

Supporting information for

**Synthesis and thermal properties of vinyl copolymers with phenyl
vinylethylene carbonate and *N*-substituted maleimides undergoing color
change with acid-base switching**

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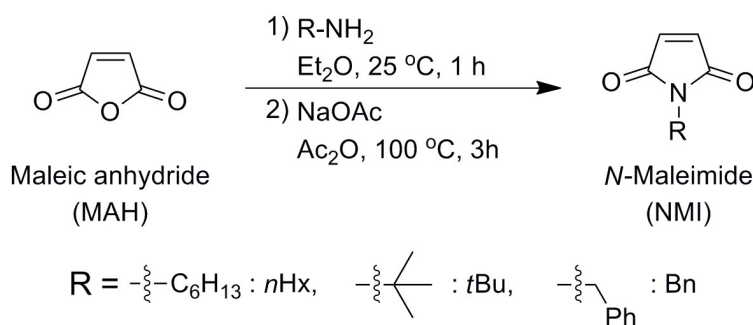
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Synthesis of *N*-substituted maleimide monomers



Scheme S1 Synthesis of *N*-substituted maleimides.

To 4.90 g (50 mmol) of maleic anhydride dissolved in 50 mL of diethyl ether added primary amines (50 mmol) in 5 mL of diethyl ether. The resulting mixture was stirred at room temperature for 1 h and a white powder of *N*-substituted maleamic acid was recovered by filtration. After a solution containing *N*-substituted maleamic acid and 2.05 g (25 mmol) of anhydrous sodium acetate in 50 mL of acetic anhydride was stirred at 100 °C for 3 h, the reaction mixture was then cooled to room temperature and was then poured into 200 mL of an ice-water mixture. The crude product was extracted with ethyl acetate and then washed with sodium hydrogen carbonate solution, water, brine. After drying with magnesium sulfate, the crude *N*-substituted maleimide was purified by silica-gel column chromatography with *n*-hexane and ethyl acetate (9:1) as an eluent.

N-Hexylmaleimide

^1H NMR (CDCl_3 , TMS): $\delta = 0.84$ (t, 3H, $-\text{CH}_3$, $J = 6.78$ Hz), 1.14-1.31 (m, 6H, $-(\text{CH}_2)_3-\text{CH}_3$), 1.47 (quin, 2H, $\text{NCH}_2-\text{CH}_2-$, $J = 7.01$ Hz), 3.38 (t, 2H, $\text{N}-\text{CH}_2-$, $J = 7.01$ Hz), 7.01 (s, 2H, $-\text{CH}=\text{CH}-$). ^{13}C NMR (CDCl_3 , TMS): $\delta = 13.8, 21.9, 25.7, 27.8, 30.6, 37.0, 134.4, 171.1$.

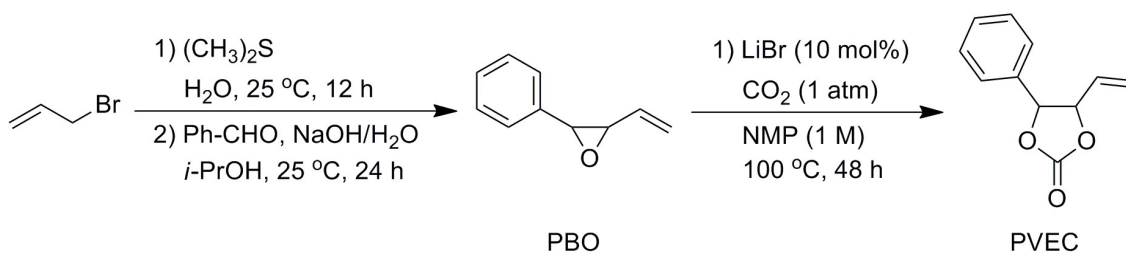
N-tert-Butylmaleimide

^1H NMR (CDCl_3 , TMS): $\delta = 1.50$ (s, 9H, $\text{C}(\text{CH}_3)_3$), 6.84 (s, 2H, $-\text{CH}=\text{CH}-$). ^{13}C NMR (CDCl_3 , TMS): $\delta = 40.4, 127.1, 128.5, 134.6, 136.6, 170.7$.

N-Benzylmaleimide

^1H NMR (CDCl_3 , TMS): $\delta = 4.59$ (s, 2H, CH_2), 7.08 (s, 2H, $-\text{CH}=\text{CH}-$), 7.21-7.35 (m, 5H, C_6H_5). ^{13}C NMR (CDCl_3 , TMS): $\delta = 28.4, 56.2, 134.2, 172.1$.

Synthesis of vinylethylene carbonate monomer



Scheme S2 Synthesis of phenyl butadiene monoxide, (PBO) and phenyl vinylethylene carbonate, (PVEC).

phenyl butadiene monoxide (*1-Phenyl-2-vinyl oxirane*), (*PBO*)

After a solution containing 54.4 g (0.45 mol) of allyl bromide and 33.6 g (0.54 mol) of dimethyl sulfide in 45 mL of water was stirred at 25 °C for 12 h, unreacted dimethyl sulfide was removed at reduced pressure by using a diaphragm pump. 31.8 g (0.3 mol) of benzaldehyde in 90 mL of 2-propanol was added to the solution at 25 °C. 18.0 g (0.45 mol) of sodium hydroxide dissolved in 45 mL of water was added slowly to the solution at 25 °C while stirring vigorously. After the solution was stirred at 25 °C for 24 h, the produced dimethyl sulfide was removed by the same method as above. The solution was extracted with ethyl acetate three times and the organic layer was washed with brine. After the organic layer was dried over MgSO₄, ethyl acetate was evaporated and the residue was purified by distillation (101-103 °C, 17 mmHg) to give a colorless liquid (41.3 g, 89%).

(*E*)-isomer: ¹H NMR (CDCl₃, TMS): δ = 3.36 (dd, 1H, CH₂=CH-CH-, *J* = 1.98 and 7.41 Hz), 3.77 (d, 1H, C₆H₅-CH-O-, *J* = 1.98 Hz), 5.34 (ddd, 1H, CH_{trans}(H_{cis})=CH-, *J* = 0.57, 1.34 and 10.4 Hz), 5.52 (ddd, 1H, CH_{cis}(H_{trans})=CH-, *J* = 0.57, 1.34 and 17.3 Hz), 5.74 (ddd, 1H, CH₂=CH-, *J* = 7.42, 10.4 and 17.3 Hz), 7.27-7.38 (m, 5H, C₆H₅-). ¹³C NMR (CDCl₃, TMS): δ = 60.21, 62.93, 119.58, 125.48, 128.23, 128.50, 132.08, 135.08.

(*Z*)-isomer: ¹H NMR (CDCl₃, TMS): δ = 3.66 (dd, 1H, CH₂=CH-CH-, *J* = 4.24 and 8.18 Hz), 4.25 (d, 1H, C₆H₅-CH-O-, *J* = 4.21 Hz), 5.27 (ddd, 1H, CH_{trans}(H_{cis})=CH-, *J* = 0.45, 1.72 and 10.4 Hz), 5.55 (ddd, 1H, CH_{cis}(H_{trans})=CH-, *J* = 0.45, 1.72 and 17.2 Hz), 5.40 (ddd, 1H, CH₂=CH-, *J* = 8.18, 10.3 and 17.3 Hz), 7.27-7.38 (m, 5H, C₆H₅-). ¹³C NMR (CDCl₃, TMS): δ = 58.83, 59.79, 121.91, 126.44, 127.71, 128.13, 132.08, 137.02.

Phenyl vinyl ethylene carbonate (4-Phenyl-5-vinyl-1,3-dioxolan-2-one), (PVEC)

A mixture of 174 mg (2 mmol) of LiBr, 2.92 g (20 mmol) of BMO-1 in NMP of 20 mL was stirring at 100 °C for 48 h under CO₂ atmosphere by using a gas balloon. The resulting solution was cooled to room temperature and washed with water and brine after the addition of ethyl acetate. After the organic layer was dried over MgSO₄, ethyl acetate was evaporated and the residue was purified by column chromatography (silica-gel, eluent: n-hexane/ethyl acetate = 4/1 [v/v]) and distillation (148-152 °C, 3 mmHg) to give a pale yellow liquid (2.00 g, 53%).

¹H NMR (CDCl₃, TMS): δ = 4.88 (ddm, 1H, CH₂=CH-CH-, J = 7.02 Hz and 8.19 Hz), 5.27 (d, 1H, C₆H₅-CH-O-, J = 8.14 Hz), 5.46 (dm, 1H, CH_B(H_A)=CH-, J = 17.3 Hz), 5.48 (dm, 1H, CH_A(H_B)=CH-, J = 10.4 Hz), 5.99 (ddd, 1H, CH₂=CH-, J = 6.99, 10.3 and 17.4 Hz), 7.34-7.85 (m, 5H, C₆H₅-). ¹³C NMR (CDCl₃, TMS): δ = 83.0, 84.74, 122.08, 125.88, 129.18, 129.71, 131.23, 134.74, 154.0.

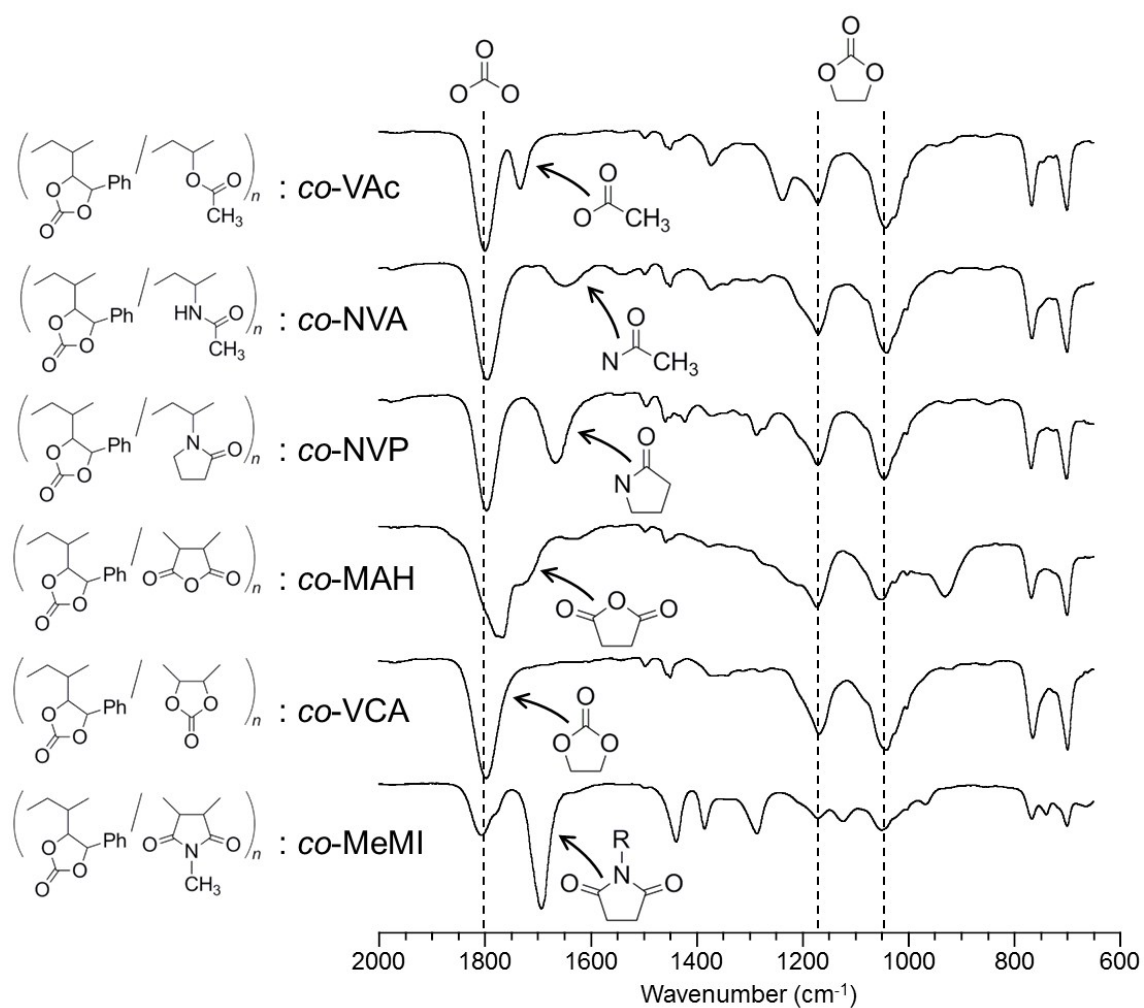


Figure S1 IR spectra of PVEC copolymers with several vinyl and cyclic monomers.

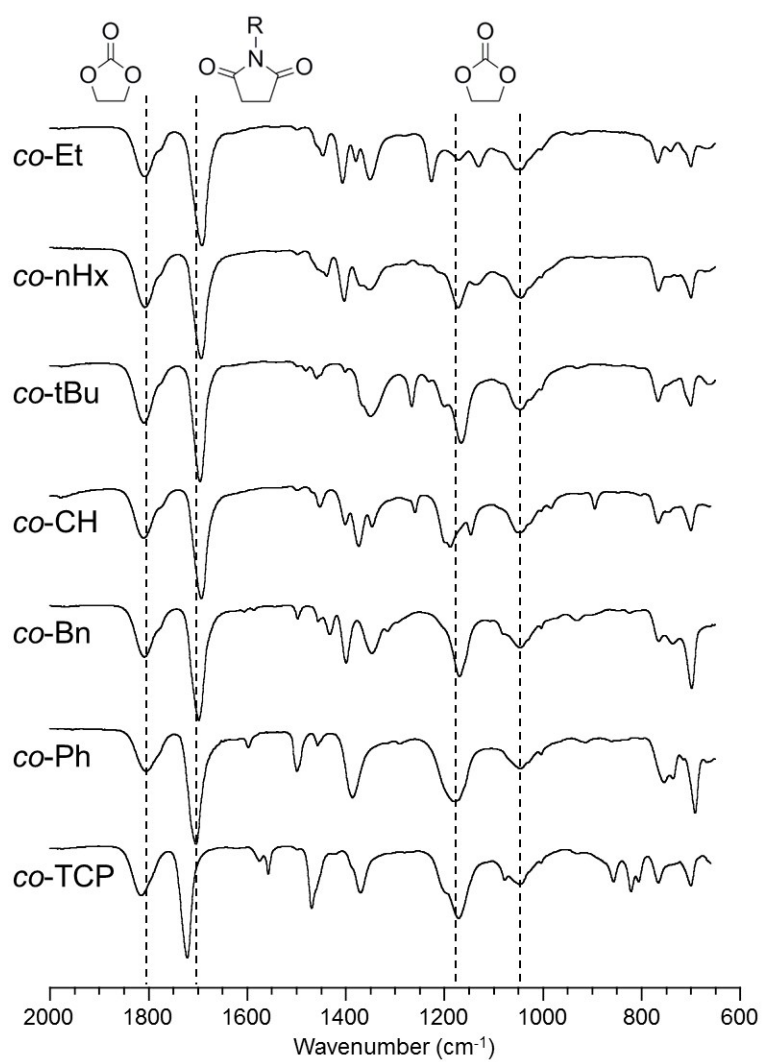


Figure S2 IR spectra of PVEC copolymers with various *N*-substituted maleimide monomers.

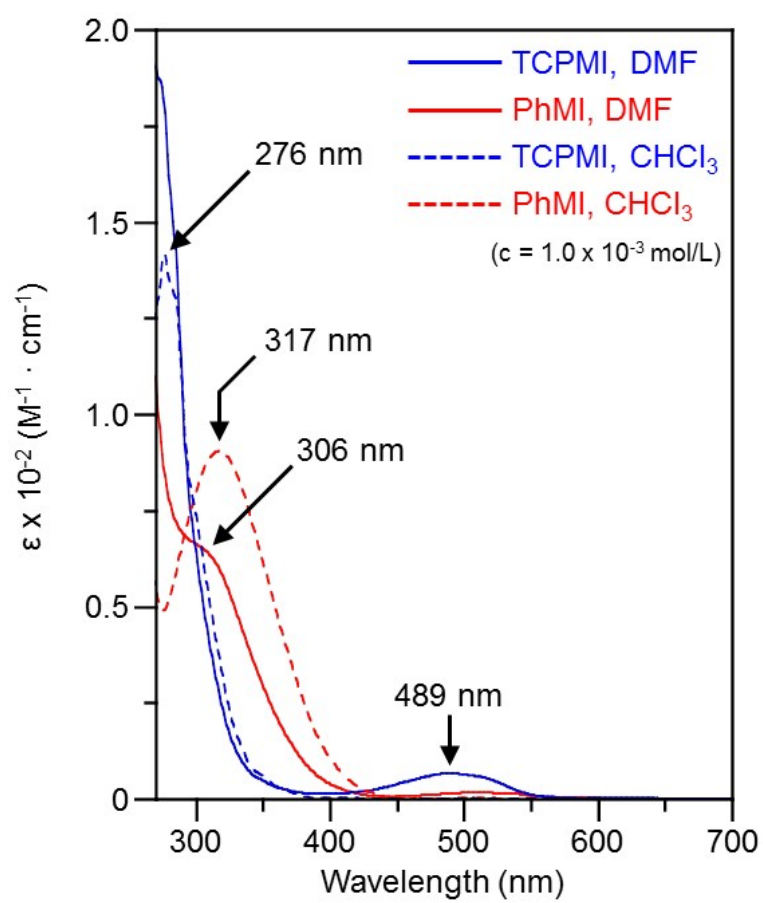


Figure S3 UV-vis spectra of PhMI and TCPMI monomers measured in DMF and CHCl_3 ($1.0 \times 10^{-3} \text{ mol/L}$).