

Cite this: DOI: 10.1039/c0xx00000x

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ARTICLE TYPE

Supporting Information for

Heat-Resistant Poly(*N*-(1-phenylethyl)maleimide-co-styrene) Microspheres Prepared by Dispersion Polymerization

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Received (in XXX, XXX) Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXX 20XX

DOI: 10.1039/b000000x

Monomer synthesis

Maleic anhydride (MAn) and DL-1-phenylethylamine were employed to synthesize *N*-(1-phenylethyl)maleimide (*N*-PEMI), as shown in Scheme 1 in the text. MAn (10.78 g, 0.11 mol) was dissolved in dimethylbenzene (50 mL) in a 250 mL three-necked flask equipped with a drop funnel, a condenser and mechanical stirring. DL-1-Phenylethylamine (12.74 mL, 0.1 mol) was added by one drop per second. The solution was stirred at room temperature for ca. 30 minutes to ensure an entire completion of the reaction. The reaction mixture was filtered and dried to give the intermediate *N*-(1-phenylethyl)maleamic acid as white powder. The intermediate (10.95 g, 0.05 mol) and dimethylbenzene (50 mL) were added to a 250 mL three-necked flask equipped with a water separator, a condenser and mechanical stirring. Triethylamine (6 mL), phosphoric acid (5 mL) and nickel sulfate hexahydrate aqueous solution (nickel sulfate/water = 1/7) (0.2 mL) were added in that order to the flask. The reaction was carried out at 135 °C (oil bath) for about 2–3 h, until there was no more water separated. The reaction mixture was washed by water for 3 times after it was cool down to room temperature to remove the residual raw materials. The dimethylbenzene-soluble mixture was collected and distilled in vacuum to obtain the monomer *N*-PEMI in 60% yield as a pale yellow crystalline solid, melting point 38–39 °C.

FT-IR (KBr) (see Fig. S1): 3096, 829 (=C-H), 3057, 3031, 762, 659 (Ar-H), 1705 (C=O), 1584 (C=C), 1390 (CO-N-CO), 1221 (C-N). ¹H NMR (CDCl₃, 600 MHz, 25 °C): δ = 1.82–1.85 (CH₃), 5.34–5.38 (CH), 6.62–6.65 (=C-H), 7.27–7.28 (para H in aromatic ring), 7.31–7.34 (ortho H in aromatic ring), 7.41–7.43 (meta H in aromatic ring). ¹³C NMR (CDCl₃, 600MHz, 25 °C): δ = 17.60–17.83 (CH₃), 49.52–49.72 (CH), 127.07–128.97 (unsubstituted C in aromatic ring), 133.91–134.13 (C=C), 140.20–140.36 (substituted C in aromatic ring), 170.39–170.71 (C=O).

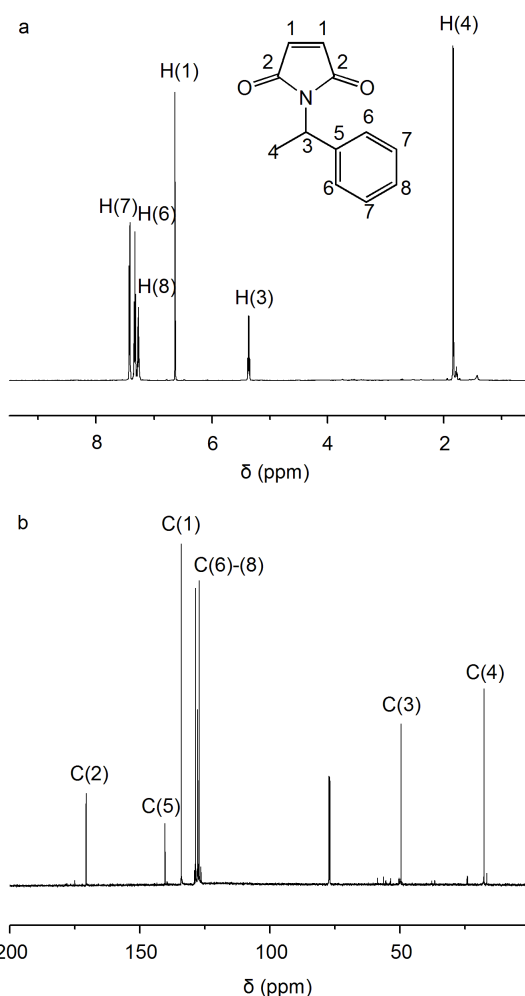


Fig. S1 ¹H NMR spectra (a) and ¹³C NMR (b) of *N*-PEMI. Measured in CDCl₃

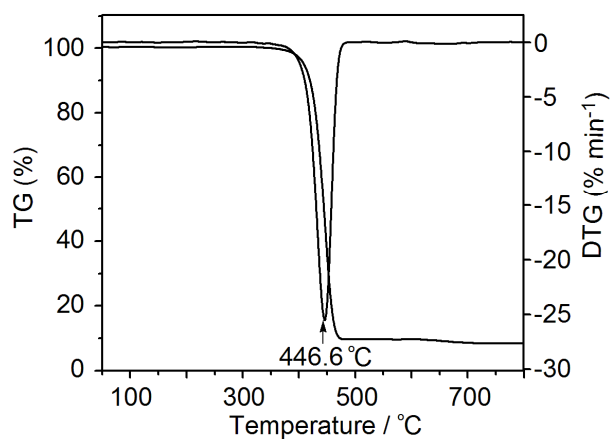


Fig. S2 TGA thermogram of poly(*N*-PEMI-*co*-St) in CHCl₃ at 75 °C. [*N*-PEMI] = [St] = 0.5 mol L⁻¹, [BPO] = 0.035 mol L⁻¹. Measurements were carried out in N₂ at a heating rate of 10 °C /min.

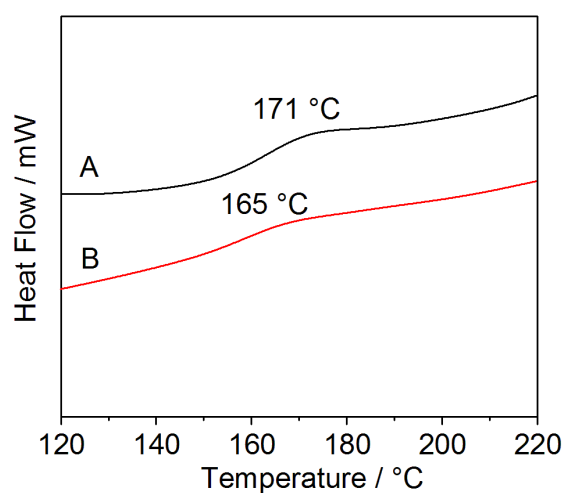


Fig. S3 DSC thermograms of poly(*N*-PEMI-*co*-St) obtained by solution polymerization (A) and poly(*N*-PEMI-*co*-St) microspheres obtained by dispersion polymerization (B) (run 2 in Table 1).

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