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Article

Catalyst-Free Synthesis of Next-Generation Biobased High-Toughness Polyesters Enabled by Knoevenagel Chemistry

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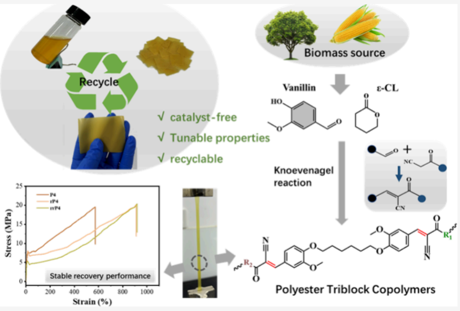

ABSTRACT: Despite being among the most prevalent polymers, conventional thermoplastic polyesters are petroleum-derived, and their production relies on energy-intensive processes with high temperature and vacuum and involves toxic catalysts. Herein, we presented a novel biobased multiblock thermoplastic polyester material from lignocellulosic-derived monomers, i.e., vanillin-based aldehyde monomer and polycaprolactone-based cyanoacetate, via a catalyst-free Knoevenagel condensation melting polymerization under low-temperature conditions (190 °C). By precisely tuning the molecular weight (2000 and 4000 g/mol) and molar ratio of soft segments, the material demonstrated exceptional performance with a tensile strength of 30.55 MPa, elongation at break of 871%, and toughness of 138.59 MJ M^{-3}, surpassing most commercial elastomers (e.g., SBS). Thanks to its good processing adaptability and low processing energy consumption, the resulting multiblock thermoplastic polyester material could be processed by melting spinning, thermoforming, and twin-screw extrusion and could be efficiently reclaimed from mixed plastic waste through a solvent-casting closed-loop recycling strategy. The melting-spinning fibers demonstrated notable elongation at break exceeding 600%, while regenerated films exhibited substantially enhanced toughness achieved through molecular reorganization. This work establishes a green paradigm for sustainable high-performance polymers, integrating environmental compatibility with engineering feasibility, and paves the way for the transition of biobased polyesters toward a circular economy.

■ INTRODUCTION

Polymers have been widely used in our daily life, bringing us great convenience, but most polymer products are derived from nonrenewable fossil resources. This puts constant pressure on the depletion of petroleum-based resources.[1−8] Besides, polymer waste is usually recycled through physical crushing,[9−12] microplastics are contaminating human food through their integration into the food chain and production processes.[13] To date, the long-term effects of microplastic waste on human health and the ecological environment have not been determined.[14] Therefore, the development and recycling of biobased high-performance polymers has become a critical problem. Thermoplastic polymers, including plastics, can be reprocessed by mechanical methods, but due to repeated heat and force, it inevitably leads to deterioration of material properties.[15,16] The chemical recovery of thermoplastic polymers has gradually become a research hotspot, which usually refers to the depolymerization of polymers into monomers,[17,18] but the current depolymerization strategy usually involves high temperature and pressure, toxic catalysts, and other strict reaction conditions.[19−23] Therefore, a more feasible and sustainable recovery strategy that avoids performance loss and excessive energy input is urgently needed. This will also promote the development of a circular economy of thermoplastic polymers.

Polyester, which has been widely used in packaging, electronic appliances, automotive, and construction industries, is one of the most widely used polymers.[24−26] The synthesis of traditional polyester materials usually involves high temperatures (above 240 °C), a high vacuum environment, or harmful organic and metallic catalysts, such as tetrabutyl titanate (TBT) and Sn $(Oct)_2$.[27−32] The green and simple synthesis methods of polyester materials need to be continuously explored. Moreover, in order to ensure the mechanical properties of polyester materials, long-term high-temperature polymerization is needed to increase the molecular weight, which inevitably increases the energy input, and usually only polymers with a single property can be obtained. The introduction of a monomer with the same end-group in a block polymer overcomes the limitations of precise stoichiometric matching of the end-group and allows for the adjustment of the monomer feed composition to produce different high molecular weight polymers. However, as

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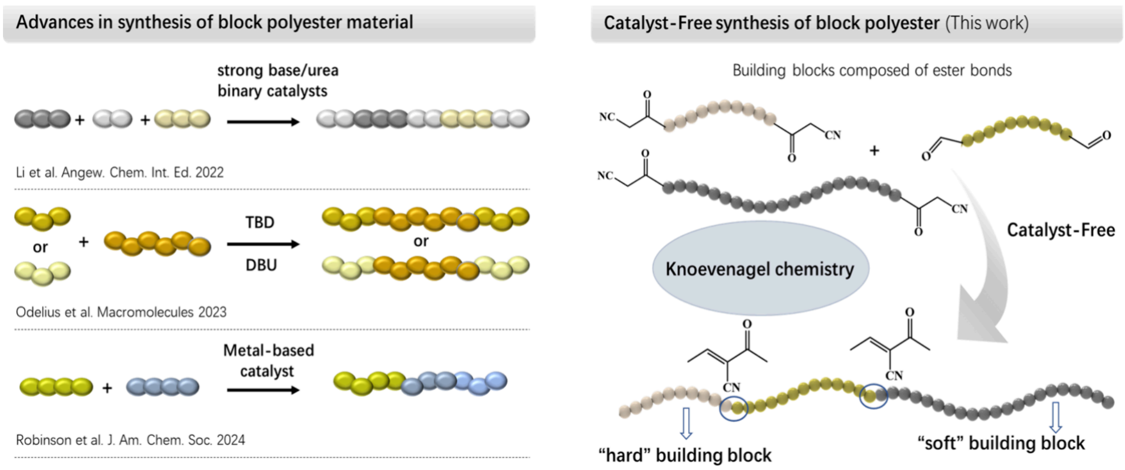
Scheme 1. Typical Examples of a Sustainable Block Polyester



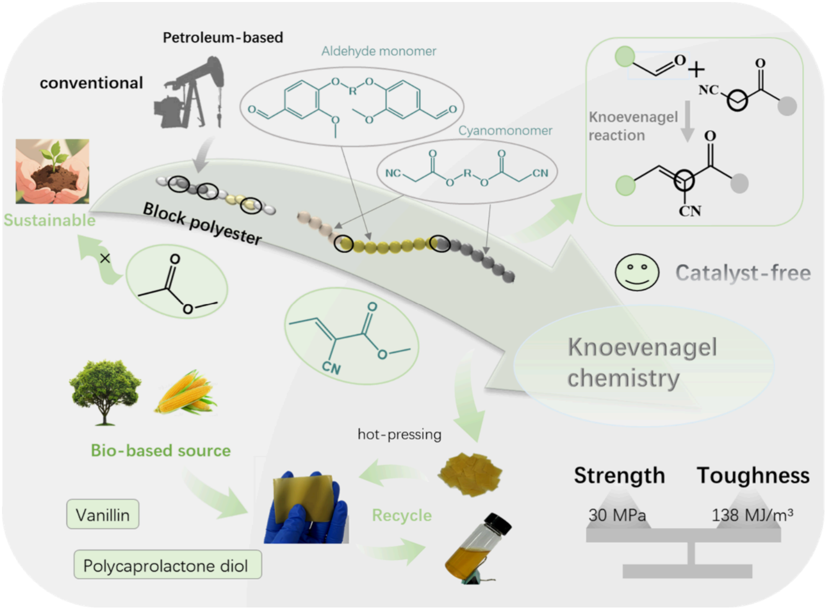


Figure 1. Biobased source and preparation mechanism of the polyester multiblock polymer.

described in Scheme 1, recent high-level reports of polyester block polymers still rely on organic/inorganic and metal-based catalysts, which also involve the support of petroleum-based monomers. Biobased polyester, such as furan-based polyester materials, also needs to break through the limit of high molecular weight.[33,34] Sun et al. found that the mechanical properties of the furan-based polyester elastomer can be improved by adding lignin cross-linking agents, but the fracture strain (610%) was still not ideal.[35] Moreover, the mechanical strength of the recovered polymer was unknown; simple recycling and effective separation from mixed plastics are still bottlenecks in the development of sustainable biobased polyesters.

We believe that the main challenge for biobased polyester materials will require the introduction of a novel polymerization strategy that avoids the use of toxic catalysts and high energy inputs, as well as overcoming the limitations of precise stoichiometry. Addressing this multifaceted challenge necessitates a fundamentally different approach. In this context, the Knoevenagel condensation reaction emerges as a uniquely promising solution, offering catalyst-free conditions, significantly lower reaction temperatures, and, crucially, the inherent ability to circumvent strict stoichiometric requirements—thereby directly tackling the key limitations of conventional polyester synthesis methods. Based on Knoevenagel condensation, Wang et al. successfully designed and synthesized a recyclable high-strength (tensile strength of 102 MPa) thermosetting material. However, due to side reactions such as double bond oxidation and cyanogen oxidation under repeated high-temperature post-treatment conditions, the mechanical properties of the recovered polymer decreased.[36] Similarly, the mechanical properties of dynamic thermosetting materials based on α-cyanate and aldehydes cannot be guaranteed after recovery due to the aging of samples during repeated high-temperature reprocessing.[37] However, it is difficult for currently reported polymers to achieve good thermodynamic properties and recyclability while avoiding the use of petroleum-based feedstocks. Vanillin, as one of the important phenolic compounds of biomass, is a new generation of biobased platform compounds after furan dicarboxylic acid.[38−41] Through simple chemical modification, a biobased vanillin monomer, which is easy for condensation, can be

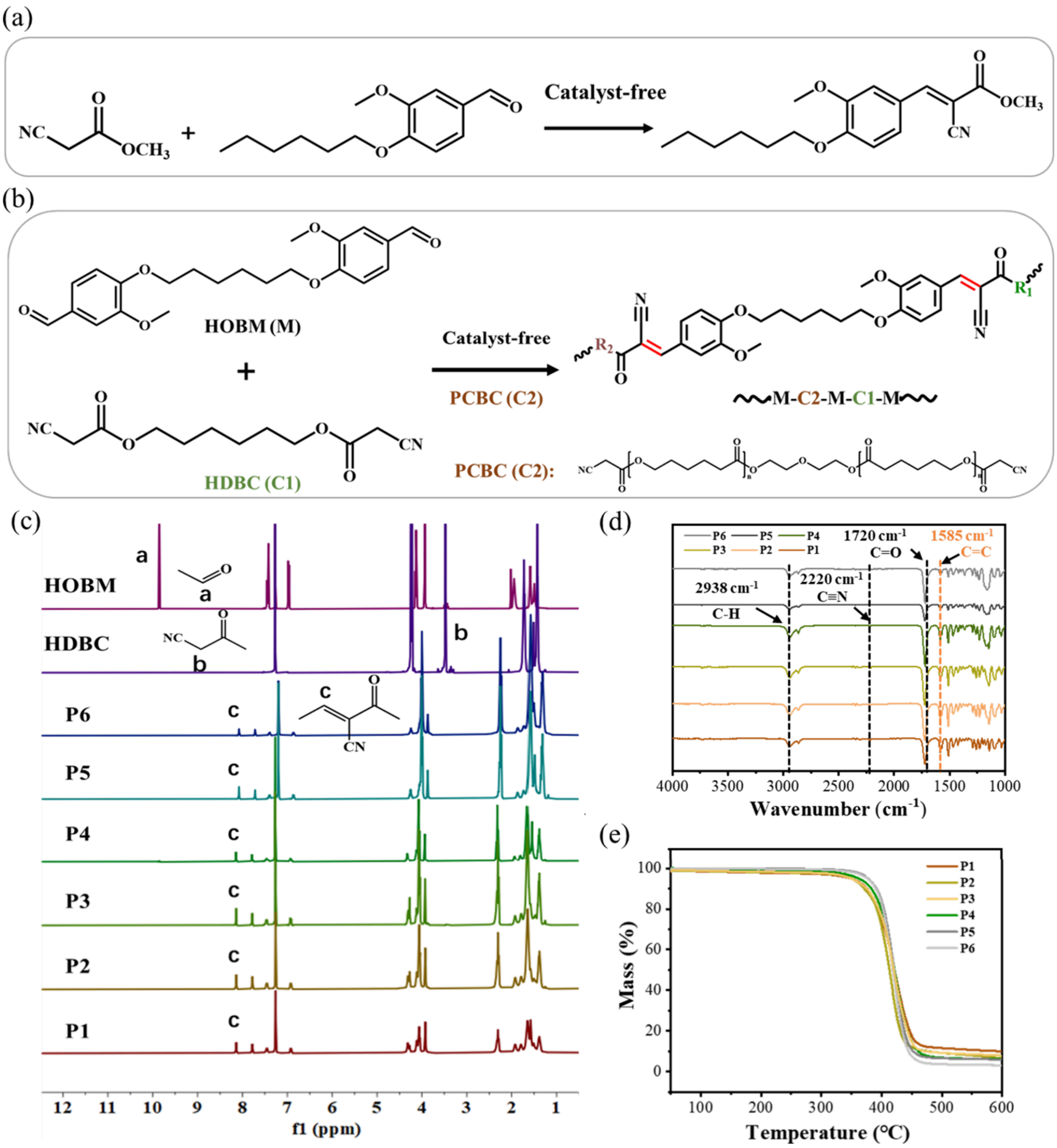


Figure 2. Model reaction of Knoevenagel condensation (a) and the synthesis of multiblock polyester (b); ^{1}H NMR spectrum (c) of HOBM and HDBC monomer and the prepared polymers; FT-IR spectrum (d) and TGA curve (e) of the prepared polymers.

obtained, providing a feasible way to prepare new biobased polyester materials by Knoevenagel condensation reaction.

Here, we developed a novel thermoplastic polyester material designed based on the Knoevenagel reaction, which uses its unique block structure and chemical properties to solve the above bottleneck. These high-performance polyester-based multiblock polymers consisted of vanillin-based aldehyde monomer and polycaprolactone-based cyanoacetate, as shown in Figure 1. Block polymers with different thermodynamic properties can be obtained by adjusting the content and molecular weight of the polycaprolactone-based cyanoacetate. The maximum strength and elongation at break of polymers can reach 30.55 MPa and 871%. The stress defects of polymer samples are remedied by simple solvent casting, and the tensile strength and elongation at break of the regenerated polymer films are increased. Compared to traditional polyester synthesis, this novel synthetic approach (catalyst-free and low-temperature polymerization), combined with solvent recovery, provides a groundbreaking strategy for the preparation and recycling of biobased polymers. Furthermore, the application potential of the resulting polymer is robustly demonstrated by the successful production of high-toughness fibers via melt spinning. Critically, this study establishes that the Knoevenagel condensation reaction offers unique and inherent advantages for sustainable polyester synthesis, representing a significant breakthrough compared with conventional methods.

■ RESULTS AND DISCUSSION

Polymer Preparation and Characterization. As the first application in polymer preparation, the feasibility of the Knoevenagel reaction was verified by the model reaction (Figures 2a and S4) of methyl cyanoacetate and vanillin aldehyde monomer in tetrahydrofuran. ^{1}H NMR spectroscopy proved that the Knoevenagel adduct was successfully synthesized at 50 °C for 3 h without a catalyst (Figures S5

Table 1. Properties of the Multiblock Polyester

polymer	M_n[a] (kDa)	M_w[a] (kDa)	$Đ$[a] (M_w/M_n)	T_g[b] (°C)	T_m[b] (°C)	X_c[c] (%)	σ_b[d] (MPa)	ε_b[d] (%)	U_T[d] (MJ M^{-3})	$T_{d,5\%}$[e] (°C)
P1	31.73	89.04	2.80	3.2	163	11	14.35	448.73	43.78	349
P2	23.14	57.38	2.43	−24.5	141	10	24.25	724.45	89.12	349
P3	34.84	99.07	2.84	−26.6	101	5	12.28	738.88	48.32	350
P4	44.83	97.45	2.17	−1.4	156	30	19.61	573.10	73.56	371
P5	53.87	120.87	2.24	−9.2	113	28	23.92	726.65	87.90	377
P6	59.94	120.47	2.00	−20.7	99	25	30.55	871.52	138.59	376

[a] The molecular weights and dispersities of the polymers were determined by gel permeation chromatography (GPC). [b] The glass transition temperature (T_g) and melting temperature (T_m) were determined using differential scanning calorimetry (DSC). [c] The crystallinity was determined by X-ray diffraction (XRD). [d] The breaking strength (σ_b) and elongation at break (ε_b) were determined by uniaxial tensile elongation testing, tensile toughness determined from stress-strain curve area. [e] Temperature at a molecular weight loss of 5% determined by thermogravimetric analysis.

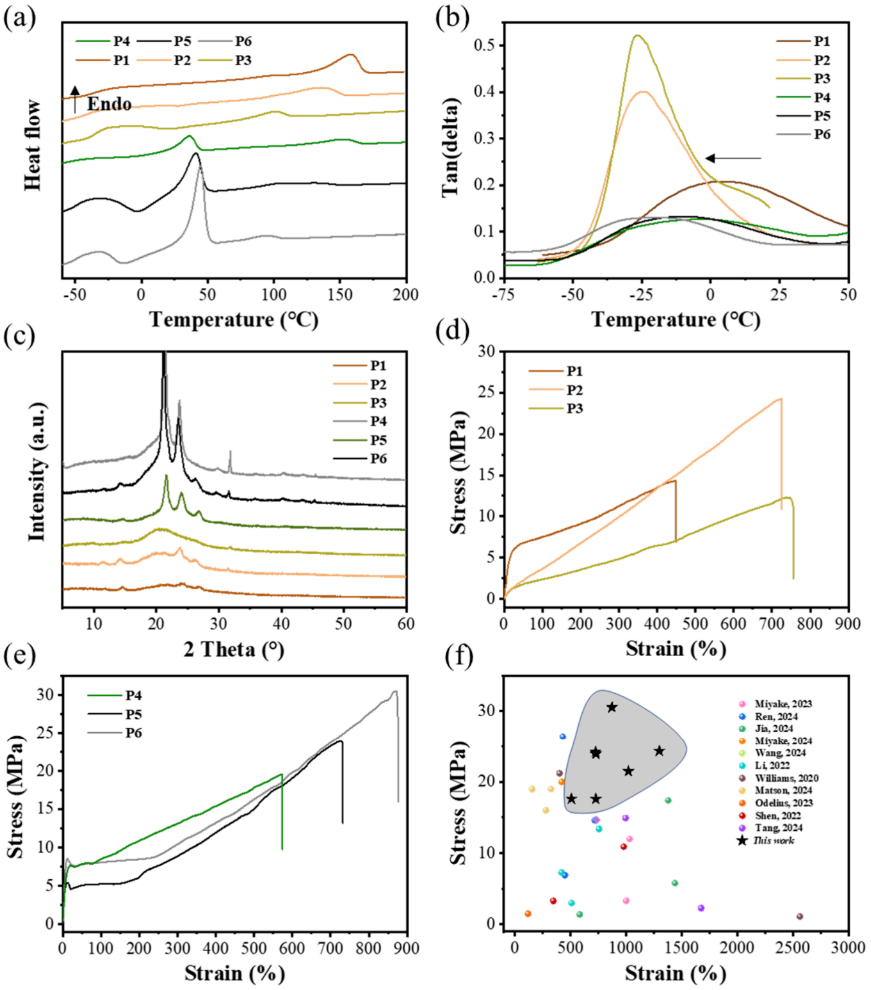


Figure 3. DSC curves (a), tan δ curves (b), XRD curves (c), and stress−strain curve (d, e) of the prepared polymers; comparison of mechanical properties with those of other typical biobased block polyesters (f).

and S6). Inspired by the above Knoevenagel compounds, biobased monomers with similar structures to the model monomers were synthesized, as shown in Figures S7−S10, and the synthesized monomers showed high purity. The initial thermal decomposition temperatures ($T_{d,5\%}$) of the two small molecular monomers shown in Figures S11 and S12 reached 299 and 234 °C, respectively. Based on good thermodynamic stability, we synthesized a variety of block polymers by adjusting the content of the two cyanomonomers (Figure 2b), and the composition of polyester multiblock polymers is shown in Table S1. The polycondensation temperature was optimized at 190 °C based on maximizing both intrinsic viscosity ([η]) and reaction yield, which served as the primary selection criteria, and the specific data are presented in Table S2. In the whole reaction process, the byproduct was only water. Different from the two small molecular monomers, the six polymers showed similar NMR absorption peaks near 8.1 ppm in Figure 2c, which was attributed to H on the newly formed C═C bond, proving that the multiblock polymers were successfully prepared based on the Knoevenagel reaction. In Figure 2d, the infrared absorption peak at 1585 cm^{-1} assigned to the newly formed C═C bond appeared, further demonstrating the successful preparation of the polymers.[42] In addition, the initial decomposition temperatures of the six polymers in Figure 2e and Table 1 were between 349 and 380 °C. These prepared polyester block polymers, according to different proportions, all showed good thermodynamic stability.

Due to the block arrangement of polymer segments and the influence of different molecular weights and molar fractions of the PCBC monomer, polyester multiblock polymers exhibited different thermodynamic properties, as shown in Table 1. The six polymers prepared in this work all exhibited narrow molecular weight distributions (GPC spectra in Figures S13−18). Furthermore, no unreacted monomers were detected in the nuclear magnetic hydrogen spectrum of the polymers (Figures S19−24). When the molecular weight of PCBC was 2000, with the increase of PCBC content, P1, P2, and P3 showed successively decreasing melting temperatures of 163, 141, and 101 °C, respectively, in Figure 3a. In the polymer chain segment, PCBC acted as the component of the soft segment, and the increase of the soft content segment made it difficult for the hard segment to form a complete crystalline structure, resulting in the decrease of the melting point of the polymer. Similarly, as shown in Table 1 and Figure 3c, the crystallinity of the three polymers also gradually decreased. Besides, when the content of the soft segment increased, the flexibility of the polymer molecular chain increased, and the chain segment was easier to move at a lower temperature, so that the glass transition temperature was reduced from 3.2 to −26.6 °C, as shown in Figure 3b. As the molecular weight of the soft segment increased to 4000, the block polymer showed a distinct melting peak of the soft segment between 0 and 50 °C, which was due to the excessive molecular weight of the soft segment, resulting in increased incompatibility between the soft segment and the hard segment in the block polymer, resulting in microphase separation.[43] The microregions of soft and hard segments melted at different temperatures, respectively. This also explained why the crystallinity of the polymer P4−P6 was significantly higher than that of P1−P3 in Table 1 and Figure 3c, but the melting temperature was basically unchanged. In the block polymer, the increase of the molecular weight of the soft segment was beneficial to the crystallization of the polymer; therefore, the glass transition temperature (Figure 3b) of the polymer did not show a stable decreasing trend.

Mechanical properties are key to evaluating the application value of polymers. As shown in Figure 3e, the stress−strain curves of P4−P6 exhibit characteristic features of semicrystalline polymers, including distinct yield points followed by strain hardening. This behavior originates from their crystalline architecture, where lamellae act as physical barriers restricting chain segment mobility, thereby inducing yield phenomena and promoting postyield orientation hardening.[44] Crystalline domains primarily function as physical cross-links and reinforcing fillers at the microscale. They significantly enhance the material's stiffness (modulus) and yield strength by restricting polymer chain mobility and bearing the majority of the applied load.[45] As demonstrated by P6, it achieved the highest tensile strength (30.55 MPa) and elongation at the break (871.52%), corresponding to a toughness of 138.59 MJ M^{-3}. The amorphous phase contributes to energy dissipation during deformation through effective chain slippage and segmental mobility, which is critical for achieving high ductility (elongation at break) and toughness (fracture resistance). As shown in Table 1, increasing soft segment content (P4 to P6) raised the elongation at break from 570 to 871% and toughness from 73 to 138.59 MJ M^{-3}. During this process, the amorphous phase absorbs energy via a viscous flow and molecular rearrangements. Strong interfacial interactions between the crystalline and amorphous phases enable efficient stress transfer from the softer amorphous matrix to the stiffer crystalline regions. This synergy prevents premature failure, thereby delivering a superior mechanical performance. Although the addition of crystalline soft segments may lead to a decrease in the crystallinity of the polymer (30−25%), by enhancing the continuity of the crystal region network and improving the interface bonding between the crystal region and the amorphous region, it reduces the risk of defects and fractures. The strength of the polymer still shows an increasing trend. The fundamental reason for the change in tensile strength is the compensation effect of the soft segment crystalline region on intermolecular forces and structural continuity, rather than simply depending on the degree of crystallinity. Therefore, we further investigated the effect of a higher soft segment content on polymer properties. It was found that the higher content of soft segment would lead to a decrease in polymer strength. The breaking strength and elongation of P7 were only 17.61 MPa and 725.77%, respectively. As expected, P7 exhibited the same high thermal stability, as shown in Figure S25. From the perspective of aggregation structure, moderate soft segments can promote the formation of a more uniform microstructure, make the stress dispersion more uniform, and improve the toughness and impact strength to a certain extent.[46] However, excessive soft segments will lead to excessive phase separation of the polymer, a decrease in crystallinity, and an increase in the disorder of molecular arrangement within the polymer, thus reducing the strength of the material. In contrast, due to the low crystallinity of P1−P3, its stress−strain curve did not show an obvious yield phenomenon, no neck phenomenon occurred during stretching, and the stress will continue to rise at a slower rate when continuing to stretch until fracture shown in Figure 3d, especially P2, which was similar to the tensile law of hard elastic materials. Similarly, the mechanical strength of P1−P3 increased first and then decreased with the increase in soft segment content.

It can be seen from Figure 3f that the strength of the block polymer prepared in this work was at a superior level compared with the recently reported high level block polymer and polyolefin elastomers.[19,20,22,43,47−53] Specific comparative data of mechanical properties are shown in Table S3. The mechanical properties of this material were similar to those of traditional TPEs, such as SBS (Styrene-butadiene-styrene) block copolymers.[54] The advantage of simple recycling makes it a competitive alternative. This is mainly due to its unique microcrystalline structure. In this structure, the amorphous region enclosed the crystalline region, and the molecular chains were tightly wound. The amorphous region provides the material's initial softness and high ductility, while the crystalline region acts as a strong physical cross-link, allowing the polymer to exhibit high mechanical properties.[55] Furthermore, as summarized in Table S4,[56] the mechanical strength of our synthesized polyester significantly surpasses that of PBS-like materials, though it remains lower than commercial PET. Crucially, its thermal stability is comparable to PET and markedly higher than PBT, PLA, and other common alternatives. This combination demonstrates a high application potential.

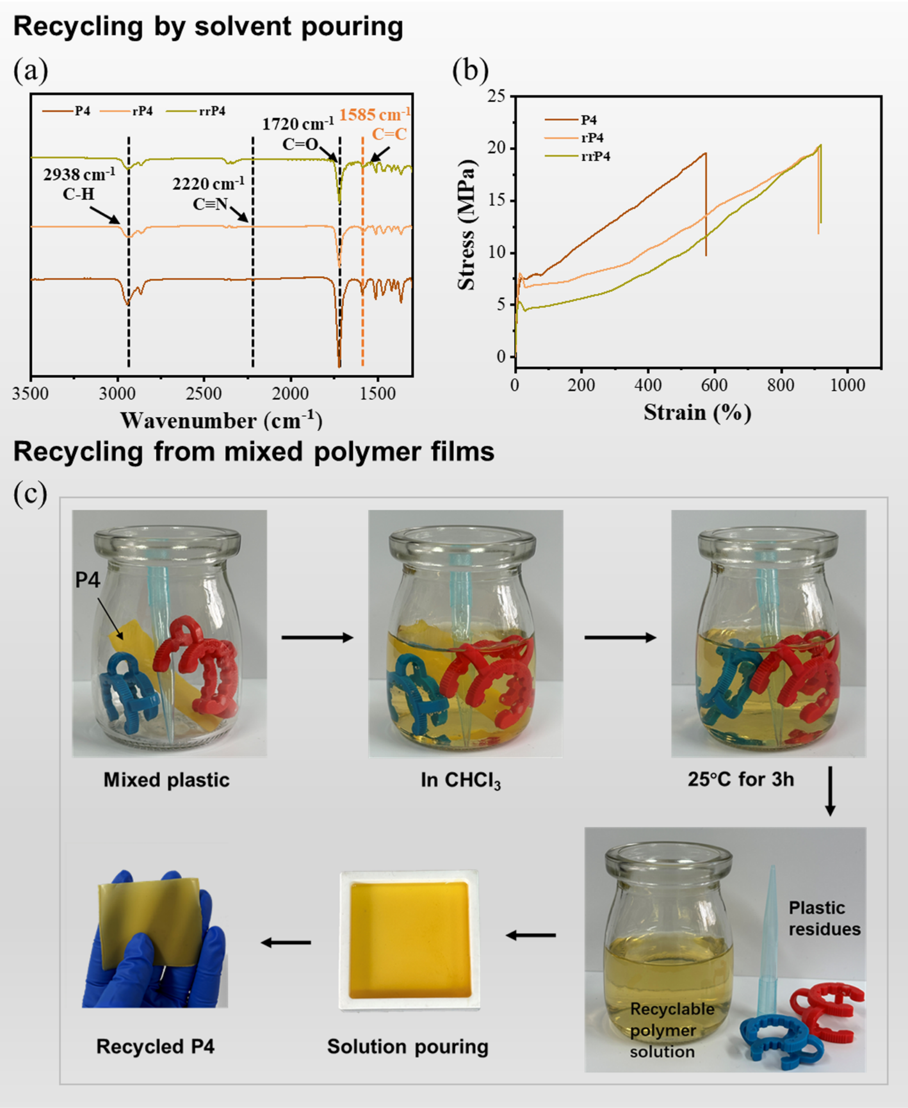


Figure 4. Infrared spectrum (a) and stress−strain curves (b) of the recycled polymer; the recovery effect (c) of the polymer from the mixed polymer samples containing polyoxymethylene (red), polyamide (dark blue), and polypropylene (light blue).

Acid−base and solvent tolerance are also important aspects of the polymer, which determine its stability in practical applications. From Figure S26, it can be found that after 24 h soaking, P1−P6 still remained intact, and the four commonly used solvents and acid−base solutions remained colorless and transparent, indicating that the polymer had not undergone significant dissolution and decomposition. Figure S27 shows the mass retention rate of the polymer in six solvents, especially in water, ethanol, and two acid−base solutions; the mass of the polymer was maintained above 90%. This indicated that the polymer has potential application stability.

Polymer Recycling and Separation. The simple recycling of polymers has a positive effect on their application in real life and the reduction of environmental pressure. The cut polymer fragments can still form the same polymer film as before after pouring the solution, forming a good polymer−polymer closed-loop recovery process. The infrared spectrum of the polymer after twice recovering is shown in Figure 4a, and it can be found that the characteristic peak (1585 cm^{-1}) on the polymer remained unchanged before and after recovery. The first film formation of the polymer was through hot pressing, and the breaking strength and elongation at break reached 19.61 MPa and 573.10%, respectively. As shown in Figure 4b and Table S5, after two solvent recoveries, the strength and elongation of the polymer film were significantly improved, with the breaking strength reaching more than 20 MPa and the elongation greater than 900%, and the toughness of the polymer increased from 73 to 108 MJ M^{-3}. This was due to the stress defect formed by the uneven stress or heat in the process of hot pressing, resulting in low mechanical strength of the polymer. It is worth noting that after solvent recovery, the polymer molecular chain was fully extended, and the stress defect formed by hot pressing was compensated, and the polymer sample showed better mechanical properties.

In real life, the recovery of mixed polymers is an urgent problem that needs to be solved. Here, we mixed polymer bottle mouth clamps of polyformaldehyde (POM), polyamide (PA), and 1 mL centrifuge tubes (polypropylene, PP), dissolved in trichloromethane. These three polymers remained in their original state, and no obvious swelling or dissolution phenomena occurred after 3 h immersion at room temperature. The polymer film prepared in this work can be well dissolved into uniform yellow solutions from the mixed polymer and recast to form films in Figure 4c. This proved the high efficiency and easy recycling performance of this polymer, which provided a new inspiration for the recovery of high-performance thermoplastic polymers.

Polymers: Various Processing Methods. In recent years, there has been an increasing demand for high-performance and versatile biobased polyester materials. Based on the excellent comprehensive properties of the block polymer prepared in this work, we have demonstrated a variety of processability of this polymer, including casting film, melt extrusion, and hot pressing. As shown in Figure S28, the polyester multiblock polymer prepared in this work formed a uniform polymer solution in trichloromethane, and after a simple solution pouring and volatilizing the solvent at room temperature, a yellow film of uniform thickness can be obtained. The film with a thickness of about 0.2 mm has good optical permeability and flexibility and can be folded into any shape. In addition, based on the good thermal stability, crystallinity, and melt fluidity of the polymer, we further investigated the spinning properties of the polymer. With P2 as an example, As shown in Figure S29, at 180 °C and 120 r/min, the polymer showed good spinnability. It was found that the tensile strength of the polymer fiber was stable at about 0.96 cN/dtex, and the elongation at break was higher than 600% after stretching (3.5 times tensile ratio) and heat treatment (50 °C).[57] Block polymers can also be made into different shapes by hot pressing. Figure 5 exhibited the practical application of the multiblock polymer, which can be processed into polymer plates, polymer washers, polymer films, gears, and blocks (such as for educational toys), and polymer fibers related to industrial production. Therefore, flexible processing methods and stable mechanical properties give the polymer a wide range of product adaptability, environmental protection, and sustainability.

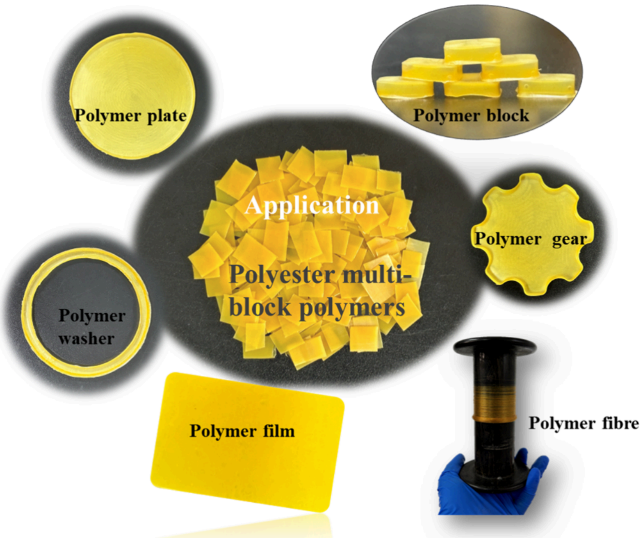


Figure 5. Demonstration of the application effect.

■ CONCLUSIONS AND PROSPECTS

In conclusion, we achieved a breakthrough in sustainable polymer science by designing biobased polyester multiblock materials via Knoevenagel condensation, addressing the limitations of conventional polyesters in energy consumption, toxicity, and recyclability. The integration of vanillin-derived rigid segments and tunable polycaprolactone diol soft segments enabled dynamic control over material properties: increasing the soft-segment molecular weight from 2000 to 4000 g/mol enhanced crystallinity to 30% but reduced ductility, while elevating the soft-segment molar ratio from 30 to 70% significantly improved toughness from 43 to 138 MJ M^{-3}, alongside high strength (30.55 MPa) and ductility (871.52%). The solvent-casting recovery strategy overcame performance degradation in thermal reprocessing, achieving a 48% toughness boost in regenerated films and efficient separation from mixed plastics, offering a novel solution for complex waste recycling. The material exhibited exceptional stability in acidic/alkaline (0.1 mol/L HCl/NaOH) and organic solvents (mass retention >90%). The high toughness fiber (elongation at break >600%) prepared by melt spinning highlights its application potential in textile, packaging, and flexible electronics. Mechanistic insights revealed that balanced soft-segment design optimized crystalline−amorphous structures: microcrystalline domains provided strength via physical cross-linking, while amorphous regions ensured flexibility for synergistic performance improvement. This work not only establishes a green synthesis-recycling framework but also advances thermoplastics toward circular manufacturing through a ″polymer-to-polymer″ closed-loop paradigm. Good processing adaptability, environmental protection, and sustainability make the polymer extremely competitive. Future directions include exploring diverse soft-segment chemistries (e.g., polylactic acid and polycarbonate) to broaden performance scope, developing low-temperature polymerization for scalable production and assessing long-term environmental stability to accelerate commercial adoption.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.5c01106.

> Materials and characterization methods, synthesis route of HDBC, PCBC, HOBM, model compound, and block polymer, ^{1}H NMR spectrum of HDBC, PCBC-2, PCBC-4, HOBM, model compound, and the prepared polymers, TG curve of HDBC, HOBM, and P7 polymer, GPC curves of the prepared polymers, comparison of mechanical properties, composition of polyester multiblock polymers, effect of polycondensation temperature on inherent viscosity and yield, comparison of recovery properties of P4 polymers, images and quality retention rate of P1−P6 polymers splines after 24 h of solvent immersion, diversity of processing methods for polyester block polymers, and mechanical properties of P2 fibers with 3.5 draw ratios (PDF)

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Notes

The authors declare no competing financial interest.

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