Supporting Information

Efficient and Low-Carbon Synthesis of Colorless Transparent Polyimides

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Contents

Experimental Section

Characterization

Fourier Transform Infrared Spectroscopy (FT-IR): The molecular structure and imidization degree of the PI films were analyzed using a Nicolet iS 50 FT-IR spectrometer (Thermo Scientific, USA) with the Attenuated Total Reflection (ATR) method. The wavenumber range was 4000-500 cm^{-1} at room temperature.

Nuclear Magnetic Resonance Spectroscopy (NMR): The molecular structure and imidization degree of the PI were analyzed using a Bruker Advance III NMR spectrometer (Bruker, Switzerland).

Gel Permeation Chromatography (GPC): The molecular weight and molecular weight distribution were determined using an Alliance e 2695 GPC (Waters, USA). PS (polystyrene) was used as a standard, and DMF containing 0.1 M LiBr was the mobile phase. The injection volume was 50.00 μL, with a flow rate of 0.1 mL/min and a runtime of 45 minutes at room temperature.

UV-Vis Spectrophotometry: The U-3900 UV-vis spectrophotometer (Hitachi, Japan) was used to test the optical properties of the PI films with a scanning wavelength range of 200-800 nm. The thickness of the tested films is indicated in the table.

Thermogravimetric Analysis (TGA): The glass transition temperature (T_g) of the PI films was measured using a TG 209F1 Libra TGA (Netzsch, Germany) with a sample mass of 3-5 mg, nitrogen flow rate of 20 mL/min, heating rate of 10 °C/min, and a temperature range of 30-800 °C.

Dynamic Thermomechanical Analysis (DMA): The storage modulus (E') and loss modulus (E") of the films were tested using a Q 800 DMA (TA Instruments, USA). The sample size was 8 mm × 4 mm, tested in air with a heating rate of 3 °C/min and a temperature range of 50-400 °C.

X-ray Powder Diffraction (XRD): The films were analyzed using a D-MAX 2200 VPC X-ray powder diffractometer (Rigaku, Japan) at room temperature with a scan speed of 10 °/min over a 10-60 ° range.

Densitometry: The specific gravity of the polyimide films and water was measured using an Alfa Mirage SD-200L electronic densitometer (Japan) at room temperature.

Mechanical properties: Mechanical properties were carried out on a Q 800 DMA (TA Instruments, USA), in which the tensile test was measured at the ramp force of 3 N min^{-1}, n=3.

Peel Performance: The peel strength was tested by 90 ° peel tester (AISRY, China) at a rate of 5 mm min^{-1}, n=5.

ID Calculation

From the ATR-FTIR spectrum, the ratio of the peak area (S) corresponding to the C-N stretching vibration at 1363 cm^{-1} (on the imide ring) and the stretching vibration at 1490 cm^{-1} (on the benzene ring) was used to estimate the imidization degree ID_1. The imidization degree of the film after thermal imidization at 350 °C was set as 100%, and the calculation method is outlined in formula (1)[1,2].

$$\mathrm{ID}_1(\%) = \frac{(S_{1363}/S_{1490})_x}{(S_{1363}/S_{1490})_{350}} \times 100\% \quad (1)$$

^{1}H NMR spectroscopy was used for more accurate characterization of the imidization degree. The imidization degree (ID_2) was calculated based on the ratio of hydrogen atoms on the amide bonds formed by incomplete imidization to those on the aromatic rings of the repeating units, as shown in formula (2)[3].

$$\mathrm{ID}_2(\%) = \left(1 - \frac{A_{imide}}{A_{ru}/6}\right) \times 100\ \% \quad (2)$$

Here A_{imide} refers to the number of hydrogen atoms on the amide bonds around 10.7 ppm, and A_{ru} refers to the number of hydrogen atoms on the aromatic rings of the repeating units in the 7.7 ppm to 8.3 ppm range.

Calculation of Hansen Solubility Parameter (HSP) and interaction distance (Ra)

The Hansen Solubility Parameter was first proposed by Hansen[4], and is decribed as formula (3). δ_t is the total energy of vaporization of components considering the different molecular interactions, and δ_d, δ_p, δ_h are the dispersive forces, polar (dipole-dipole) forces and hydrogen bonding components in order., which can represent the x, y, z coordinates in a Hansen sphere model[5]. The compatibility between a solvent and a polymer can be quantitatively evaluated by interaction distance (R_a), which can be calculated according to formula (4), by the distance between the polymer and the solvent. R_0 is the radius of interaction in the solubility sphere. The Relative Energy Difference (RED) is then defined as the ratio, as shown in formula (5). A solvent is considered a "good solvent" if RED≤1.

$$\delta_t = \sqrt{({\delta_d}^2 + {\delta_p}^2 + {\delta_h}^2)} \quad (3)$$

$$R_a = \sqrt{4({\delta_{d2}}^2 - {\delta_{d1}}^2) + ({\delta_{p2}}^2 - {\delta_{p1}}^2) + ({\delta_{h2}}^2 - {\delta_{h1}}^2))} \quad (4)$$

$$RED = \frac{Ra}{R_0} \quad (5)$$

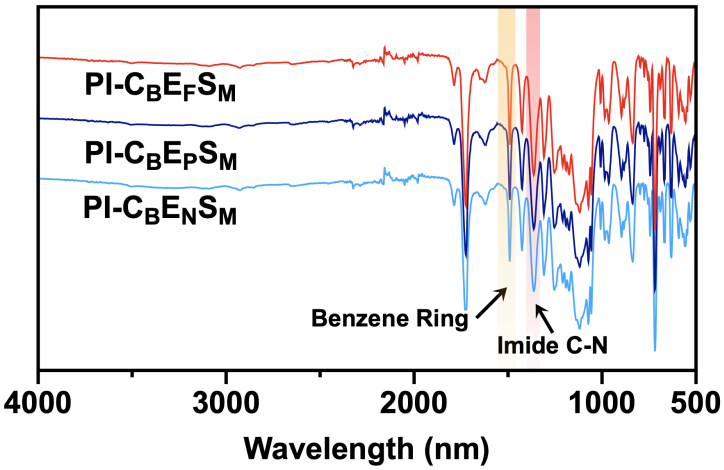

Figure S1. ATR-FTIR spectrum of films prepared with different end-capping agents.

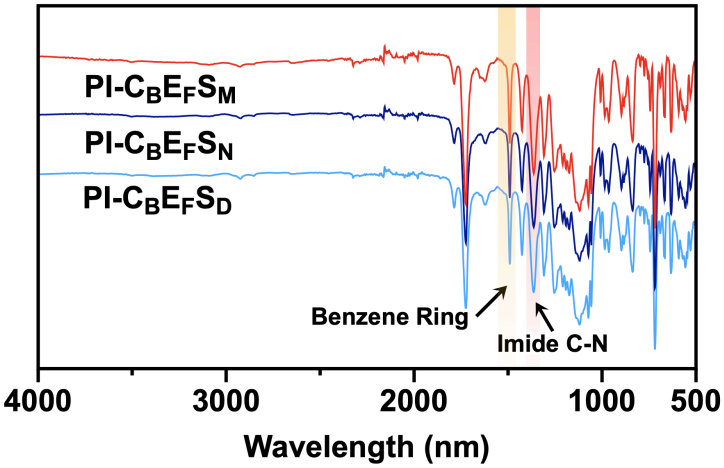

Figure S2. ATR-FTIR spectrum of films prepared with different solvents.

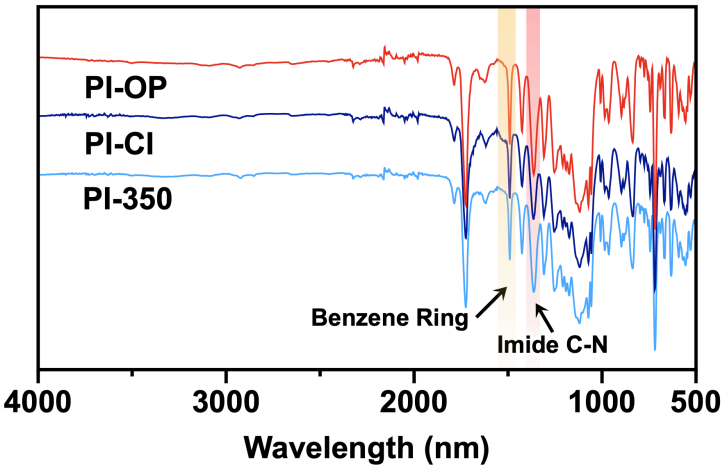

Figure S3. ATR-FTIR spectrum of films prepared by one pot method, chemical imidization method and heat imidization as control.

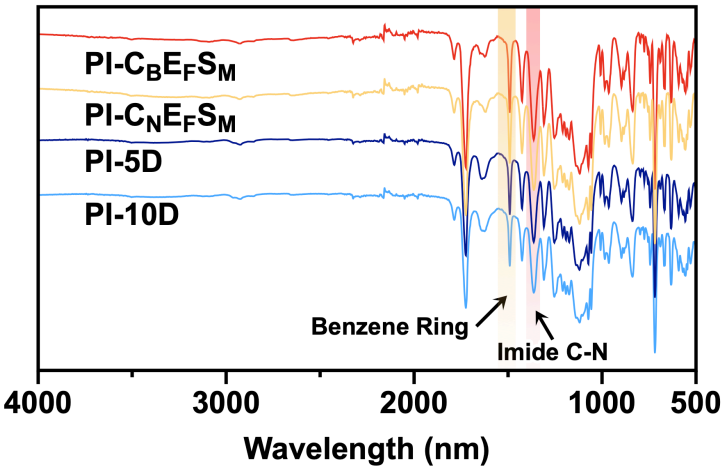

Figure S4. ATR-FTIR spectrum of films prepared by DABA self-catalyzed one-step method.

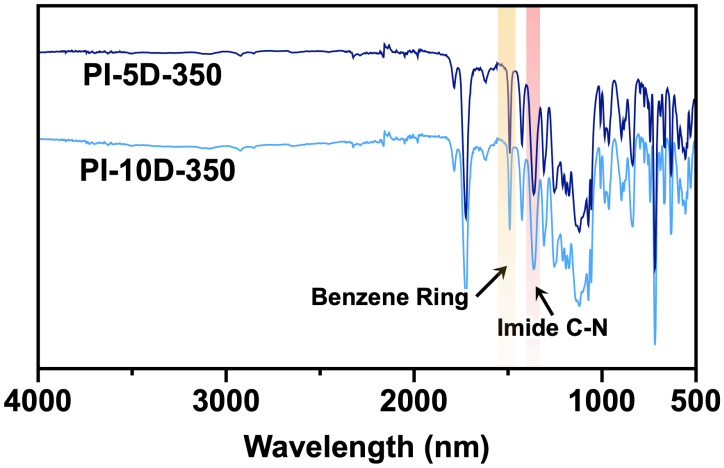

Figure S5. ATR-FTIR spectrum of DABA-6FDA-TFMB films prepared by heat imidization as control.

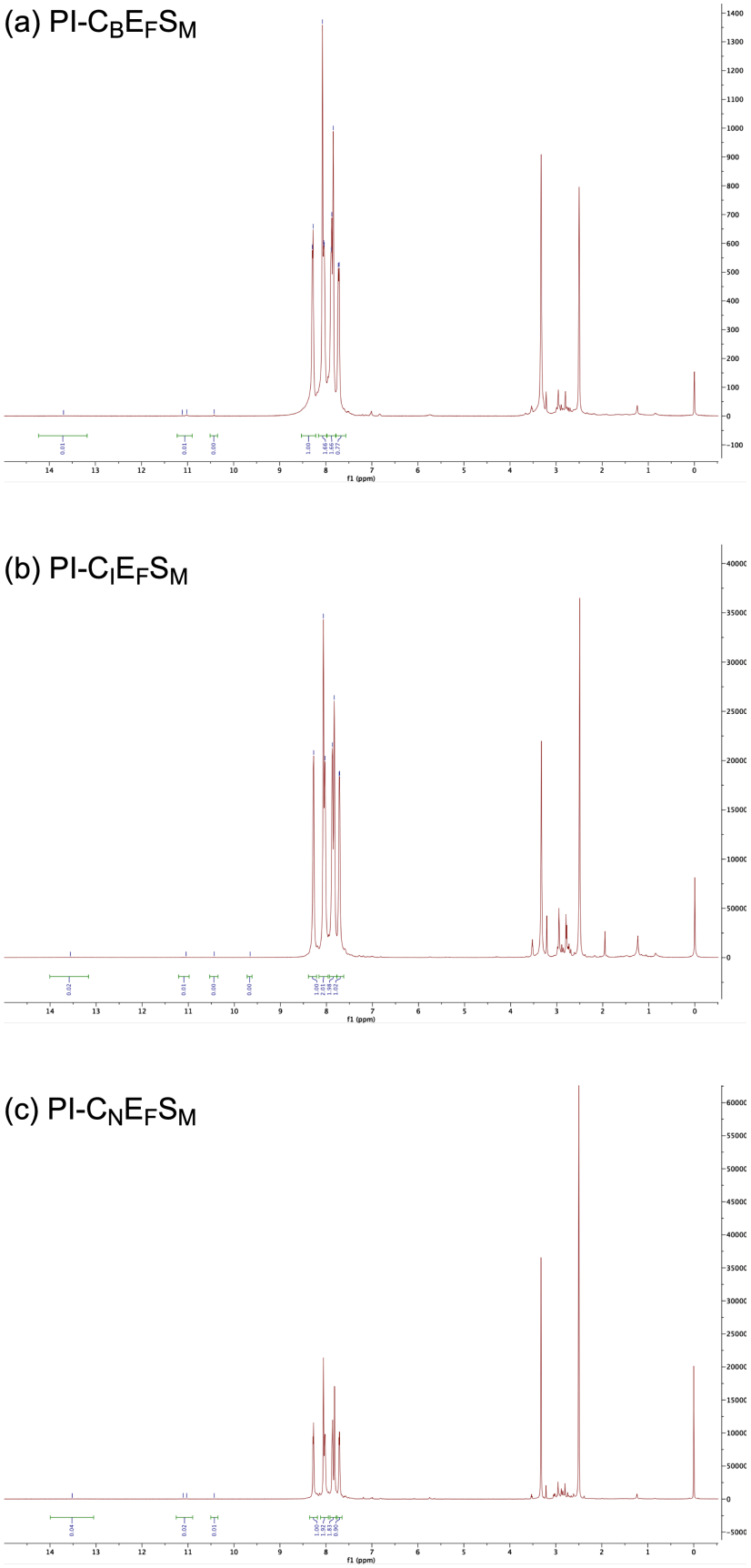

Figure S6. ^{1}H NMR spectrum of films prepared with differen catalyststst.

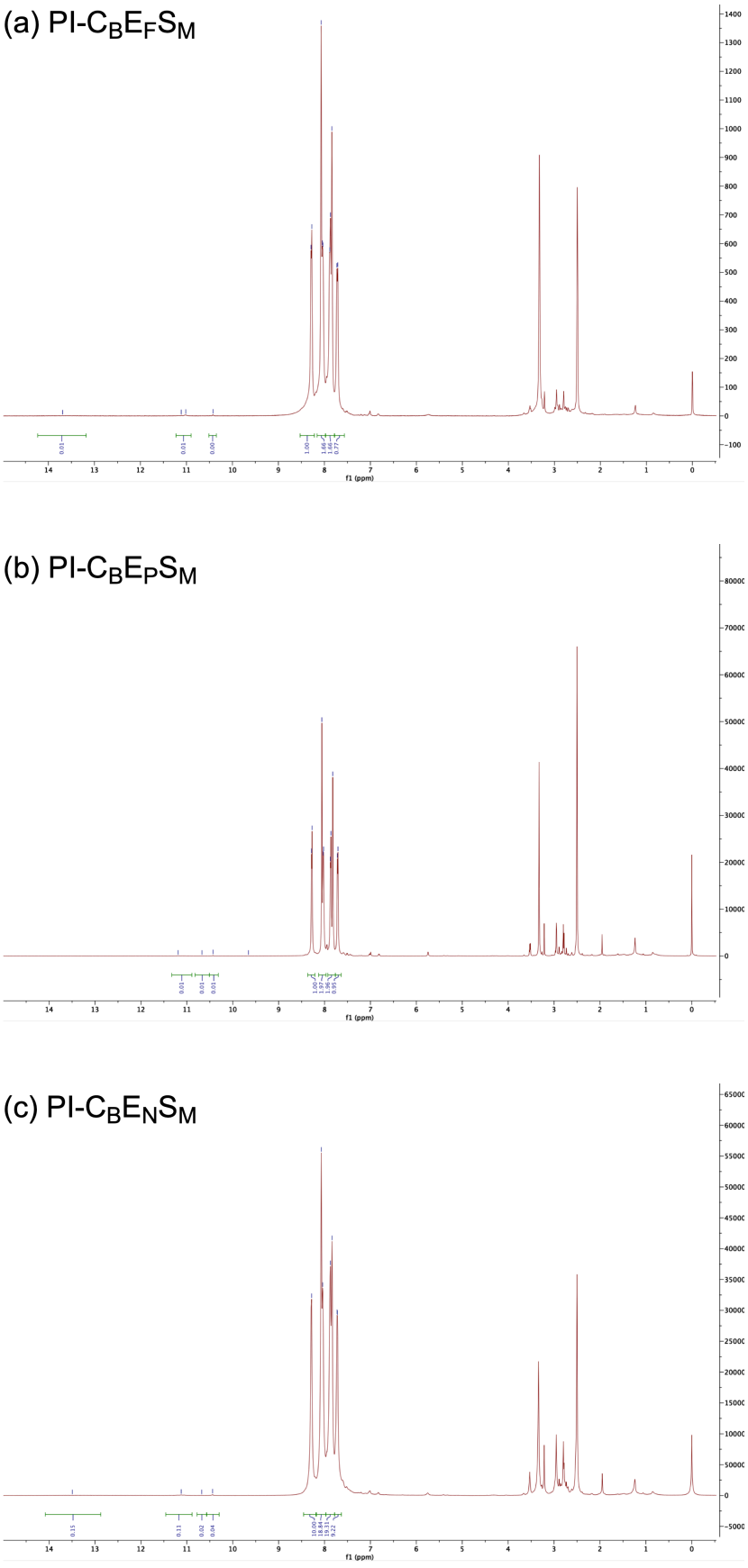

Figure S7. ^{1}H NMR spectrum of films prepared with different end-capping agents.

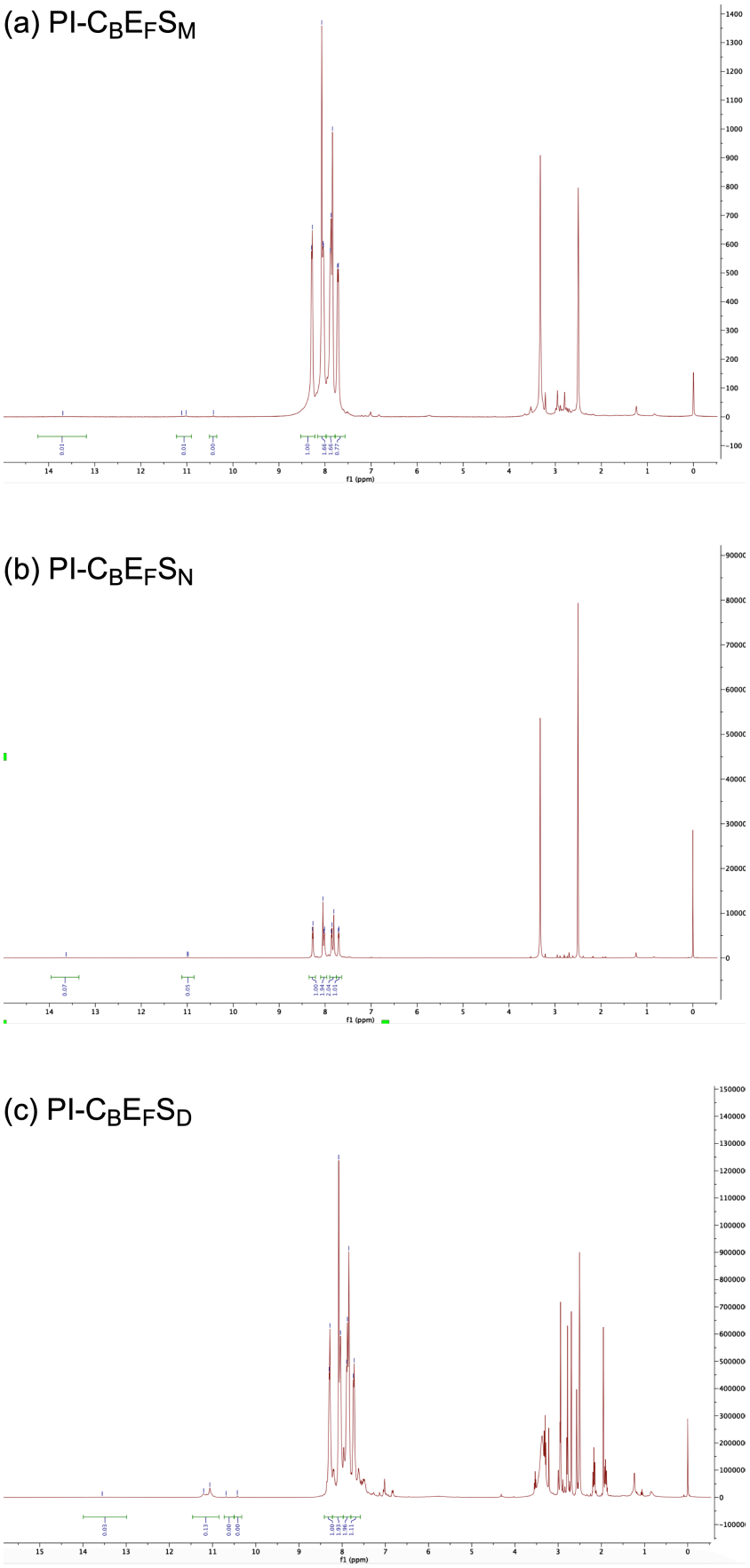

Figure S8. ^{1}H NMR spectrum of films prepared with different solvents.

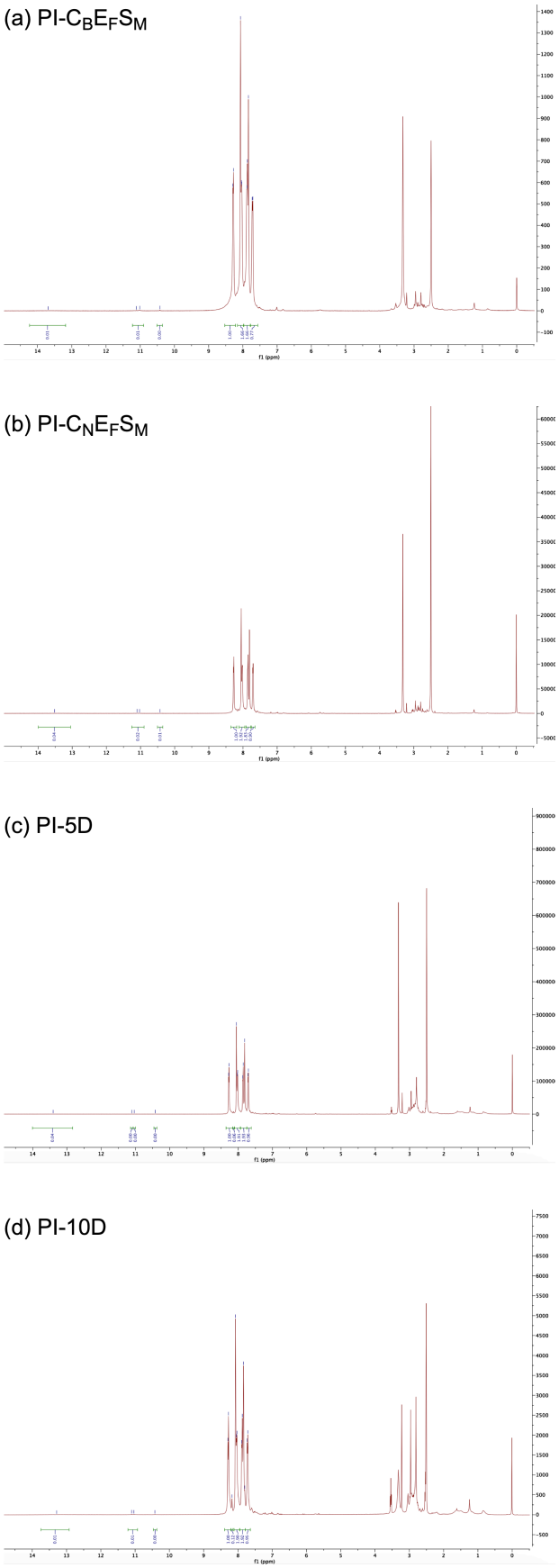

Figure S9. ^{1}H NMR spectrum of films prepared by DABA self-catalyzed one-step method.

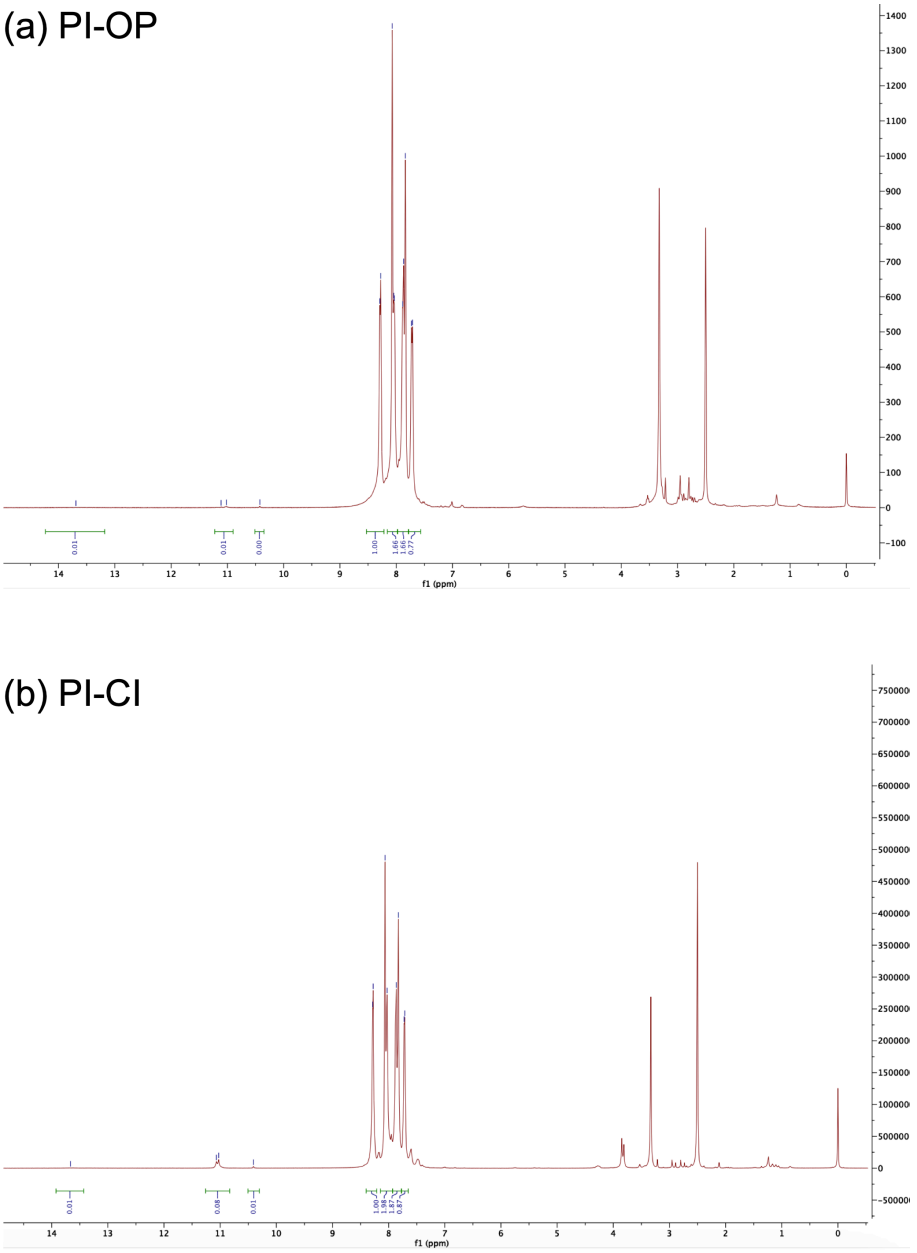

Figure S10. ^{1}H NMR spectrum of films prepared by one-pot method, chemical imidization method.

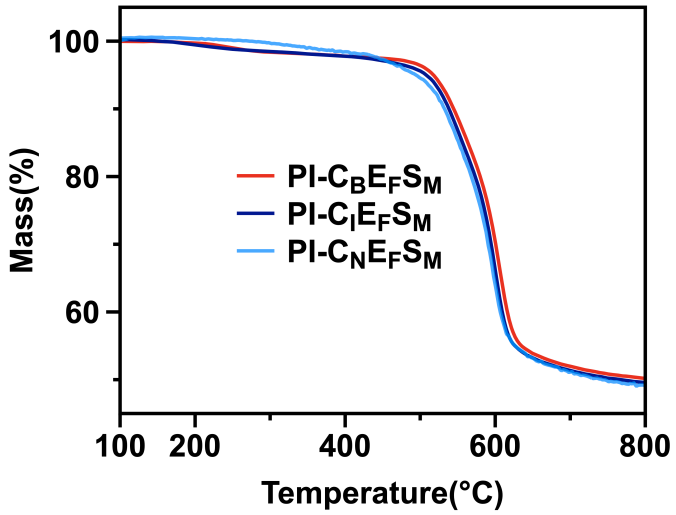

Figure S11. TGA curves of PI films prepared with different catalysts.

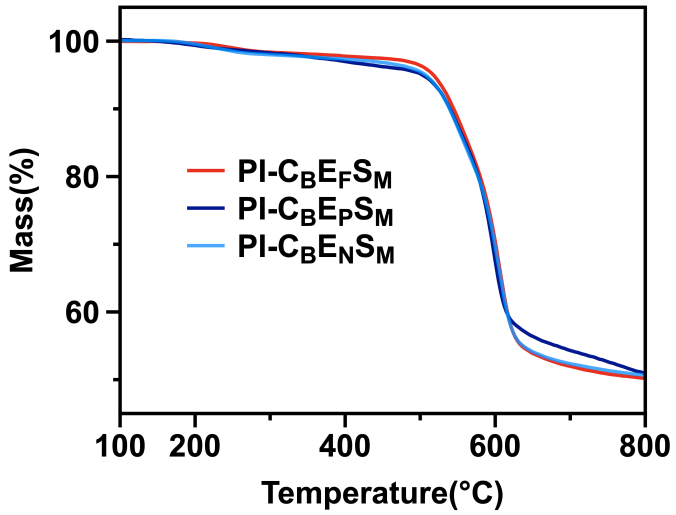

Figure S12. TGA curves of PI films prepared with different end-capping agents.

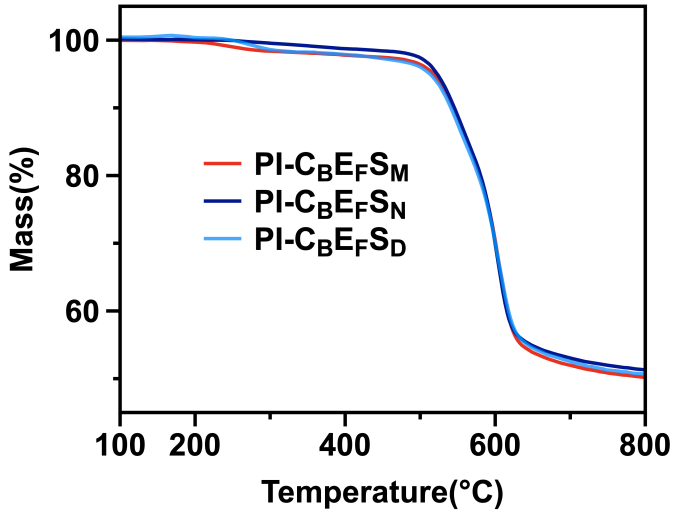

Figure S13. TGA curves of PI films prepared with different solvents.

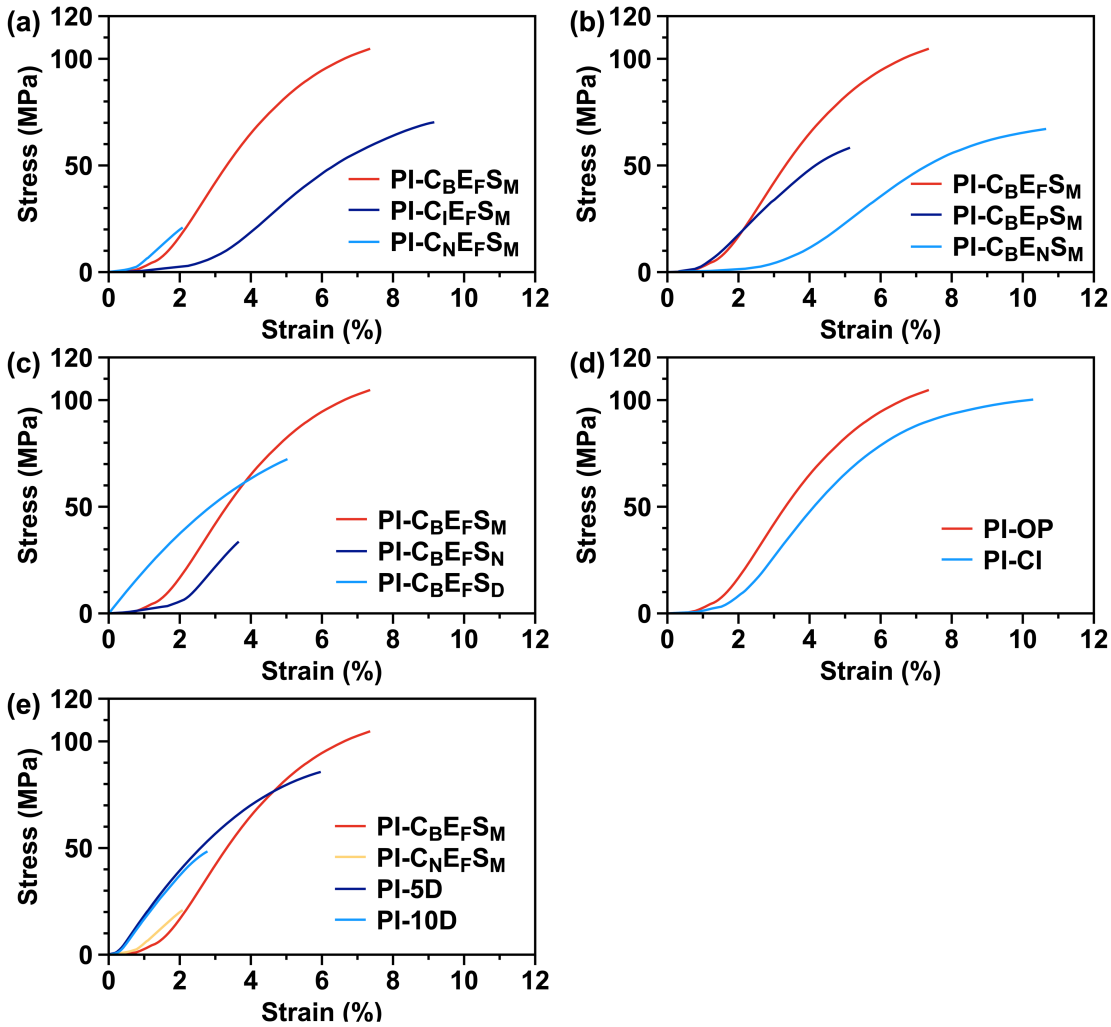

Figure S14. Stress-strain curves of PI films. (a) Stress-strain curves of PI films prepared with different catalysts; (b) Stress-strain curves of PI films prepared with different end-capping agents; (c) Stress-strain curves of PI films prepared with different solvents; (d) Stress-strain curves of films prepared by chemical imidization method and one pot method; (e) Stress-strain curves of films prepared by DABA self-catalyzed one-step method.

Table S1. GHS hazard statements of common solvents for one-step preparation of polyimide.

Solvent	Code	Hazard Statement	Class
NMP	H372	Causes damage to organs through prolonged or repeated exposure	STOT-RE Category 1
	H360Fd	May damage fertility. Suspected of damaging the unborn child	Reproductive Toxicity Category 1B
	H360FD	May damage fertility. May damage the unborn child	Reproductive Toxicity Category 1B
	H360F	May damage fertility	Reproductive Toxicity Category 1B
	H360Df	May damage fertility. Suspected of damaging the unborn child	Reproductive Toxicity Category 1B
	H360D	May damage the unborn child	Reproductive Toxicity Category 1B
	H360	May damage fertility or the unborn child	Reproductive Toxicity Category 1B
	H335	May cause respiratory irritation	Specific target organ toxicity - single exposure Category 3 (respiratory tract irritation)
	H318	Causes serious eye damage	Serious Eye Damage Category 1
	H315	Causes skin irritation	Skin Corrosion / Irritation Category 2
	H302	Harmful if swallowed	Acute Toxicity (Oral) Category 4
***m*-Cresol**	H335	May cause respiratory irritation	Specific target organ toxicity - single exposure Category 3 (respiratory tract irritation)
	H314	Causes severe skin burns and eye damage	Skin Corrosion/Irritation Category 1B
	H318	Causes serious eye damage	Serious Eye Damage Category 1
	H370	Causes damage to organs	STOT - SE Category 1
	H361fd	Suspected of damaging fertility. Suspected of damaging the unborn child	Reproductive Toxicity Category 2
	H361f	Suspected of damaging fertility	Reproductive Toxicity Category 2
	H361d	Suspected of damaging the unborn child	Reproductive Toxicity Category 2
	H361	Suspected of damaging fertility or the unborn child	Reproductive Toxicity Category 2
	H411	Toxic to aquatic life with long lasting effects	Chronic Aquatic Hazard Category 2
	H301	Toxic if swallowed	Acute Toxicity (Oral) Category 3
	H311	Toxic in contact with skin	Acute Toxicity (Dermal) Category 3

Continue Table S1. GHS hazard statements of common solvents for one-step preparation of polyimide.

Solvent	Code	Hazard Statement	Class
DMAc	H360Fd	May damage fertility. Suspected of damaging the unborn child	Reproductive Toxicity Category 1B
	H360FD	May damage fertility. May damage the unborn child	Reproductive Toxicity Category 1B
	H360F	May damage fertility	Reproductive Toxicity Category 1B
	H360Df	May damage fertility. Suspected of damaging the unborn child	Reproductive Toxicity Category 1B
	H360D	May damage the unborn child	Reproductive Toxicity Category 1B
	H360	May damage fertility or the unborn child	Reproductive Toxicity Category 1B
	H319	Causes serious eye irritation	Eye Irritation Category 2
	H350i	May cause cancer by inhalation	Carcinogenicity Category 1A
	H350	May cause cancer	Carcinogenicity Category 1A
	H301	Toxic if swallowed	Acute Toxicity (Oral) Category 3
	H300	Fatal if swallowed	Acute Toxicity (Oral) Category 2
MDMPA	H371	May cause damage to organs	STOT-SE Category 2
	H373	May cause damage to organs through prolonged or repeated exposure	STOT-RE Category 2
	H361fd	Suspected of damaging fertility. Suspected of damaging the unborn child	Reproductive Toxicity Category 2
	H361f	Suspected of damaging fertility	Reproductive Toxicity Category 2
	H361d	Suspected of damaging the unborn child	Reproductive Toxicity Category 2
	H361	Suspected of damaging fertility or the unborn child	Reproductive Toxicity Category 2
	H319	Causes serious eye irritation	Eye Irritation Category 2

Notes: data from European Chemical Agency (ECHA) Classification & Labelling Inventory.

Table S2. The Hansen Solubility Parameters (HSP), Interaction Distance (R_a) and Relative Energy Difference (RED)

	δ_d (Mpa$^{1/2}$)	δ_p (Mpa$^{1/2}$)	δ_h (Mpa$^{1/2}$)	R_a	RED
Average of 6FDA-based[5]	18.0	7.8	7.7	7.1(R_0)	-
MDMPA	17.2	10.9	9.5	3.9	0.55
NMP	18.0	12.3	7.2	4.5	0.63
DMAc	16.8	11.5	9.4	4.7	0.66

Table S3. Inventory of chemicals consumption for different methods of producing polyimide films.

Compoent	Unit	Amount Required (One Pot)	Amount Required (Chemical Imidization)
Polymer synthesis			
6FDA	mmol	5.05	5.05
TFMB	mmol	5	5
Solvents (MDMPA, NMP, DMAc)	g	12	22
Anhydrous xylene	g	4	0
Ac_2O	g	0	5.10
Pyridine	g	0	2.19
Benzoic Acid	g	0.038	0
Polymer Washing			
Ethanol	g	0	440
Varnish Preparation			
Solvents	g	0	22

Table S4. Energy consumption calculation for each process.

Component	Equipment	Power Rating (kW)	One Pot		Chemical Imidization	
			Operating Time (h)	Energy Consumption (kWh)	Operating Time (h)	Energy Consumption (kWh)
Polymer synthesis	Magnetic stirrer with hot plate[6]	0.6	4 h	2.4	0	0
	Magnetic stirrer[6]	0.008	0	0	24 h	0.2
Polymer Washing	Magnetic stirrer[6]	0.008	0	0	24 h	0.2
	Vacuum oven[6]	1.6	0	0	12 h	19.2
	Vacuum pump[6]	-	-	-	-	2.2
Varnish Preparation	Magnetic stirrer[6]	0.008	0	0	4 h	0.03
Membrane Drying	Vacuum oven[6]	1.6	4 h	6.4	4 h	6.4
	Vacuum pump[6]	-	-	4.3	-	4.3
Total				13.1		32.5

References

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(2) C. Pryde, *J. Polym. Sci. Part Polym. Chem.*, 1993, **31**, 1045–1052.

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(4) C. Hansen, *J. Paint Technol*., 1967, **39**, 104.

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