

Supporting Information

Graphene Oxide Modified by Betaine Moieties for Improvement of Electrorheological Performance

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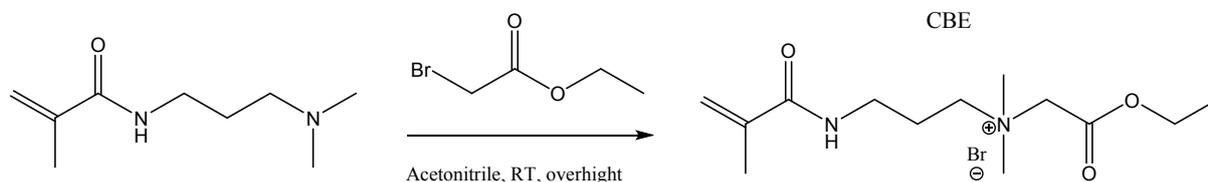
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Experimental

Synthesis of *N*-(2-ethoxy-2-oxoethyl)-3-methacrylamido-*N,N*-dimethylpropan-1-aminium bromide (CBE)



Scheme S1: Synthesis of *N*-(2-ethoxy-2-oxoethyl)-3-methacrylamido-*N,N*-dimethylpropan-1-aminium bromide (CBE)

The synthesis of *N*-(2-ethoxy-2-oxoethyl)-3-methacrylamido-*N,N*-dimethylpropan-1-aminium bromide (CBE) was performed according to Scheme S1.

N-(3-dimethylamino)propylmethacrylamide (5 mL, 27.6 mmol) was added to 20 mL acetonitrile followed by dropwise addition of ethyl bromoacetate (4.6 mL, 41.4 mmol). The reaction was stirred overnight at RT under nitrogen atmosphere. The solution was re-precipitated into diethyl ether (3x, 7 mL) to get product in form of white powder (CBE, 7.32 g, 91 %). The ¹H NMR and FTIR spectra are shown in Figure S1 and Figure S3, respectively.

^1H NMR (400 MHz, D_2O) δ : 5.61 (s, 1H, $-\text{C}=\text{CH}_2$), 5.37 (s, 1H, $-\text{C}=\text{CH}_2$), 4.14-4.22 (m, 4H, $\text{O}-\text{CH}_2-\text{CH}_3$ and N^+-CH_2), 3.47-3.53 (m, 2H, CH_2-N^+), 3.23-3.28 (m, 2H, $\text{NH}-\text{CH}_2$), 3.15-3.20 (s, 6H, N^+Me_2), 1.89-1.99 (m, 2H, $\text{CH}_2-\text{CH}_2-\text{CH}_2$), 1.80-1.82 (m, 3H, $\text{C}-\text{CH}_3$)

FTIR (cm^{-1}): 3232, 3026, 2931, 1758, 1660, 1610, 1469, 1435, 1228, 1190, 1150, 945, 921, 670.

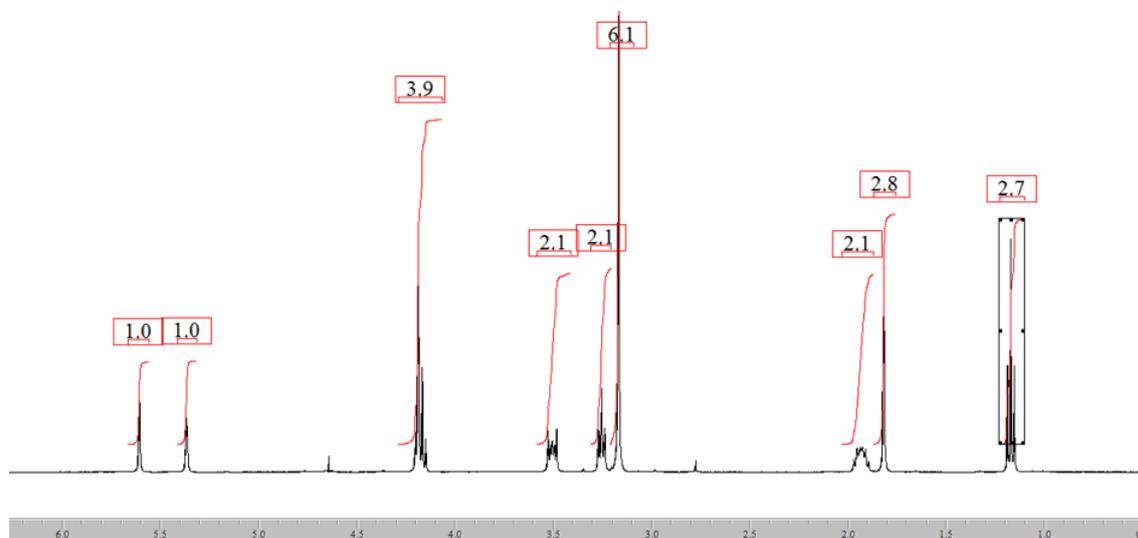
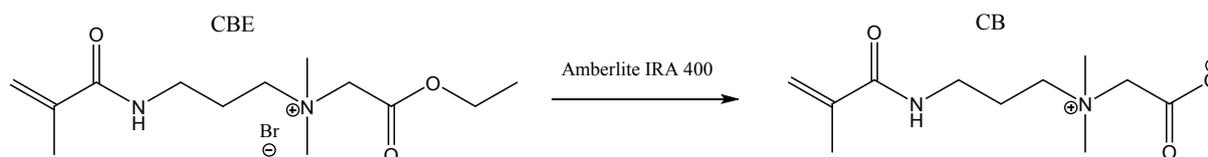


Figure S1: ^1H NMR spectra of *N*-(2-ethoxy-2-oxoethyl)-3-methacrylamido-*N,N*-dimethylpropan-1-aminium bromide (CBE)⁺

Synthesis of 2-((3-methacrylamidopropyl)dimethylammonio)acetate (CB)



Scheme S2: Synthesis of 2-((3-methacrylamidopropyl)dimethylammonio)acetate (CB)

The synthesis of 2-((3-methacrylamidopropyl)dimethylammonio)acetate (CB) was performed according to Scheme S2. The CBE (2 g, 7 mmol) was dissolved in 5 mL of distilled water and passed through Amberlite chloride IRA 400 column activated by 0.1 M NaOH aqueous solution and washed with distilled water. The product was dried under reduced pressure to obtain white powder (1.51 g, 6.6 mmol, 97 %). The ^1H NMR and FTIR spectra are shown in Figure S2 and Figure S3, respectively.

$^1\text{H NMR}$ (400 MHz, D_2O) δ : 5.58 (s, 1H, $-\text{C}=\text{CH}_2$), 5.34 (s, 1H, $-\text{C}=\text{CH}_2$), 3.74 (s, 2H, N^+-CH_2), 3.44-3.5 (m, 2H, CH_2-N^+), 3.21-3.26 (m, 2H, $\text{NH}-\text{CH}_2$), 3.08 (s, 6H, N^+Me_2), 1.84-1.94 (m, 2H, $\text{CH}_2-\text{CH}_2-\text{CH}_2$), 1.78-1.84 (s, 3H, $\text{C}-\text{CH}_3$)

FTIR (cm^{-1}): 2963, 1609, 1536, 1484, 1450, 1390, 1332, 1233, 924, 884.

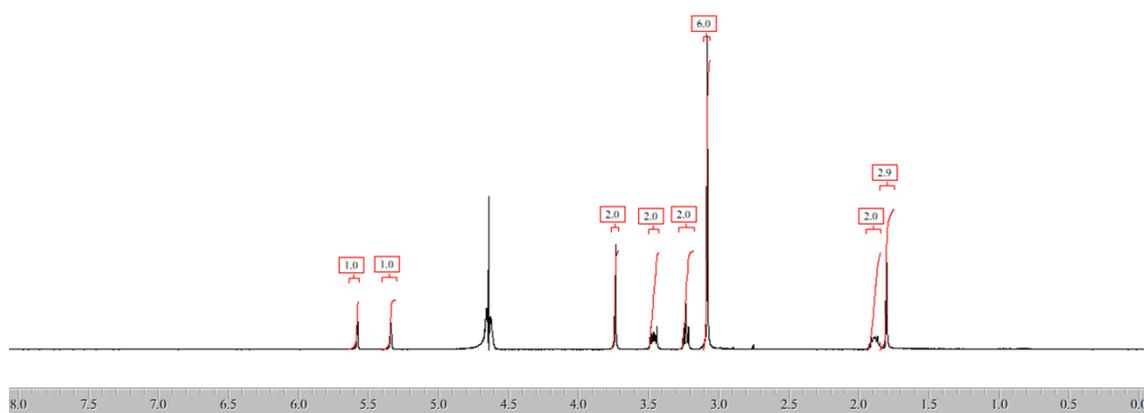


Figure S2: $^1\text{H NMR}$ spectra of 2-((3-methacrylamidopropyl)dimethylammonio)acetate(CB)

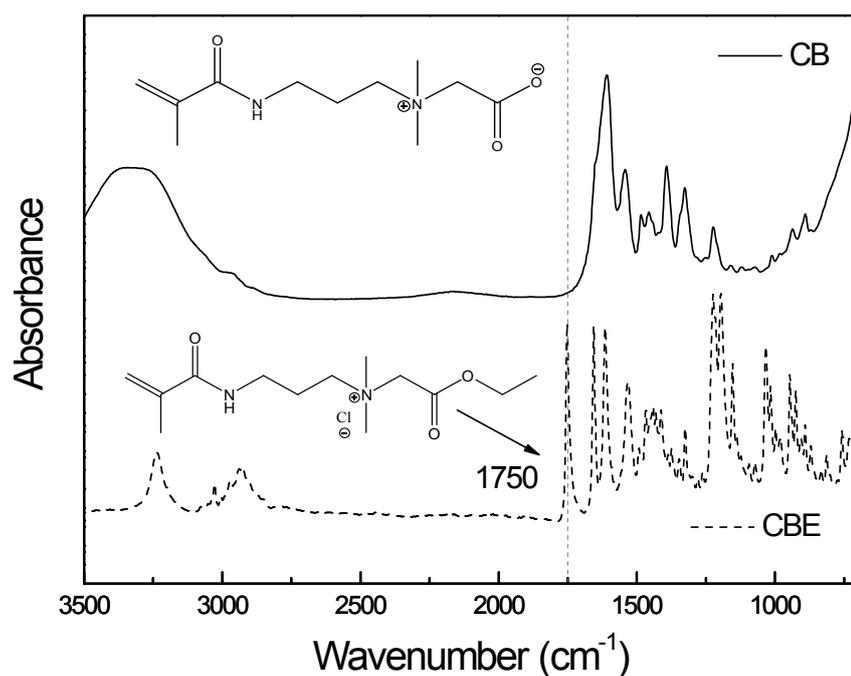


Figure S2: FTIR spectra of carboxybetaine ester (CBE) and zwitterionic carboxybetaine (CB).

The absorption of carbonyl group in carboxybetaine ester sample (CBE) at 1750 cm^{-1} shifts to lower frequencies after switch to zwitterionic form (CB).

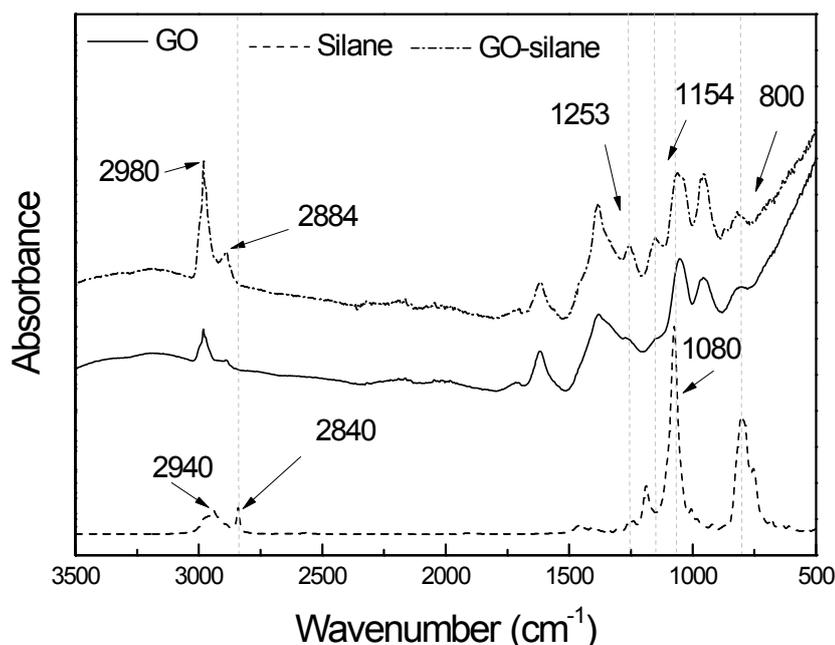


Figure S3: FTIR (ATR) spectra of neat GO, neat (3-mercaptopropyl)trimethoxysilane (silane), and silane modified GO particles (GO-silane).

The absorption bands at around 2940 cm^{-1} and 2880 cm^{-1} correspond to the asymmetric stretch of C-H in methoxy group. The band at 2840 cm^{-1} is assigned to C-H stretch in methoxy group, as is clearly visible in both silane and GO-silane spectra. In the finger-print region, the absorption peak of SiO-C at 1080 cm^{-1} can be recognized in GO-silane spectra. The new peaks at 1253 and 1154 cm^{-1} appeared, corresponding to C-H₂ twist and CH₃ rocking, respectively. The vibration at 800 cm^{-1} corresponds to Si-OC and is slightly pronounced after silanization in GO-silane spectra.

Investigation of the yield stress

Rheological data in the Fig. 9 were fit with Cho-Choi-Jhon model [1] (eq. S1).

$$\tau = \frac{\tau_y}{1 + (t_1 \dot{\gamma})^\alpha} + \eta_\infty \left(1 + \frac{1}{(t_2 \dot{\gamma})^\beta} \right) \dot{\gamma} \quad (S1)$$

Where τ_y is yield stress, α is related to decrease in the shear stress, β is exponent and falls $0 < \beta < 1$, t_1 and t_2 are time constants, and η_∞ is the shear viscosity at a high shear rate in the absence of an electric field. Six parameters of this model were determined using least square method. The parameters of the Cho-Choi-Jhon model are summarized in the tables S1-S4.

Table S1: Parameters of Cho-Choi-Jhon model fit for sample GO at various external electric field strengths.

	0.5 kV mm ⁻¹	1.0 kV mm ⁻¹	1.5 kV mm ⁻¹	2.0 kV mm ⁻¹	2.5 kV mm ⁻¹	3.0 kV mm ⁻¹
τ_y	2.49	5.75	11.94	21.86	30.18	41.67
t_1	0.03	0.03	0.05	0.05	0.09	0.09
A	2.46	2.09	2.36	1.97	1.65	1.30
η_∞	0.28	0.28	0.28	0.28	0.28	0.28
t_2	0.28	0.16	0.09	0.08	0.03	0.02
B	0.82	0.80	0.69	0.79	0.72	0.64

Table S2: Parameters of Cho-Choi-Jhon model fit for sample GO-SB at various external electric field strengths.

	0.5 kV mm ⁻¹	1.0 kV mm ⁻¹	1.5 kV mm ⁻¹	2.0 kV mm ⁻¹	2.5 kV mm ⁻¹	3.0 kV mm ⁻¹
τ_y	4.70	12.3	21.44	35.48	48.97	63.09
t_1	0.04	0.04	0.08	0.05	0.08	0.08
A	2.52	2.11	2.53	0.67	0.52	0.51
η_∞	0.28	0.28	0.28	0.280	0.28	0.28
t_2	0.29	0.17	0.09	0.08	0.07	0.02
B	0.93	0.83	0.80	0.76	0.72	0.64

Table S3: Parameters of Cho-Choi-Jhon model fit for sample GO-CB at various external electric fields strengths

	0.5 kV mm ⁻¹	1.0 kV mm ⁻¹	1.5 kV mm ⁻¹	2.0 kV mm ⁻¹	2.5 kV mm ⁻¹	3.0 kV mm ⁻¹
τ_y	4.80	14.79	24.28	37.11	53.7	70.79
t_1	0.05	0.06	0.03	0.04	0.06	0.07
A	2.14	1.66	1.11	0.98	1.73	1.26
η_∞	0.29	0.29	0.29	0.29	0.28	0.28
t_2	0.74	0.39	0.50	0.64	0.28	0.02
B	0.87	0.85	0.83	0.79	0.74	0.69

Table S4: Parameters of Cho-Choi-Jhon model fit for sample GO-CBE at various external electric field strengths.

	0.5 kV mm ⁻¹	1.0 kV mm ⁻¹	1.5 kV mm ⁻¹	2.0 kV mm ⁻¹	2.5 kV mm ⁻¹	3.0 kV mm ⁻¹
τ_y	7.41	17.37	30.19	48.94	69.18	96.72
t_1	0.08	0.02	0.03	0.04	0.03	0.06
A	2.16	0.32	0.64	0.02	0.94	0.55
η_∞	0.29	0.28	0.28	0.28	0.28	0.28
t_2	0.89	0.77	0.48	0.03	0.23	0.02
B	0.87	0.89	0.87	0.81	0.80	0.75

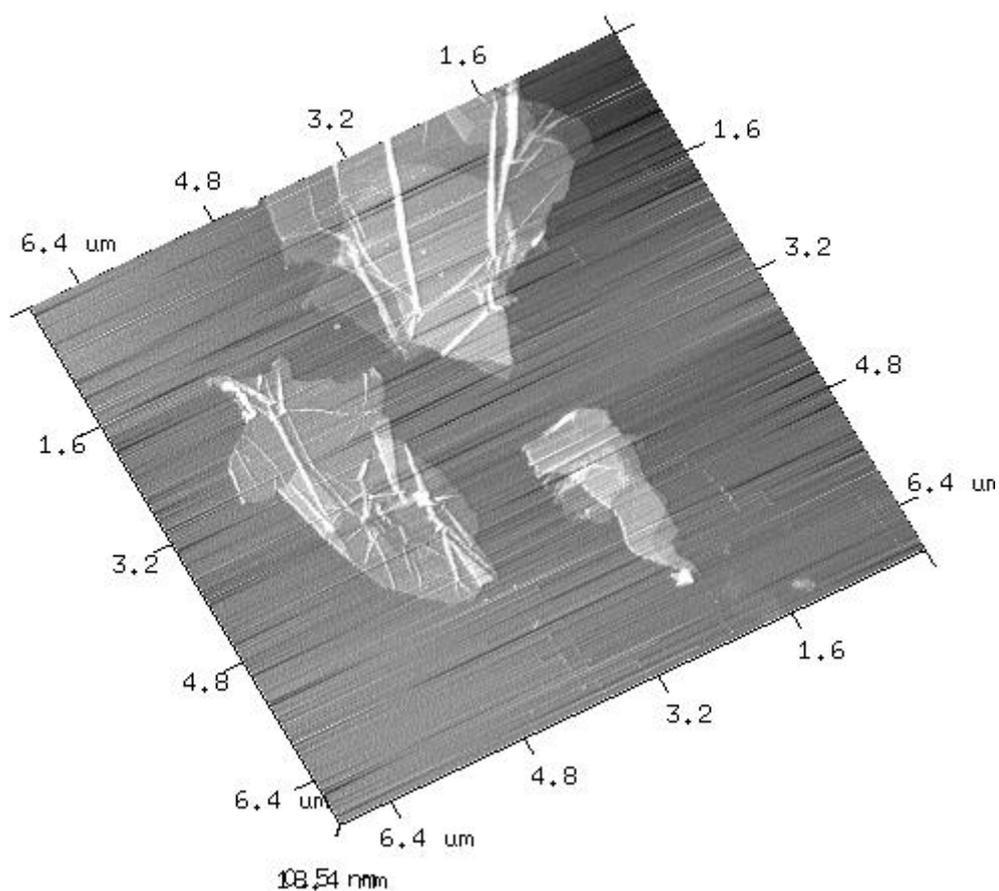


Figure S4: AFM image of neat GO deposited on silicone wafer.

[1] M. S. Cho, H. J. Choi and M. S. Jhon, *Polymer*, 2005, 46, 11484.