF at 80 (runs 1-5), 90 (runs 11 and 12) or 100 °C (runs 6-10) for 40 h. ^b Weight grafting ratio as determined by TGA or elemental analysis; $G_r = W_{\text{graft polymer}}:W_{\text{GO}}$. ^c Grafting efficiency indicating weight ratio of grafted copolymer to feeded copolymer. ^d Molar grafting ratio calculated by equation $G_p = G_r/M_n(\text{NMR})$. ^e Water contact angle.

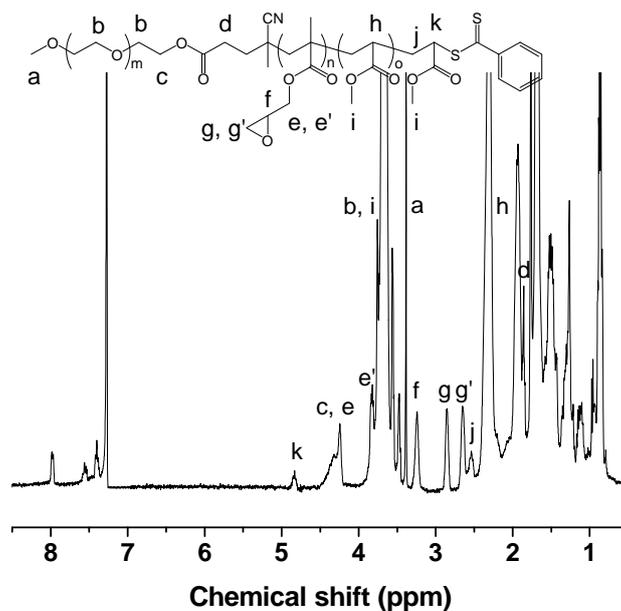


Figure S1. ¹H NMR spectra of PEG₄₅-*b*-PGMA₄-*b*-PMA₇₂ triblock copolymer.

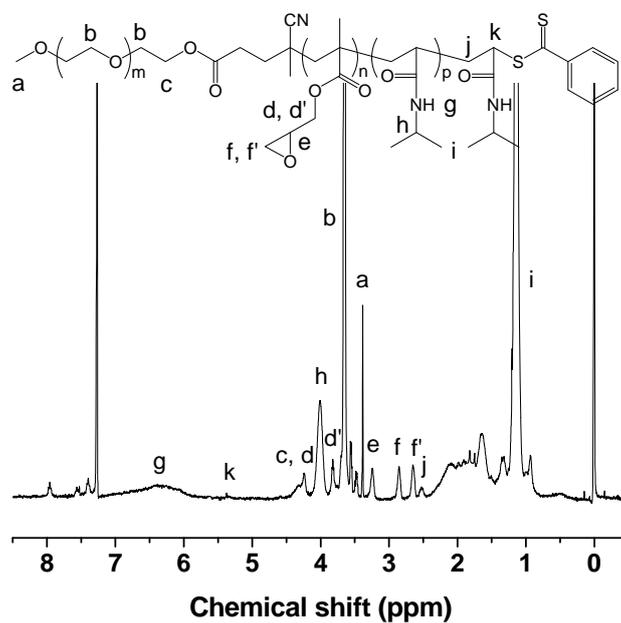


Figure S2. ¹H NMR spectra of PEG₄₅-*b*-PGMA₄-*b*-PNIPAM₃₂ triblock copolymer.

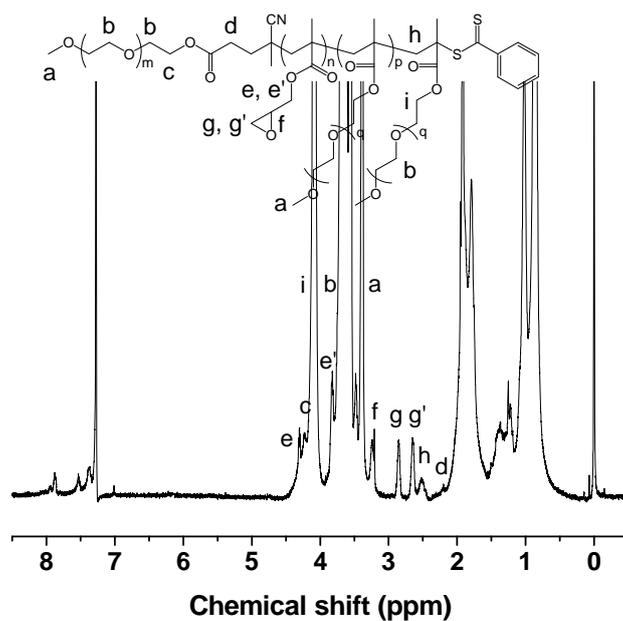


Figure S3. ¹H NMR spectra of PEG₄₅-b-PGMA₄-b-PPEGMA₅₃ triblock copolymer.

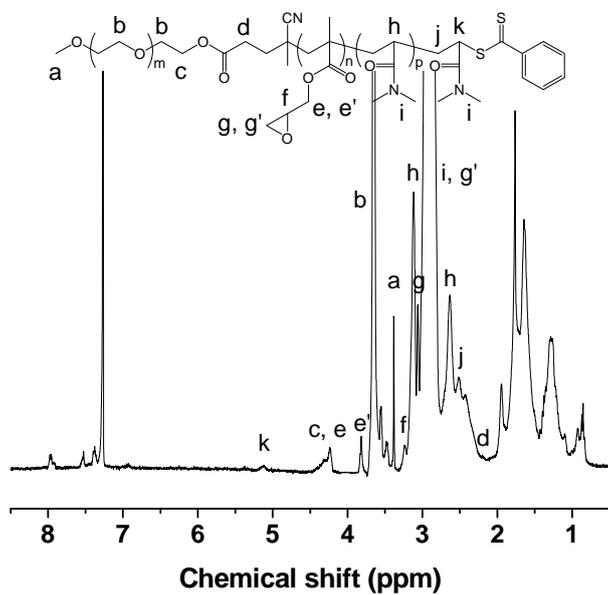


Figure S4. ¹H NMR spectra of PEG₄₅-b-PGMA₄-b-PDMA₈₄ triblock copolymer.

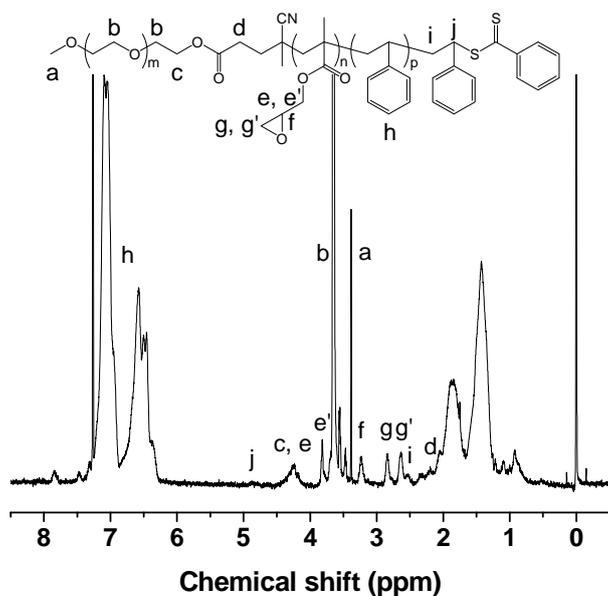


Figure S5. ¹H NMR spectra of PEG₄₅-b-PGMA₄-b-PSt₆₈ triblock copolymer.

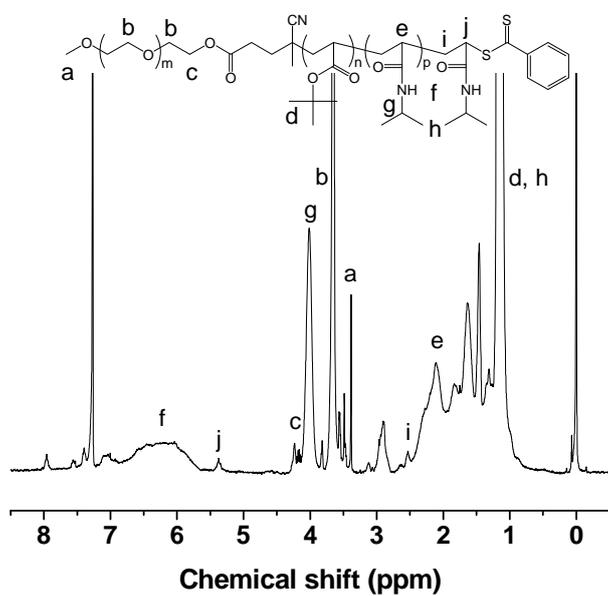


Figure S6. ¹H NMR spectra of PEG₄₅-b-PtBA₃-b-PNIPAM₄₇ triblock copolymer.

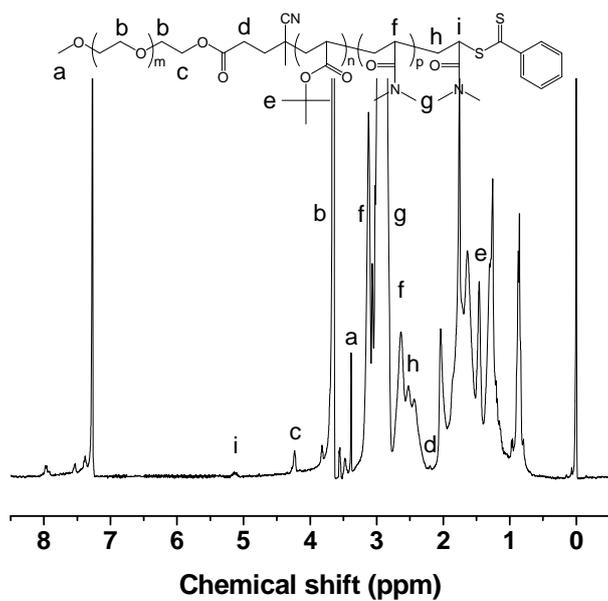


Figure S7. ¹H NMR spectra of PEG₄₅-b-PtBA₃-b-PDMA₉₅ triblock copolymer.

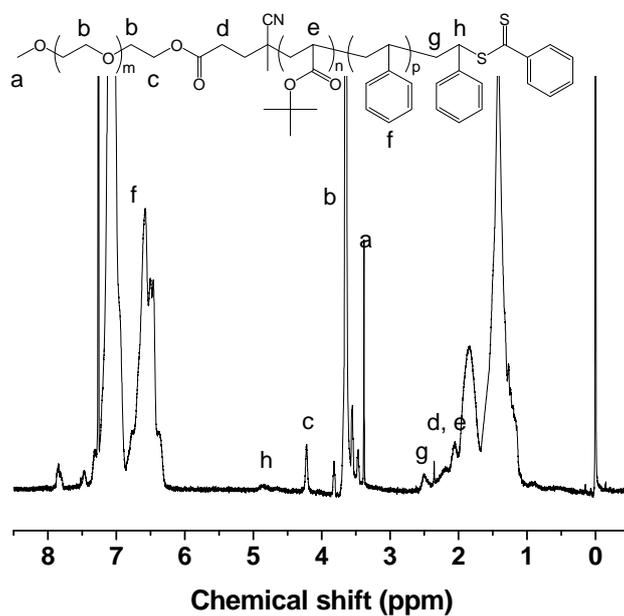


Figure S8. ¹H NMR spectra of PEG₄₅-b-PtBA₃-b-PSt₅₄ triblock copolymer.

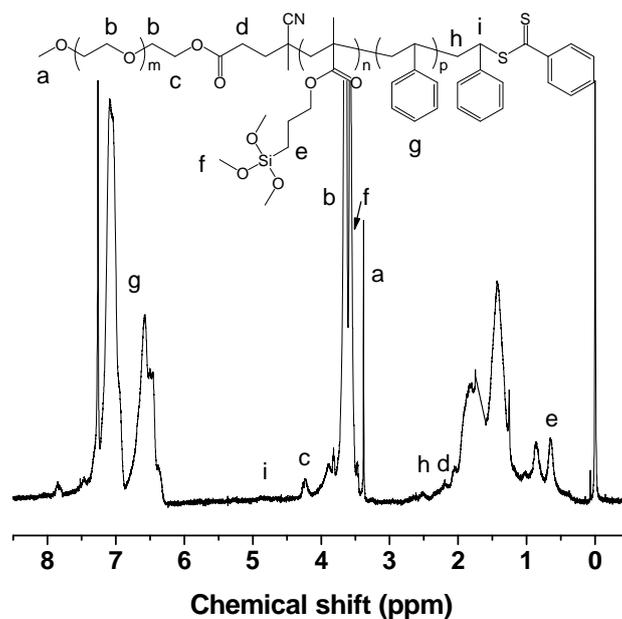


Figure S9. ^1H NMR spectra of $\text{PEG}_{45}\text{-}b\text{-PMPS}_7\text{-}b\text{-PSt}_{43}$ triblock copolymer.

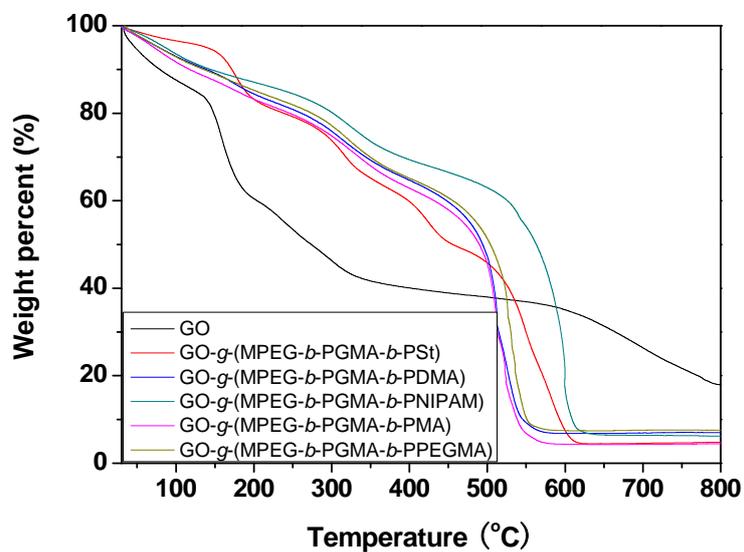


Figure S10. TGA curves of GO and GO grafted with V-shaped copolymers obtained by carboxyl-epoxy coupling reactions. Graft reaction was performed in DMF at 80 °C for 40 h. See Table S2 for detailed conditions.

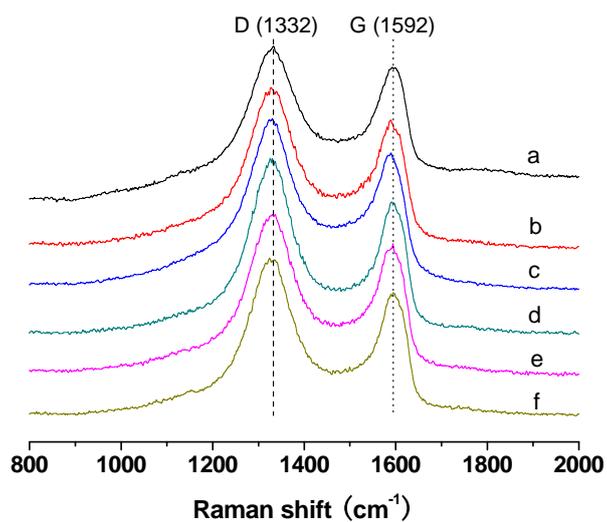


Figure S11. Raman spectra of GO (a) and various GO-*g*-(MPEG-*b*-PGMA-*b*-PM₂) samples (b-f): M₂ = PEGMA (b), St (c), NIPAM (d), DMA (e) and MA (f).

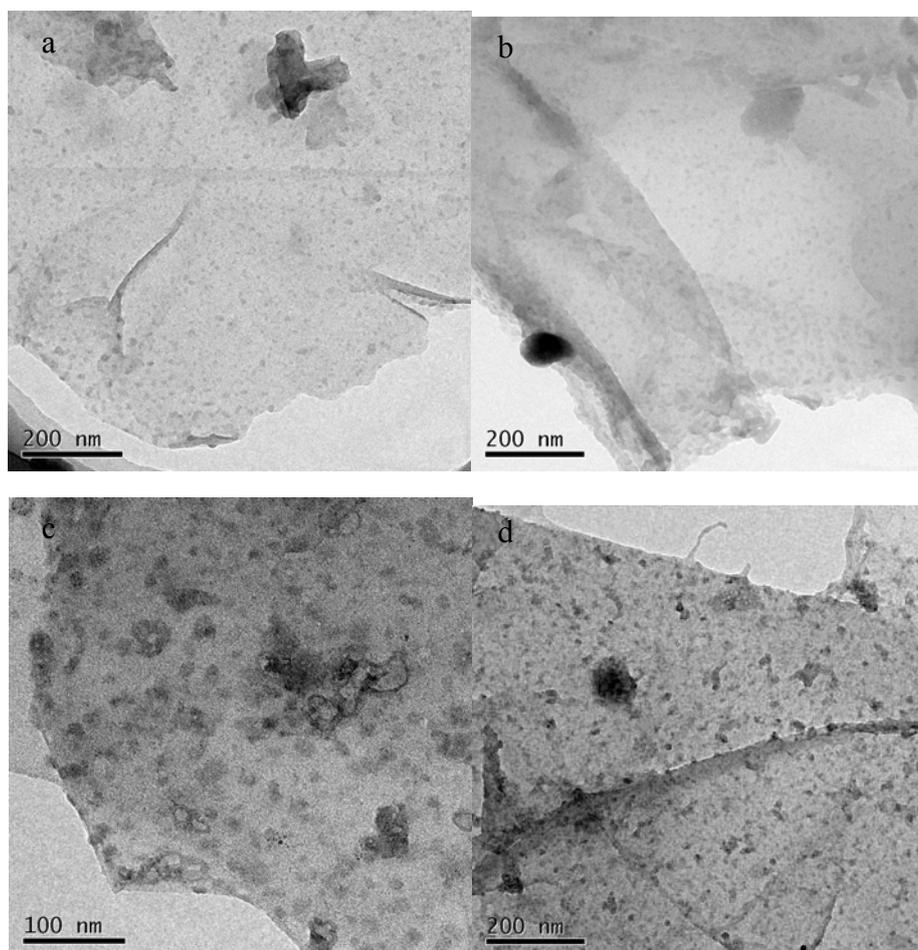


Figure S12. TEM images of GO-*g*-(MPEG-*b*-PAA-*b*-PNIPAM). The sample was originally dispersed in hexane (a), toluene (b), THF (c), and chloroform (d) with a concentration of 0.02 mg/mL.



(a) GO

(b) GO-g-(MPEG-*b*-PGMA-*b*-

(c) GO-g-(MPEG-*b*-PGMA-*b*-PSt)

(d) GO-g-(MPEG-*b*-PGMA-*b*-PNIPAM)

(e) GO-g-(MPEG-*b*-PGMA-*b*-PDMA)

(f) GO-g-(MPEG-*b*-PGMA-*b*-PMA)

Figure S13. Photographs of GO and GO grafted with V-shaped copolymers dispersed in various solvents. Solvents were hexane, toluene, acetone, THF, chloroform, DMF and water (from left to right), and sample concentration was 0.50 mg/mL. Samples were subjected to ultrasonic treatment and then stood for 15 min at ambient temperature.

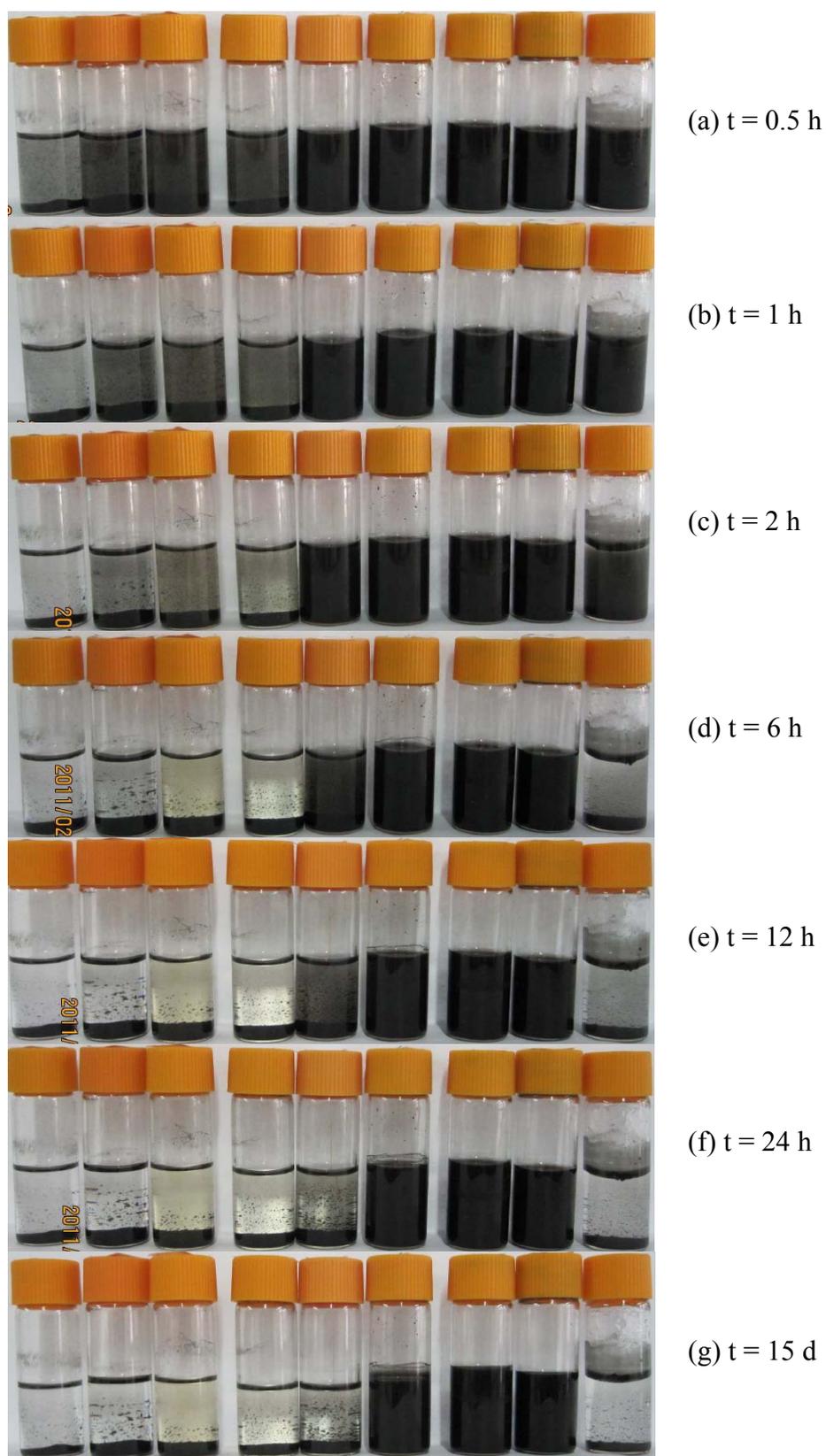


Figure S14. Photographs of GO-g-(MPEG-*b*-PAA-*b*-PSt) dispersed in various solvents for various times. Solvents were hexane, toluene, methanol, acetone, THF, chloroform, DMF, NMP and deionized water (from left to right), and sample concentration was 1.0 mg/mL.

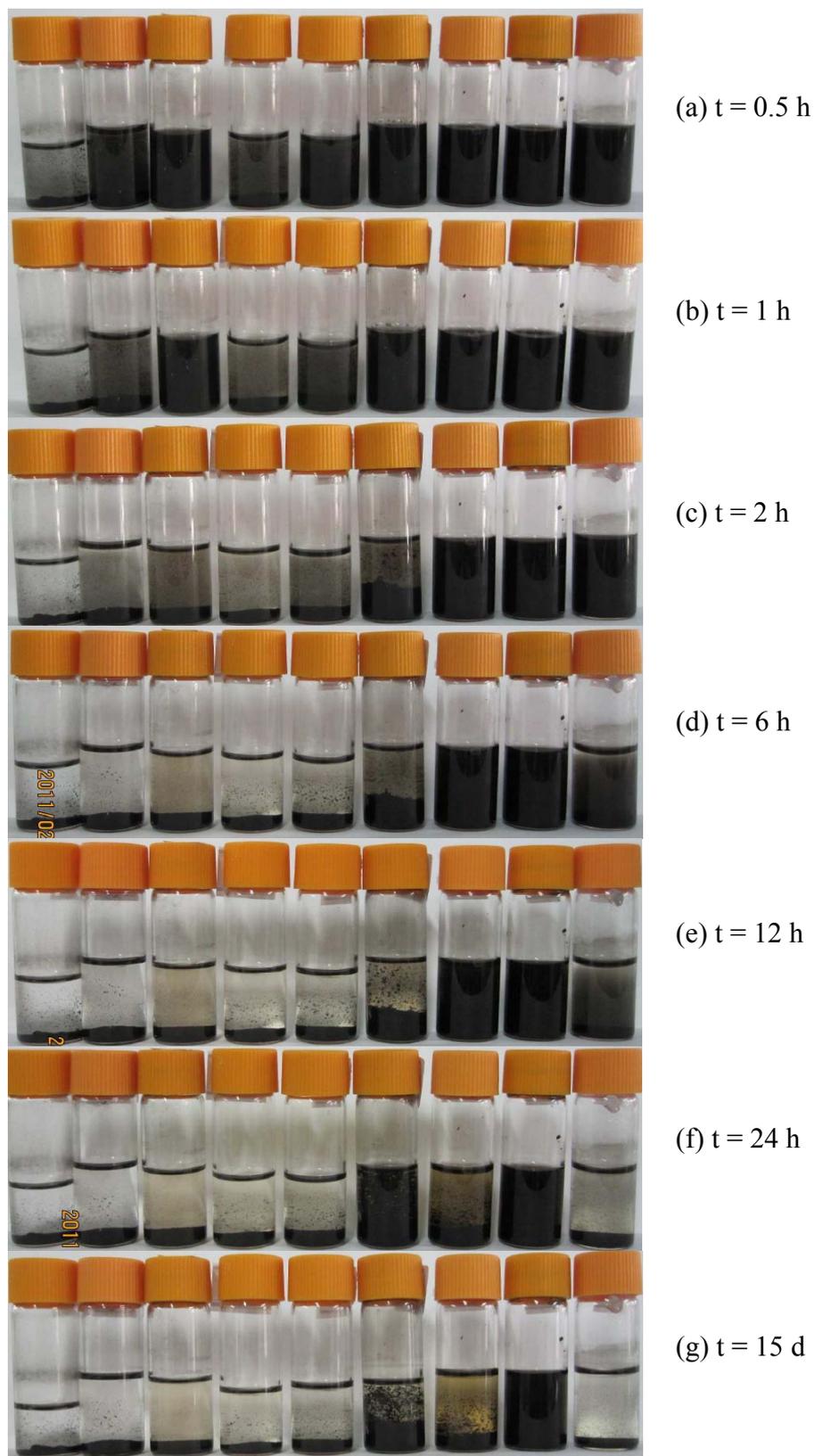


Figure S15. Photographs of GO-g-(MPEG-*b*-PAA-*b*-PNIPAM) dispersed in various solvents for various times. Solvents were hexane, toluene, methanol, acetone, THF, chloroform, DMF, NMP and deionized water (from left to right), and sample concentration was 1.0 mg/mL.