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Efficient and low-carbon synthesis of colorless transparent polyimides†

Jiahui Liu,[a] Chuying Li,[a] Yanwei He,[b] Bo Deng,[a] Haitao Huang,[a] Siwei Liu [a] and Yi Zhang *[a]

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The widespread use of polyimide varnish in semiconductors, packaging, and flexible displays has created increasing demand for efficient and environmentally friendly preparation. Compared to polyamic acid varnish, polyimide varnish offers enhanced stability and significantly improved process control, as it eliminates the need for chemical reactions during subsequent production steps. However, traditional polyimide varnish synthesis involves the preparation of polyamic acid followed by chemical imidization, a complex and time-consuming process that includes precipitation, washing, and dissolution. This method is not only costly but also poses environmental and safety risks. In this study, we propose a high-temperature one-step process to prepare a colorless polyimide varnish using the environmentally friendly solvent 3-methoxy-*N*,*N*-dimethylpropionamide (MDMPA) and benzoic acid as a catalyst. The process requires only 4 h to obtain the high molecular weight polyimide varnish without aftertreatment. The varnish can be easily converted into a transparent film through low-temperature drying. Additionally, by introducing a small amount of 3,5-diaminobenzoic acid (DABA) for copolymerization, polyimide synthesis can be successfully achieved without external catalysts. The resulting polyimide exhibits a higher imidization degree and significantly improved peel strength between the polyimide and copper foil. This one-step process not only maintains the superior properties of colorless transparent polyimides (CPIs) but also reduces reliance on toxic solvents, enhances production efficiency, and provides an environmentally sustainable solution for the large-scale production of high-performance polyimides.

Green foundation

1. Our work advances green chemistry by developing a one-step synthesis method that reduces the use of harmful solvents and improves production efficiency, aligning with green chemistry principles.
2. We achieved a green chemistry breakthrough by using an environmentally friendly solvent to synthesize a high molecular weight, transparent polyimide in just 4 h. The method reduces the polymerization time by 94%, cuts electricity use by 60%, and decreases reagent consumption by up to 95%, making the process more efficient and environmentally sustainable.
3. Future research will focus on developing a lower-temperature one-step process, making it compatible with more eco-friendly solvents. This will significantly reduce energy consumption and further enhance the sustainability of polyimide production.

Introduction

Polyimide (PI) is a class of polymers with aromatic heterocycles containing amide groups in the main chain. In recent years, colorless transparent polyimides (CPIs) have found widespread use in optoelectronic devices, such as flexible solar cell substrates, flexible display substrates and covers, and flexible circuit boards,[1–8] owing to their excellent thermal stability, mechanical properties, and optical transparency. However, existing preparation methods still face significant limitations, including high solvent toxicity, excessive catalyst usage, high costs, and complex processing steps. Consequently, overcoming these technical barriers is crucial to meeting the growing demands of emerging fields, particularly in flexible displays.

The commonly used methods for synthesizing polyimides in both laboratory and industrial settings involve the solution polycondensation of dianhydrides and diamines, which can be

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[a] *PCFM Lab, GD HPPC Lab, Guangdong Engineering Technology Research Centre for High-performance Organic and Polymer Photoelectric Functional Films, GBRCE for Functional Molecular Engineering, State Key Laboratory of Optoelectronic Materials and Technologies, School of Chemistry, Sun Yat-sen University, Guangzhou 510275, China. E-mail: ceszy@mail.sysu.edu.cn*

[b] *Wuxi Shunxuan New Materials Co., Ltd, Wuxi 214037, China*

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Table 1 Physical and chemical properties of MDMPA compared with other solvents

Solvents	B.p.	M.p.	pK_a	Density (293.15 K, g cm^{-3})	Viscosity (293.15 K, mPa s)	Refractive index	Surface tension (298.15 K, mN m^{-1})	Color
NMP	204	−25	−0.41	1.03	1.9	1.47	40.0	Colorless
m-Cresol	202	11	10.1	1.04	8.9 (303.15 K)	1.54	35.7	Colorless
DMAc	164	−19	−0.41	0.94	0.98	1.44	33.1	Colorless
MDMPA	216	−49	−0.56	0.99	2.3	1.45	34.2 (296.15 K)	Colorless

categorized into thermal imidization, chemical imidization, and one-step processes. Although traditional polyimide synthesis processes are well-established, they still present several drawbacks. For example, thermal imidization generally requires high temperatures above 300 °C, which may cause oxidative degradation and reduce the optical properties of polyimides. Additionally, if the intermediate polyamic acid (PAA) in thermal imidization is left for extended periods or stored improperly, it may degrade, leading to a reduction in molecular weight. The chemical imidization process is complex, comprising multiple steps such as polymerization, cyclization, washing, filtration, drying, dissolution, and coating. It requires several molar equivalents of catalysts and hundreds of times the volume of organic solvents, leading to high consumption of time, energy, and reagents, thus driving up preparation costs and increasing the burden of chemical waste disposal. Both methods are incompatible with the demands for sustainable development and environmental protection, hindering their broader application.

In comparison, the high-temperature one-step process offers a shorter reaction time. However, it typically requires high-boiling solvents, whose toxicity has become a major obstacle to widespread industrial adoption, especially given the increasing emphasis on sustainable development and environmental protection. Since the 1980s, researchers have employed the one-step method to prepare high-strength, high-modulus aromatic polyimide fibers.[9] In 1996, Hiroshi Inone and colleagues demonstrated that solvents with hydroxyl groups on the benzene ring could be used in the one-step method.[10] According to the Globally Harmonized System of Classification and Labeling of Chemicals (GHS) and the European Chemical Agency Classification & Labelling Inventory (ECHA), commonly used phenolic solvents in laboratories, such as *m*-cresol and *p*-chlorophenol, are highly toxic. More recently, *N*-methyl-2-pyrrolidone (NMP) and *N*,*N*-dimethylacetamide (DMAc) have been used in one-pot processes; however, they are toxic to specific organs and the reproductive system and can irritate the skin and eyes. DMAc is also suspected of being carcinogenic. Furthermore, NMP tends to generate colored impurities at high temperatures, darkening the film color, making it less suitable for applications requiring colorless polyimides. The colorless and heat-resistant solvent γ-butyrolactone (GBL)[11] has also been classified as a controlled precursor chemical. The prolonged and extensive use of these solvents poses serious health risks to operators and demands substantial investment in pollution control measures. As a result, developing green, environmentally friendly, and efficient processes for colorless transparent polyimides has become a significant research focus. There is an urgent need to find environmentally friendly solvents with good solubility, high boiling points, and no noticeable color change, enabling low-carbon and economically sustainable one-step processes.

In contrast, the new environmentally friendly solvent 3-methoxy-*N*,*N*-dimethylpropionamide (MDMPA) presents a potential alternative due to its eco-friendliness (see Table S1†). MDMPA is a biodegradable aprotic polar solvent with a high boiling point and stable physical properties.[12] It is a colorless liquid at room temperature and atmospheric pressure (see Table 1). Although chemically similar to traditional amide solvents, MDMPA exhibits lower toxicity to human health and the environment, with no carcinogenic or ecotoxic effects identified. In industrial applications, the use of green solvents such as MDMPA reduces health and safety risks while reducing environmental pollution control costs.

Experimental section

Reagents

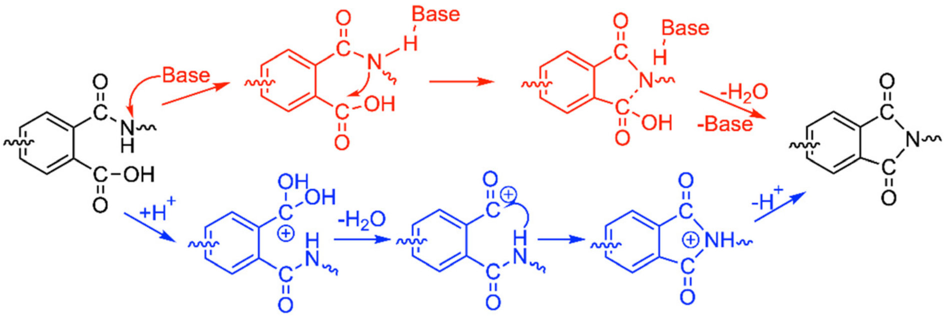
2,2′-Bis(3,4-dicarboxylicacid) hexafluoropropane dianhydride (6FDA) and 2,2′-bis(trifluoromethyl)-4,4′-diaminobiphenyl (TFMB) were purchased from Tianjin Zhongtai Technology Co., Ltd and sublimed using a sublimation apparatus; 3,5-diaminobenzoic acid (DABA) was purchased from Tianjin Zhongtai Technology Co., Ltd and purified by decolorization; 3-methoxy-*N*,*N*-dimethylpropionamide (MDMPA) was purchased from Guangzhou Ruiyue Trading Co., Ltd; *N*,*N*-dimethylacetamide (DMAc) and xylene were purchased from Beijing Bailingwei Technology Co., Ltd; *N*-methyl-2-pyrrolidone (NMP) was purchased from Anhui Zesheng Technology Co., Ltd; pyridine (Py), benzoic acid (BA), isoquinoline (IQL), and phthalic anhydride (PA) were purchased from Aladdin Reagent Co., Ltd; acetic anhydride (Ac_2O) was purchased from Guangzhou Chemical Reagent Factory.

Preparation of the colorless transparent PI varnish

(1) High-temperature one-step method for preparing the 6FDA–TFMB colorless transparent PI varnish (Table 2, sample a–g). The polyimides prepared by different processes are denoted as PI-$C_XE_YS_Z$, where C_X, E_Y and S_Z represent the catalyst, end-capping agent, and solvent, respectively. For example, using benzoic acid (C_B) or isoquinoline (C_I) as the catalyst, or no catalyst (C_N), 6FDA (E_F) or PA (E_P) as the end-capping agent, or no end-capping agent (E_N), and MDMPA (S_M), NMP (S_N), or

Table 2 One-step preparation of the 6FDA–TFMB varnish using different processes

No.	CPIs	Description	Solvents	Catalysts	End-capping reagent	Reaction temperature (°C)	Reaction time (h)	Drying temperature (°C)
a	PI-C$_B$E$_F$S$_M$	To explore the influence of catalysts	MDMPA	BA	6FDA	185	4	220
b	PI-C$_I$E$_F$S$_M$			IQL				
c	PI-C$_N$E$_F$S$_M$			—				
d	PI-C$_B$E$_P$S$_M$	To explore the influence of end-capping reagents	MDMPA	BA	PA			
e	PI-C$_B$E$_N$S$_M$				—			
f	PI-C$_B$E$_F$S$_N$	To compare MDMPA with common solvents	NMP	BA	6FDA			
g	PI-C$_B$E$_F$S$_D$		DMAc					
h	PI-CI	To compare one pot synthesis with chemical imidization	MDMPA	Py/Ac$_2$O	6FDA	Room temperature	12	220
i	PI-5D	Autocatalytic one pot synthesis	MDMPA	DABA	6FDA	185	4	220
j	PI-10D							
x	PI-350	Heat imidization as control	MDMPA	—	6FDA	Room temperature	12	350
y	PI-5D-350			DABA				
z	PI-10D-350			DABA				



Scheme 1 The imidization process of polyamic acid in the presence of alkaline or acidic catalysts.

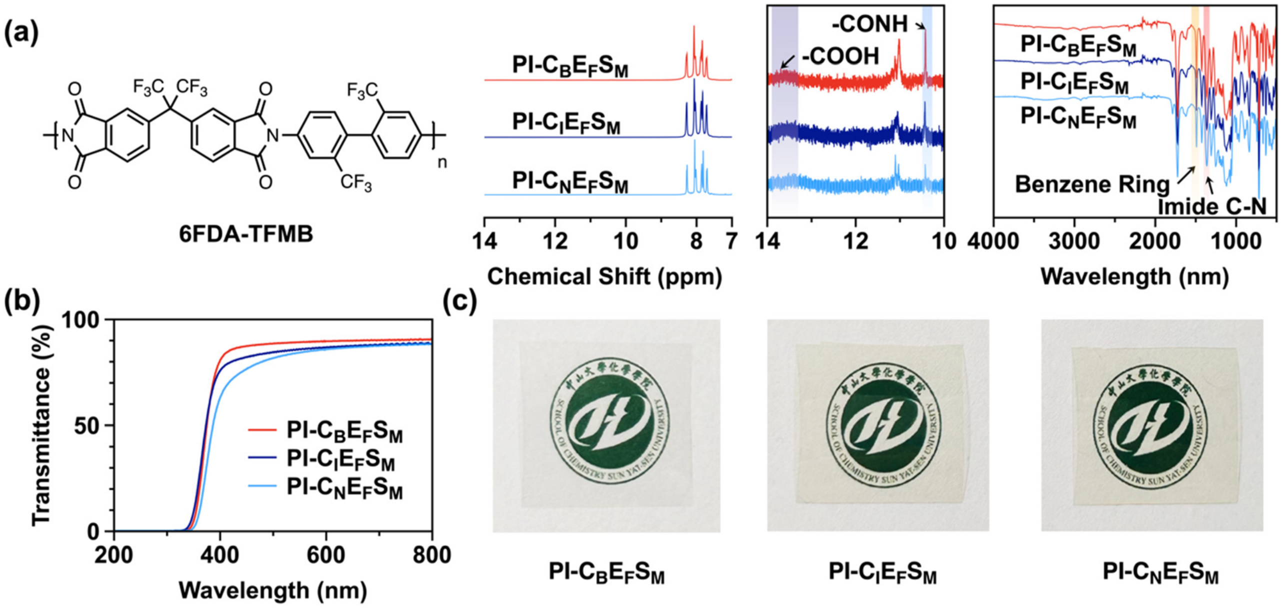


Fig. 1 Characterization of various properties of PI films prepared with different catalysts. (a) Polyimide structure, ^{1}H NMR spectrum, with an enlargement of the 10–14 ppm region on the right, and ATR-FTIR spectrum. (b) UV-vis curves; the thicknesses of PI-C$_B$E$_F$S$_M$, PI-C$_I$E$_F$S$_M$ and PI-C$_N$E$_F$S$_M$ are 18.5 μm, 15.4 μm, and 30.3 μm in order. (c) PI films.

Table 3 Properties of 6FDA–TFMB films prepared by different processes

No.	CPIs	ID_1 (%)	ID_2 (%)	T_{400} [a] (%)	$T_{360-800}$ [b] (%)	Thickness (μm)	$T_{5\%}$ [c] (°C)	M_n (kDa)	M_w (kDa)	PDI	Breaking elongation (%)	Tensile strength (MPa)
a	PI-$C_BE_FS_M$	88	99.6	80.7	87.3	18.5	517	70	100	1.40	8.13 ± 1.24	102.31 ± 2.18
b	PI-$C_IE_FS_M$	90	99.8	75.7	84.6	15.4	508	61	93	1.53	9.65 ± 0.69	69.23 ± 1.46
c	PI-$C_NE_FS_M$	100	99.1	63.0	81.8	30.3	495	30	46	1.56	2.41 ± 0.36	17.88 ± 2.79
d	PI-$C_BE_PS_M$	86	99.4	75.0	85.4	11.0	503	50	78	1.55	6.14 ± 1.36	56.66 ± 4.55
e	PI-$C_BE_NS_M$	90	99.6	72.0	82.4	17.4	507	69	110	1.65	9.81 ± 0.85	79.10 ± 10.44
f	PI-$C_BE_FS_N$	99	100	67.0	84.9	25.0	523	47	56	1.27	4.38 ± 0.56	68.08 ± 6.93
g	PI-$C_BE_FS_D$	88	99.6	76.0	86.3	30.0	513	38	50	1.30	5.04 ± 0.014	60.48 ± 16.72

[a] Transmittance at 400 nm wavelength, obtained from UV-vis testing. [b] Transmittance in the 360–800 nm range, obtained from UV-vis testing. [c] Temperature at 5% weight loss under a nitrogen atmosphere, obtained from TGA testing. The spectra are shown in Fig. S11–13.†

DMAc (S_D) as the solvent, several types of PIs were prepared. To prepare PI-$C_BE_FS_M$, TFMB (1.6012 g, 5.00 mmol), 6FDA (2.2434 g, 5.05 mmol) and MDMPA (12 mL) were added to a three-neck flask to prepare a 25 wt% solution. The one-step reaction setup was established, with benzoic acid (0.038 g) and anhydrous xylene (4 mL) added to the flask. Anhydrous xylene was also added to the Dean–Stark apparatus, and argon gas was bubbled continuously into the flask. The temperature was directly raised to 185 °C, and the total reaction time was approximately 4 h, yielding a light-yellow varnish. The mixture was then centrifuged at 7500 rpm for 20 min without washing.

(2) **Chemical imidization method for preparing the 6FDA–TFMB colorless transparent PI solution (control, Table 2, sample h).** The PI solution prepared by this method is denoted as PI-CI. 6FDA (2.2434 g, 5.05 mmol) and TFMB (1.6012 g, 5.00 mmol) were added to a sample bottle, followed by the addition of MPA (22 mL). The mixture was reacted at room temperature under magnetic stirring for 12 h to form a colorless PAA solution. Acetic anhydride and pyridine were added to the PAA solution at a molar ratio of n (carboxyl group) : n (acetic anhydride) = 1 : 5, and a volume ratio of V (acetic anhydride) : V (pyridine) = 7 : 3. The mixture was stirred magnetically at room temperature for 12 h to form a colorless PAA solution. The PAA solution was then slowly poured into ethanol (20 times its volume) to precipitate PI fibers. The fibers were purified by Soxhlet extraction with ethanol for 12 h and then dried in a vacuum oven at 80 °C for 12 h to obtain white PI fibers. MPA (22 mL) was used as the solvent to prepare the PI solution from the fibers.

(3) **Self-catalyzed method for preparing the DABA–6FDA–TFMB system PI varnish (Table 2, samples i and j).** The PI solution prepared by this method is denoted as PI-nD, where "n" indicates the molar fraction of DABA in the polymer composition. For example, 6FDA–$DABA_{0.05}$–$TFMB_{0.95}$ is named PI-5D. To prepare PI-5D, DABA (0.0380 g, 0.25 mmol), TFMB (1.5211 g, 4.75 mmol), 6FDA (2.2221 g, 5.00 mmol), and MDMPA (12 mL) were added to a three-neck flask to prepare a 25 wt% solution. The one-step reaction was carried out following the procedure described in step (1). The same procedure was applied to prepare PI-10D.

Preparation of colorless PI films

The solution was degassed under vacuum and then coated onto a glass plate and dried at 80 °C for 2 h on a hot plate. The film was then placed in a reducing gas oven with the following temperature program: room temperature to 150 °C for 0.5 h, 150 °C for 1 h, 150 to 220 °C for 0.5 h, and 220 °C for 1 h. This was followed by a gradient heating step to remove the solvent and obtain the PI film. The structure of the PI films was confirmed by ATR-FTIR and NMR spectroscopy (the data are provided in the ESI, Fig. S1–S10†).

Thermal imidization to prepare PI films for imidization degree comparison (Table 2, sample x–z)

One-step solutions, without catalysts or end-capping agents, were stirred at room temperature for 12 h. The solution was degassed under vacuum, coated onto a glass plate, and dried at 80 °C for 2 h on a hot plate. The films were then placed in a nitrogen oven with the following heating program: room temp-

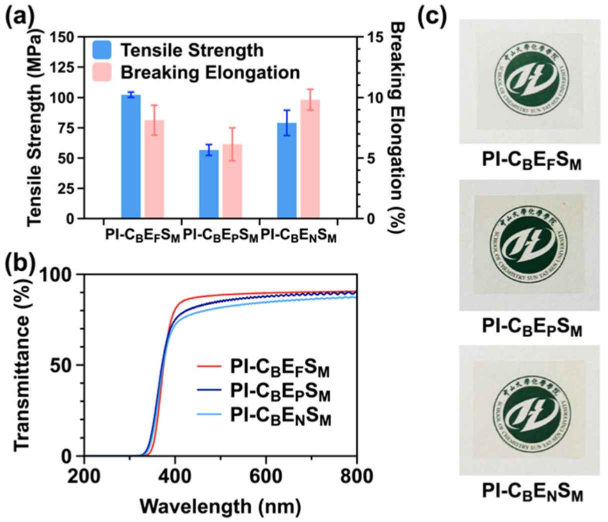


Fig. 2 Characterization of various properties of PI films prepared with different end-capping agents. (a) Tensile strength and elongation at break. (b) UV-vis curves; the thicknesses of PI-$C_BE_FS_M$, PI-$C_BE_PS_M$ and PI-$C_BE_NS_M$ are 18.5 μm, 11.0 μm, and 17.4 μm in order. (c) PI films.

erature to 350 °C for 2 h, followed by 350 °C for 1 h, to remove the solvent and prepare the completely imidized PI films.

Results and discussion

One-step polymerization performance using different catalysts in MDMPA

The performance of one-step reactions with different catalysts in MDMPA was studied to identify the most suitable catalyst for CPIs and to verify the feasibility of using MDMPA in one-step polymerization. The one-step method typically employs organic bases (*e.g.*, quinoline and isoquinoline) or organic acids (*e.g.*, benzoic acid and hydroxybenzoic acid) as catalysts. The catalytic mechanisms of organic bases and organic acids are different (Scheme 1). Base catalysts, such as isoquinoline and imidazole, may replace the bound solvents and form hydrogen bonds with the –CONH group. This increases the electron density of the nitrogen atom, enhances its nucleophilicity, and significantly lowers the reaction energy barrier. Kuznetsov *et al.* proposed a catalytic mechanism involving carboxyl groups in polyimide synthesis.[13] Acidic catalysts protonate the carbonyl oxygen atom, increasing the reactivity of the acyl cation and thereby promoting the imidization reaction. Thus, benzoic acid, isoquinoline, and the no-catalyst condition were chosen for the one-step polymerization.

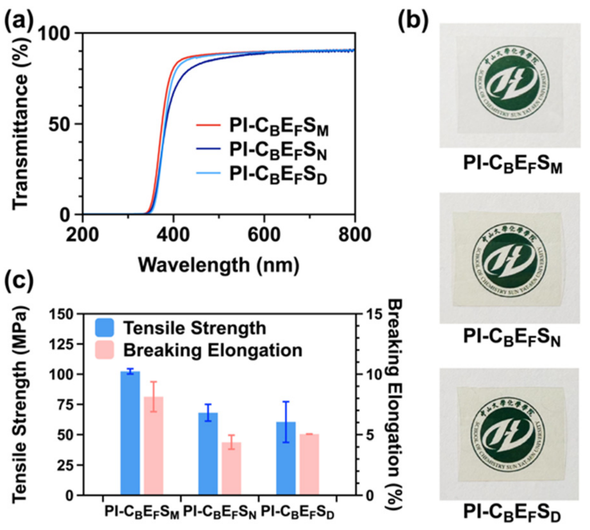
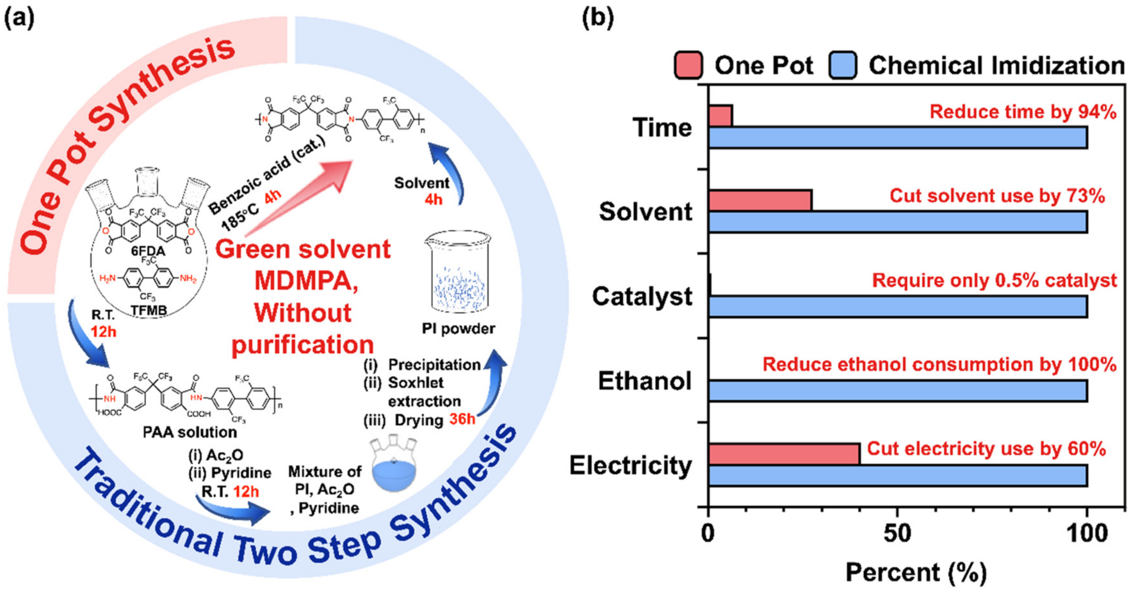


Fig. 3 Characterization of various properties of PI films prepared with different solvents. (a) UV-vis curves; the thicknesses of PI-$C_BE_FS_M$, PI-$C_BE_FS_N$ and PI-$C_BE_FS_D$ are 18.5 μm, 25.0 μm, and 30.0 μm in order. (b) PI films. (c) Tensile strength and elongation at break.

The experimental setup is summarized in Table 2, samples a–c and the reaction products were analyzed using various characterization techniques. The ATR-FTIR spectrum and ^{1}H NMR spectrum (Fig. 1a and Fig. S6†) confirm the successful synthesis of polyimides in all three cases, with the imidization degree (ID) calculated from the two spectra, data provided in Table 3, samples a–c (the calculations are provided in the ESI†). ATR-FTIR spectroscopy is the most commonly used method to analyze the ID of PI. However, as the imidization level increases, infrared spectroscopy becomes less effective in distinguishing variations in imidization levels.[14,15] Residual amide solvents may exhibit infrared absorption at 1363 cm^{-1} and 1490 cm^{-1}, interfering with the absorption peaks of polyimide. Moreover, the ATR mode only provides surface chemical information and does not reflect the overall structure of the



Scheme 2 (a) Schematic comparison of the implementation plan between the high-efficiency low-carbon one-step method and the traditional two-step method. (b) Inventory of chemicals; energy consumption for different methods of producing polyimide films. Solvent includes reaction solvents and the dehydrating agent.

film. Therefore, the ^1H NMR spectrum was used for a more accurate characterization of the imidization degree in this study.

^1H NMR results indicate that when benzoic acid and isoquinoline were used as catalysts, the imidization degrees (ID_2) reached 99.6% and 99.8%, respectively, significantly higher than the 99.1% achieved without any catalyst. The addition of catalysts further enhances the imidization degree, demonstrating that MDMPA can be effectively used in high-temperature one-step polymerization reactions with various catalyst systems.

The UV-vis spectrum of the films is shown in Fig. 1b, and the results are summarized in Table 3. It was noted that the PI film prepared with benzoic acid was more transparent than that prepared with isoquinoline or without a catalyst. The transmittance of PI-$C_BE_FS_M$ at 400 nm was 80.7%, and the total optical transmittance from 360–800 nm was 87.3%, making the film nearly transparent.

The molecular weights and mechanical properties are shown in Table 3. Both acidic and basic catalysts were found to be beneficial for the preparation of high molecular weight polyimides compared to the catalyst-free process, with the number-average molecular weight of PI-$C_BE_FS_M$ reaching up to 70 kDa. This helps to enhance the mechanical properties of the film. PI-$C_BE_FS_M$ and PI-$C_IE_FS_M$ exhibited tensile strengths of 102.31 MPa and 69.23 MPa, with elongations at break of 8.13% and 9.65%, respectively. Considering transparency and mechanical properties, benzoic acid is the most suitable catalyst for preparing colorless transparent polyimides *via* the one-step method.

Effects of different end-capping strategies on PI performance

Building on the catalyst study, this research utilized MDMPA as the solvent and benzoic acid as the catalyst while exploring different end-capping strategies to further enhance the transparency of polyimides. Polyimide synthesis is a step-growth polymerization, and to achieve high molecular weight products, it is crucial to maintain a 1 : 1 molar ratio of functional groups. However, this ratio may be influenced by monomer purity and side reactions during polymerization. Unreacted amine groups may oxidize during the high-temperature solution reaction and film formation, adversely impacting optical properties. Thus, the oxidation of these amines can be minimized through introducing an anhydride end-capping agent to react with the residual amines, thereby improving the transparency of the films.

The effects of three end-capping strategies on polyimide performance were investigated: 6FDA self-end-capping, phthalic anhydride (PA) end-capping, and no end-capping agent (data shown in Table 3, samples a, d and e). ATR-FTIR and ^1H NMR spectra (Fig. S1 and S7†) confirm that all three end-capping methods successfully produced polyimides with a high degree of imidization. Among them, the 6FDA self-end-capping strategy promotes the formation of high-molecular-weight polymers, thereby enhancing

Table 4 Properties of 6FDA–TFMB films prepared by the high-temperature one-step method and the traditional two-step method

No.	CPIs	M_n (kDa)	M_w (kDa)	PDI	ID_1 (%)	ID_2 (%)	T_{400} [a] (%)	$T_{360-800}$ [b] (%)	Thickness (μm)	$T_{5\%}$ [c] (°C)	Density	Breaking elongation (%)	Tensile strength (MPa)	Young's modulus (GPa)
a	One pot	70	100	1.40	88	99.6	80.7	87.3	18.5	517	1.37	8.13 ± 1.24	102.31 ± 2.18	1.43 ± 0.37
h	Chemical imidization	75	120	1.61	80	99.0	84.7	88.3	15.0	523	1.35	9.17 ± 1.27	100.67 ± 5.79	1.11 ± 0.15

[a] Transmittance at 400 nm wavelength, obtained from UV-vis testing. [b] Light transmittance in the 360–800 nm range, obtained from UV-vis testing. [c] Temperature at 5% weight loss under a nitrogen atmosphere, obtained from TGA testing.

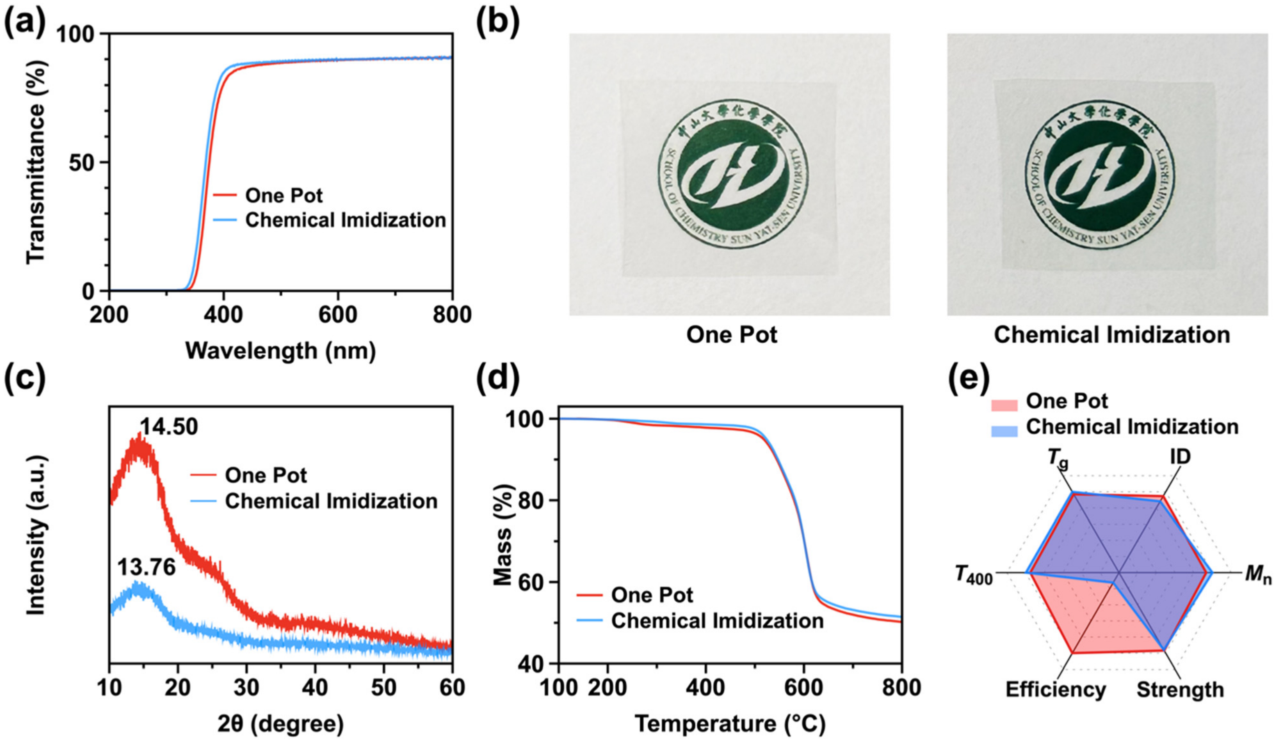


Fig. 4 Performance comparison of films prepared by the chemical imidization method and high-temperature one-step method. (a) UV-vis curves; the thicknesses of one pot and chemical imidization films are 18.5 μm and 15.0 μm in order. (b) PI films prepared by the one-step method and chemical imidization method. (c) XRD curves. (d) TGA curves. (e) Comparison of various properties of PI films.

mechanical performance (Fig. 2a and Fig. S14†). This is likely due to the fact that the monoanhydride end-capping strategy hinders further polymer chain growth. In the absence of an end-capping agent, the oxidation of amino end groups under high-temperature conditions may also lead to a reduction in polymer molecular weight. Both factors adversely affect the mechanical strength, as confirmed by experimental data.

The UV-vis spectra and photo images (Fig. 2b and c) show that polyimide films with either dianhydride or monoanhydride end-capping agents exhibit superior transparency compared to those without an end-capping agent. In particular, the film prepared with the 6FDA self-end-capping strategy exhibited the highest level of colorless transparency. Overall, employing a 1% excess of 6FDA for self-end-capping is a simple and efficient strategy that achieves an optimal balance between excellent transparency and mechanical properties.

Comparison with common solvents in one-step methods

The previous sections demonstrated that MDMPA can successfully support polyimide synthesis under various conditions, including different catalysts and end-capping methods. Among the tested conditions, the polyimide film prepared with benzoic acid as the catalyst and 6FDA as the end-capping agent exhibited the best overall performance. This section compares the performance of polyimides synthesized in MDMPA with those prepared using NMP and DMAc, following the processes outlined above (Table 3, samples a, f and g†).

The ^{1}H NMR spectra (Fig. S8†) show that the polyimide synthesized in NMP achieved a 100% imidization degree, higher than the 99.6% achieved in MDMPA and DMAc. However, the UV-vis spectra and photo images (Fig. 3a and b) revealed that the film prepared with NMP exhibited significant yellowing and reduced transmittance. In contrast, the film synthesized in MDMPA exhibited higher transparency. MDMPA also contributes to the synthesis of a high molecular weight polyimide, which is beneficial for the superior tensile strength and elongation at break (Fig. 3c and Fig. S14†). Considering transparency, mechanical properties of the film and the toxicity of the solvent, MDMPA is an ideal solvent for the one-step method, providing an environmentally friendly approach for high-performance polyimide synthesis while reducing health and safety risks.

The solubility of the solvent plays a crucial role in polyimide synthesis, influencing the polymerization process and final properties of the films. To better understand the observed differences, the Hansen solubility parameters (HSP) were considered. Based on literature values, all three solvents fall within the solubility sphere (RED < 1), confirming their general compatibility with the 6FDA-based polyimide system (Table S2, the calculations are provided in the ESI†). MDMPA exhibited the smallest RED (0.55), which is consistent with its superior performance in producing high-molecular-weight and mechanically robust CPI films. This theoretical analysis further supports MDMPA's suitability as an ideal solvent for one-step polyimide synthesis.

Characterization of the CPI synthesized by the one-step method compared to the two-step method

The improved one-step method offers several advantages over traditional chemical imidization in terms of efficiency and environmental sustainability (Scheme 2a, the quantification of input materials and energy is provided in Table S4†). First, this method significantly shortens the polymerization cycle. Traditional chemical imidization involves multiple complex steps, including polyamic acid polymerization, chemical imidization, washing with poor solvent, drying, and redissolution, with a total duration of approximately 64 h in the laboratory. In contrast, the one-step method requires only the addition of 1% catalyst relative to the monomer weight and a dehydrating agent, with a reaction time of just 4 h at a high temperature to obtain the varnish. This approach saves 94% of the time and reduces electricity consumption by 60%. Additionally, in traditional chemical imidization, the catalyst and dehydrating agent are used at approximately 15 times the molar amount of the monomers, and the volume of poor solvent used for washing is 20 times that of the reaction solvent (Scheme 2b). The one-step method can significantly reduce reagent consumption. This reduces the burden of pollution treatment and minimizes environmental impact, making it advantageous from safety, environmental, and economic perspectives. These advantages make the method well-suited for sustainable development and large-scale industrial applications.

Moreover, the film prepared using the one-step method exhibits superior performance. The ^{1}H NMR results are presented in Table 4. The film prepared *via* the one-step method exhibits a higher imidization degree, as determined by ^{1}H NMR analysis, reaching 99.6%. The optical properties of the films prepared by both methods were essentially the same (Fig. 4a and b). XRD analysis (Fig. 4c) of both reveals broad diffuse peaks, indicating that both films have an amorphous structure. The average interchain distance of the film prepared using the one-step method is smaller (calculated using Bragg's equation $d = \lambda/2(\sin\theta)$ (ref. 16)), suggesting a more tightly packed molecular structure. This observation is consistent with the density measurements reported in Table 4. The higher imidization degree likely results in more compact molecular packing, enhancing intermolecular interactions and improving mechanical properties, including tensile strength and Young's modulus. The thermal stability of both films was nearly identical (Fig. 4d).

Therefore, considering production efficiency, environmental impact, and material performance (Fig. 4e), using MDMPA as a green solvent for the one-step method offers a promising solution for the large-scale industrial production of high-performance polyimide substrates for flexible displays. Compared to the traditional method, using the efficient one-step method maintains excellent material properties while aligning with environmental protection and low-carbon principles, offering significant benefits for sustainable development.

Table 5 Properties of 6FDA–TFMB films prepared by the self-catalyzed one-step method

No.	CPIs	M_n (kDa)	M_w (kDa)	PDI	ID$_1$ (%)	ID$_2$ (%)	T_{400} ^{a} (%)	$T_{360-800}$ ^{b} (%)	Thickness (μm)	$T_{5\%}$ ^{c} (°C)	Peel strength (N mm^{-1})	Breaking elongation (%)	Tensile strength (MPa)
a	PI-$C_BE_FS_M$	70	100	1.40	88	99.6	80.7	87.3	18.5	517	0.46 ± 0.049	8.13 ± 1.24	102.31 ± 2.18
g	PI-$C_NE_FS_M$	30	46	1.56	100	99.1	63.0	81.8	30.3	495	0.40 ± 0.094	2.41 ± 0.36	17.88 ± 2.79
i	PI-5D	40	57	1.44	98	99.6	72.2	85.6	20.3	375	0.73 ± 0.033	5.87 ± 0.79	85.52 ± 4.73
j	PI-10D	43	59	1.39	95	99.8	68.3	84.4	21.8	390	0.65 ± 0.037	3.38 ± 0.85	50.51 ± 2.95

[a] Transmittance at 400 nm wavelength, obtained from UV-vis testing. [b] Light transmittance in the 360–800 nm range, obtained from UV-vis testing. [c] Temperature at 5% weight loss under a nitrogen atmosphere, obtained from TGA testing.

Self-catalyzed preparation of the colorless PI

The previous sections demonstrated that both benzoic acid and isoquinoline can effectively catalyze the synthesis of polyimides, achieving high imidization degrees and molecular weights. However, due to their high boiling points, these catalysts may not be completely removed during the low-temperature curing process, potentially affecting the purity of the final product. As evidenced by TGA (Fig. S11†), films prepared with benzoic acid or isoquinoline exhibit an additional weight loss around 200 °C, indicating the presence of residual catalysts in the final product. Although their amounts are minimal and difficult to detect by ^{1}H NMR or FTIR spectroscopy, these residuals may still influence the purity of the final films.

Considering the advantages of benzoic acid in enhancing transparency and mechanical properties, this section explores a self-catalyzed approach by introducing the benzoic acid group into the polymer backbone through the incorporation of the carboxyl group-containing diamine monomer DABA. By copolymerizing different amounts of DABA with the 6FDA–TFMB system, polyimide varnishes, including PI-5D and PI-10D, were synthesized *via* the one-step method. After solvent removal, the films were obtained, and their properties are summarized in Table 5 and Fig. 5 in comparison with those prepared using benzoic acid and those synthesized without a catalyst.

Compared with PI-$C_NE_FS_M$, the incorporation of DABA significantly increases the molecular weight ($M_n \geq 40$ kDa) and imidization degree ($ID_2 \geq 99.6\%$) (Fig. 5a), thereby enhancing the mechanical properties of the films (Fig. 5b and Fig. S14†). These results indicate that the incorporation of carboxyl groups into the polymer backbone facilitates the self-catalyzed synthesis of polyimides with a high imidization degree, achieving catalytic efficiency comparable to that of external catalysts. TGA (Fig. 5c) shows that the initial weight loss temperature of the DABA-containing polyimide system decreases to approximately 250 °C. This reduction is likely attributed to the decarboxylation of DABA prior to PI decomposition, which induces polymer crosslinking and slight mass loss.[17]

A common challenge of the application of polyimide is the insufficient adhesion between the polyimide substrate and copper, which often necessitates the use of an adhesive layer between the polymer and the metal circuit. However, this

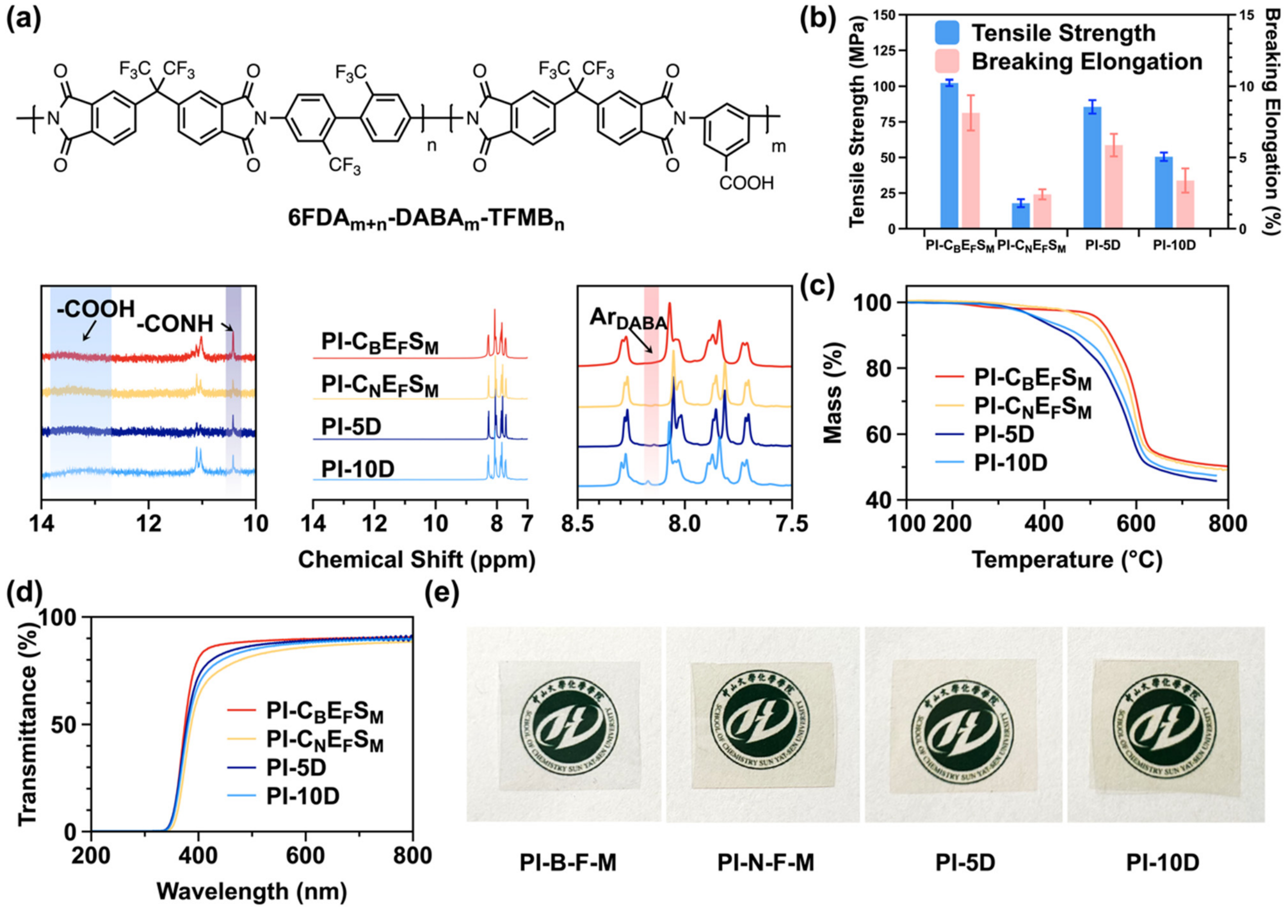


Fig. 5 Comparison between films prepared by the DABA self-catalyzed one-step method and without using a catalyst. (a) Molecular structure of 6FDA–DABA–TFMB and ^{1}H NMR curves, with the left figure showing a local enlargement from 10–14 ppm and the right figure showing a local enlargement from 7.5–8.5 ppm. (b) Tensile strength and elongation at break, (c) TGA curves. (d) UV-vis curves; the thicknesses of PI-$C_BE_FS_M$, PI-$C_NE_FS_M$, PI-5D and PI-10D are 18.5 μm, 30.3 μm, 20.3 μm, and 21.8 μm in order. (e) PI films prepared with different catalysts.

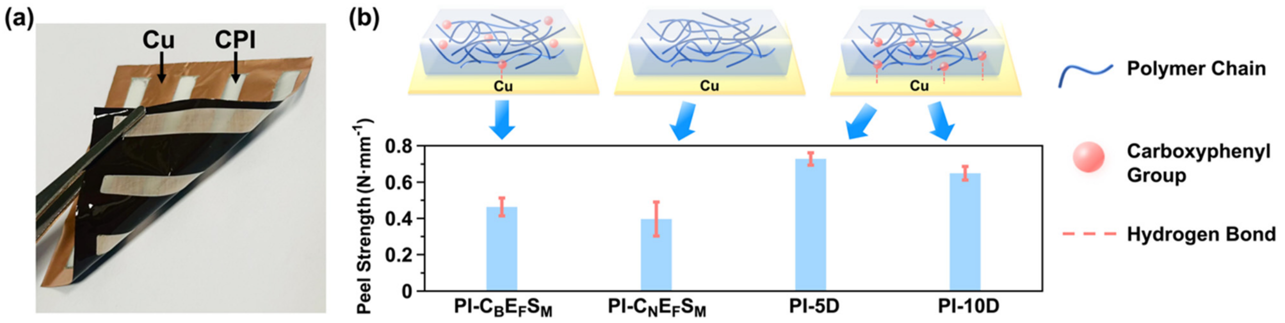


Fig. 6 (a) Photo of FCCL. (b) Peeling performance and schematic diagram of PI prepared by different catalytic methods from copper foil.

adhesive layer can increase the dielectric loss of the FCCL.[18,19] The introduction of carboxyl groups in DABA enhances hydrogen bonding, increases the dipole moment, and boosts the system's polarization, thereby improving adhesion between the polyimide and copper foil.[19]

In 90° peel tests (Fig. 6), significant differences in peel strength were observed across the various PI systems. The peel strength of films prepared without catalysts was only 0.36 N mm^{-1}, while films prepared with benzoic acid as a catalyst exhibited a peel strength of 0.49 N mm^{-1}, likely due to the residual benzoic acid in the system. In contrast, the DABA self-catalyzed system exhibited a significant improvement, with the peel strength of PI-5D reaching 0.73 N mm^{-1}, demonstrating the enhanced adhesion between the polyimide and copper foil. This may be attributed to the decrease in the molecular weight with increasing DABA content, which in turn leads to a decline in mechanical properties and consequently reduces the adhesion capability of the PI-10D.

Conclusion

In response to the growing demand for high-performance polyimide varnish, this study presents a high-temperature one-step method using the environmentally friendly solvent MDMPA for the low-carbon, efficient preparation of the 6FDA–TFMB colorless transparent polyimide. This process addresses the environmental issues associated with the use of toxic solvents in conventional polyimide synthesis, while reducing the polymerization cycle to just 6% of the original time. The resulting polyimide exhibits a higher imidization degree and a more compact molecular structure, while retaining excellent optical properties, with a transmittance exceeding 80% at 400 nm and a total transmittance of 87.3% in the 360–800 nm range. Furthermore, the one-step synthesis can be achieved without external catalysts by incorporating 5% DABA, which co-polymerizes with 6FDA–TFMB. The polyimide produced not only demonstrates a higher imidization degree but also significantly improves the peel strength of the colorless films, reaching up to 0.73 N mm^{-1}.

Overall, the one-step method proposed here offers notable advantages in terms of safety, environmental sustainability, and economic feasibility. It aligns with the principles of sustainable development and provides a practical solution for the industrial-scale production of high-performance polyimide varnish.

Author contributions

Conceptualization: Jiahui Liu and Yi Zhang. Sample preparation and characterization: Jiahui Liu, Chuying Li, Yanwei He, and Bo Deng. Project administration: Yi Zhang, Siwei Liu and Haitao Huang. Writing – original draft: Jiahui Liu and Yi Zhang. Writing – review and editing: all authors.

Conflicts of interest

The authors declare no conflict of interest.

Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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References

1 F. Bai, Y. Jiang, X. Li, J. Dong, X. Zhao and Q. Zhang, *Acta. Polym. Sin.*, 2024, **55**, 1393–1404.

2 P. Ma, C. Dai, H. Wang, Z. Li, H. Liu, W. Li and C. Yang, *Compos. Commun.*, 2019, **16**, 84–93.

3 H. Wu, T. Liu and C. Chien, *ECS J. Solid State Sci. Technol.*, 2014, **3**, Q24–Q27.

4 P. M. Hergenrother, *High Perform. Polym.*, 2003, **15**, 3–45.

5 M. Hasegawa, *Polymers*, 2017, **9**, 520.

6 T. Sekitani, U. Zschieschang, H. Klauk and T. Someya, *Nat. Mater.*, 2010, **9**, 1015–1022.

7 S. Nakano, N. Saito, K. Miura, T. Sakano, T. Ueda, K. Sugi, H. Yamaguchi, I. Amemiya, M. Hiramatsu and A. Ishida, *J. Soc. Inf. Disp.*, 2012, **20**, 493–498.

8 K. Min, T. Lee, C. P. Park, Z. Wu, H. H. Girault, I. Ryu, T. Fukuyama, Y. Mukai and D. Kim, *Angew. Chem., Int. Ed.*, 2010, **49**, 7063–7067.

9 A. Y. Ardashnikov, I. Y. Kardash and A. N. Pravednikov, *Polym. Sci. U.S.S.R.*, 1971, **13**, 2092–2100.

10 H. Inoue, Y. Sasaki and T. Ogawa, *J. Appl. Polym. Sci.*, 1996, **60**, 123–131.

11 M. Hasegawa, K. Ichikawa, S. Takahashi and J. Ishii, *Polymers*, 2022, **14**, 1131.

12 G. Yang, M. Zhang, I. Majeed, W. Fan, J. Zhao and Z. Zeng, *ACS Sustainable Chem. Eng.*, 2023, **11**, 14582–14590.

13 A. A. Kuznetsov, A. Yu. Tsegelskaya, M. Yu. Belov, V. I. Berendyaev, S. V. Lavrov, G. K. Semenova, A. L. Izyumnikov, N. V. Kozlova and B. V. Kotov, *Macromol. Symp.*, 1998, **128**, 203–219.

14 X. Jin and D. Zhu, *Eur. Polym. J.*, 2008, **44**, 3571–3577.

15 L. Cao, X. Fang and G. Chen, *J. Polym. Sci.*, 2023, **61**, 491–502.

16 X. Feng, Y. Wang, Y. Zhao, X. Yu, P. Zhang, J. Cui and M. Guo, *Acta. Polym. Sin.*, 2023, **54**, 1219–1228.

17 W. Qiu, C. Chen, L. Xu, L. Cui, D. Paul and W. Koros, *Macromolecules*, 2011, **44**, 6046–6056.

18 J. Hur, *Colloids Surf., A*, 2022, **645**, 128880.

19 A. Li, H. He, Y. Shen and Q. Li, *Colloids Surf., A*, 2023, **140**, e54596.