

Mechanical, Heat-resistant, Crystallographic and Dynamical Mechanical Properties of Nylon 6/P(N-phenylmaleimide-alt -styrene) Blends

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1. General Methods.

The 400 MHz ¹H and 101 MHz ¹³C NMR spectra were recorded on a Bruker Ascend400 spectrometer. The ¹H and ¹³C NMR spectra were referenced internally to the solvent peaks.

FTIR spectra were recorded on a ThermoFisher Nicolet iS50 spectrometer.

GPC analyses were performed in THF (1.0 mL/min, 30 °C) using a Viscotek TDA302 with a WL. M GPC solvent/sample module.

2. Materials

Maleic anhydride (MAH) was purchased from Tianjin Damao Chemical Reagent Factory and used as received. Hydroquinone was purchased from Tianjin Comma Chemical Reagent Co. LTD and used as received. Styrene (St, CR) was purchased from Sinopharm Chemical Reagent Co. LTD and was passed over an aluminum oxide column before usage to remove any inhibitor. Benzoyl peroxide was recrystallized from methyl alcohol and stored in the fridge. Aniline was purchased from Chengdu Jinshan Chemical Reagent Co.

LTD and used as received. Acetic anhydride and acetone were purchased from Chongqing sichuan east chemical (group) co. LTD and used as received. N,N-dimethyl formamide was purchased from Taicang Hushi test reagent co. LTD and used as received. Cyclohexanone was purchased from Chengdu kelong chemical reagent plant and used as received. Sodium acetate anhydrous and thionyl chloride was purchased from Chengdu kelong chemical reagent plant and used as received.

3. Syntheses

Synthesis of N-Phenylmaleimide (IUPAC-name: 1-phenyl-1H-pyrrole-2,5-dione; NPMI)

The solution of aniline (93.06g, 1mol) in N,N-dimethyl formamide (DMF, 100mL) was gradually added over a period of 15min to a well-stirred solution of maleic anhydride (98.1g, 1mol) in DMF(500mL). The solution was stirred for 2h at room temperature. Then dusty sodium acetate (12.0g), hydroquinone(10g) and acetic anhydride (50ml) was added to the resulting clear solution and heated up to 50 °C in an oil bath for 2 hours. A light yellow mass of N-Phenylmaleimide (NPMI), obtained by adding the solution to crushed ice, was washed several times with water and then dried in an air oven at 50–60°C. Yield: 96.2% (166.5g). ¹H NMR (400 MHz, CDCl₃) δ 7.47 (t, J = 7.6 Hz, 2H), 7.41 – 7.31 (m, 3H), 6.86 (s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 169.35 (s), 134.03 (s), 131.02 (s), 128.98 (s), 127.80 (s), 125.90 (s). FT-IR: 3095.1(–

$CH=CH-$), 1709.8 (maleimide C=O), 1593.2, 1507.6, 1394.7 (benzene carbon skeleton).

Free radical copolymerization of P(NPMI-alt-St) (PNS)

The free radical copolymerization of P(NPMI-alt-St) was carried out in a 5 L mouth flask purged with dry nitrogen. The polymerization process is as follows: NPMI (217 g) and St (104 g) were added and dissolved in cyclohexanone (3 L) by stirring at 76 °C for 40 min before the initiator, BPO (7.5 g), was added. The reactor was heated by external circulating heated silicon oil, and the copolymerization was carried out at 100 °C for 4 h under nitrogen atmosphere and then cooled down to room temperature. The copolymer was then dissolved in acetone and the solution was poured into an excess of methanol to remove residual monomers and initiator. This procedure was repeated twice, and the final product was dried under vacuum at 100 °C up to constant weight. The predicted chemical structure of P(NPMI-alt-St) is shown in Scheme 1. GPC: $M_{n, GPC}=12200 \text{ g mol}^{-1}$, $M_{w, GPC}=18300 \text{ g mol}^{-1}$, $D = 1.50$

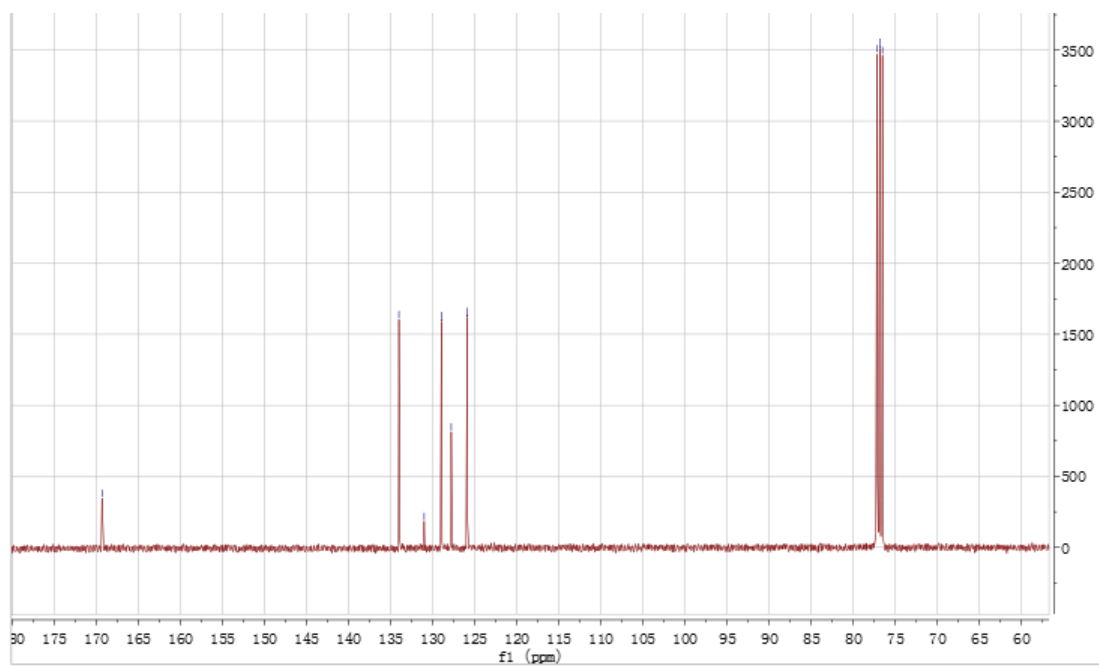
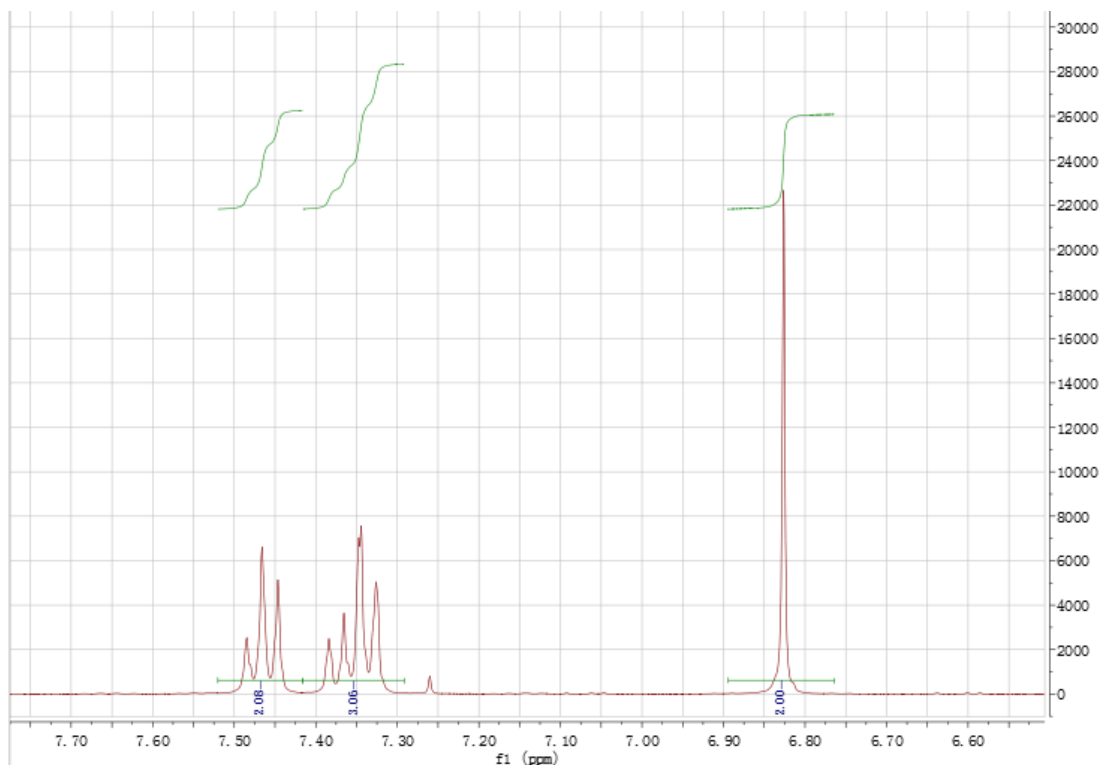


Figure S1 ^1H and ^{13}C NMR spectra of NPMI in CDCl_3

Additional Spectral Data for Polymers

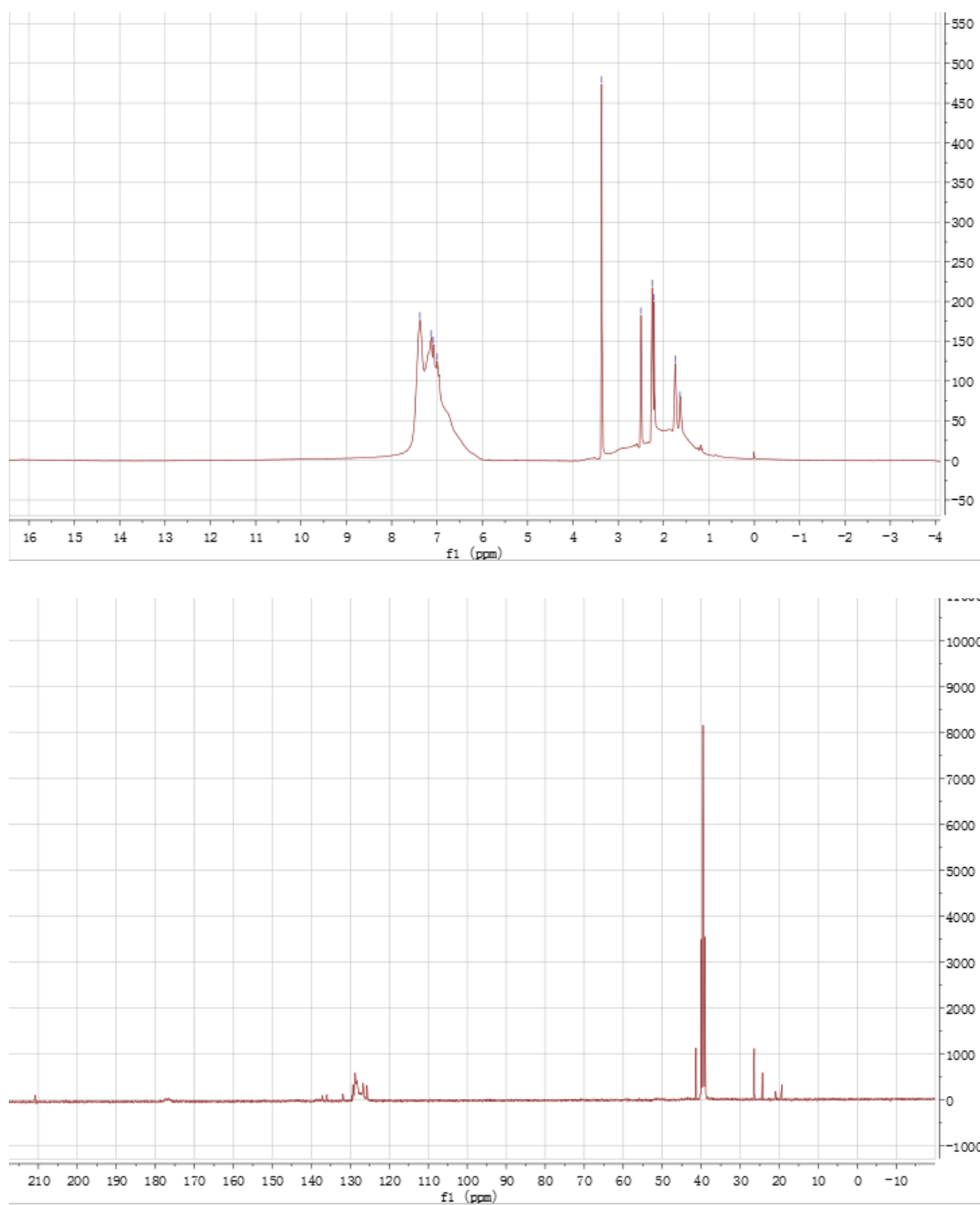


Figure S2 ^1H and ^{13}C NMR spectra of PNS in DMSO

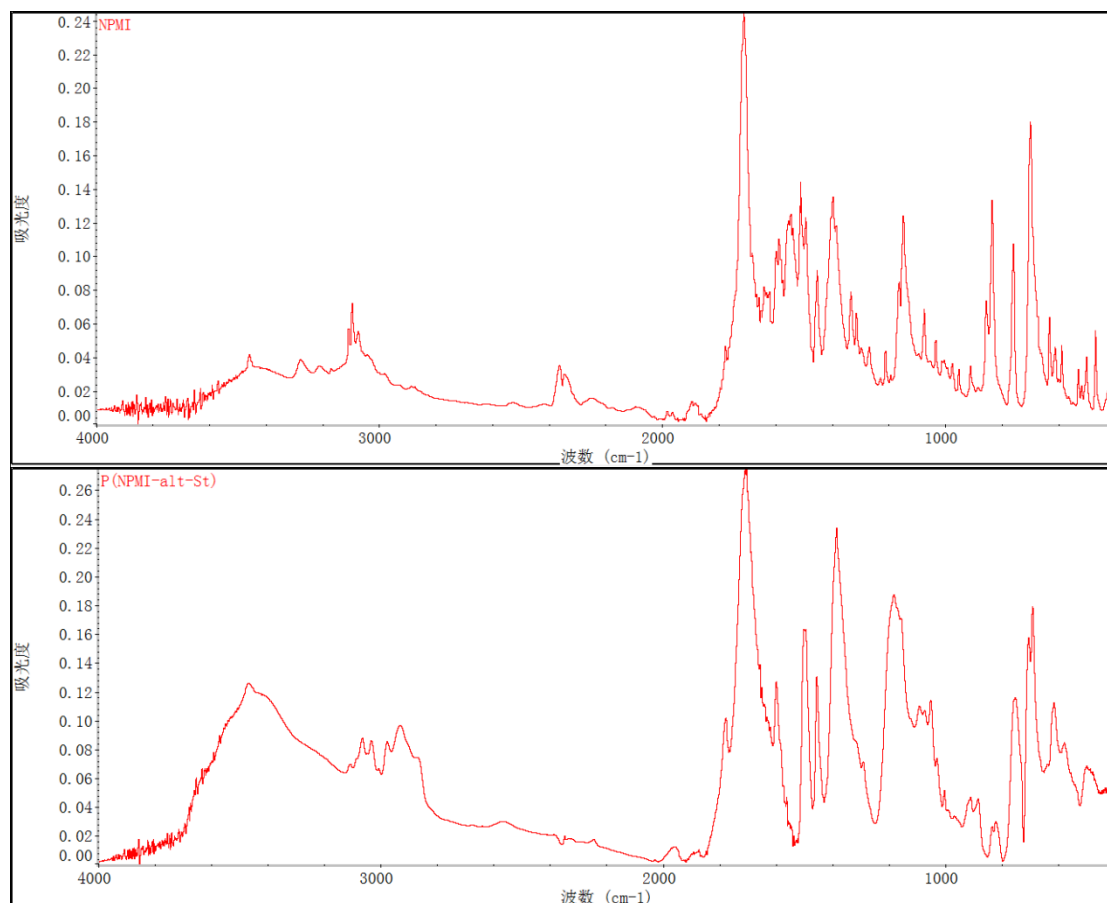


Figure S3 FT-IR spectra of the synthesized NPMI and PNS