

# Polymer Single-Crystal Functionalization Applications

Subjects: Polymer Science

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Polymer physics has evolved significantly over the past century, transitioning from the early recognition of the chain structure of polymers to a mature field integrating principles from statistical mechanics, thermodynamics, and condensed matter physics. As an important part of polymer physics, polymer single crystals are crucial for understanding molecular structures and behaviors, enhancing material properties, and enabling precise functionalization. They offer insights into polymer crystallization kinetics, serve as templates for nanofabrication, and have applications in electronics, sensors, and biomedical fields.

Keywords: polymer single crystal ; crystallization strategy ; functionalized application

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## 1. Introduction

In 1920, Hermann Staudinger proposed for the first time that polymers are linear structures consisting of monomers connected by covalent bonds, thus founding modern polymer science <sup>[1][2]</sup>. In the course of one hundred years of development, polymer materials have gradually become an indispensable part of our daily lives. Scientists have gradually deepened their research on polymer chemistry and polymer physics, especially on polymer crystallization.

A polymer single crystal is defined as a highly ordered arrangement of polymer chains in a three-dimensional lattice structure, wherein all the molecules are aligned in a specific orientation with respect to each other. Unlike polymer polycrystals, which consist of multiple crystal domains with varying orientations, polymer single crystals exhibit uniformity and perfect geometric symmetry. It was first thought that it was difficult for polymer chains similar to random line clusters to be ordered, and that there was a very high thermodynamic energy barrier for the untangling and movement of molecular chains. However, experimental results showed that under appropriate crystallization conditions, polymer chains will spontaneously form geometrically symmetric structures similar to small molecule crystals. The structure of the crystal reflects the stacking of the lattice, and the close arrangement of the molecular chains also leads to excellent mechanical or optoelectronic properties.

The key to preparing high-quality single crystals is to ensure that they crystallize under low supercooling and a low concentration. Single crystals of polymers can usually only be obtained under special conditions, and are generally produced by slow crystallization in very dilute solutions (0.01% to 0.1%). Within the single crystal, the molecular chains are arranged in a highly regular three-dimensional order, with the chains oriented perpendicular to the surface of the lamellar single crystal. When the degree of supercooling or the concentration of the solution is slightly higher, the growth of polymer crystals is no longer limited to lateral growth, but can form multiple crystals containing a number of overlapping crystals of equal thickness. Helical dislocations in these crystals provide a step that can be grown continuously without restriction, culminating in the formation of helical-stepped multilayer crystals.

## 2. Polymer Single-Crystal Functionalization Applications

### 2.1. Single-Crystal Template Modification

The typical structures of polymer crystals include spherulites <sup>[3][4][5][6]</sup>, dendritic crystals <sup>[7][8][9]</sup>, extended-chain crystals <sup>[10][11][12][13]</sup>, fibrous crystals <sup>[14][15][16]</sup>, and lamellar crystals <sup>[17][18][19][20]</sup>. Among them, polymer single crystals are lamellar crystals with regular geometrical shapes, usually formed by folding molecular chains back and forth <sup>[21]</sup>. For now, there are limited studies using single crystals as a functional template <sup>[22]</sup>.

The advantage of polymer single crystals is that when the end-functionalized polymers form monolithic folded-sheet single crystals, the chain ends are excluded from the crystal surface and can be coupled to various nanoparticles (NPs) to form nanosandwich structures. After the coupling reaction and dissolution of the polymer single crystals, free Janus nanoparticles (with a non-centrosymmetric structure and single nuclei surrounded by a separated coronal structure) can

be obtained, providing a unique approach to the preparation of asymmetric nanoparticles [23]. When polymer single crystals are used as substrates, the method is referred to as the “polymer single crystal templating” (PSCrT) method [23][24][25][26][27][28][29][30][31][32][33][34][35][36][37][38][39]. PSCrT uses surface chemical coupling similar to that of self-assembled monolayers (SAMs), and the advantage of using polymer single crystals for nanoparticle assembly is that the SAMs are usually confined to solid substrates [40][41][42][43], whereas PSC is solution-independent. Yuren Li's group proposed the PSCrT method and has been working on this unique application of polymer single crystal for years.

In 2006, Yuren Li's group first reported the application of polymer layered single crystals as a solid substrate to create a graphically functional (thiol) surface and immobilize gold nanoparticles (AuNPs) [24]. Two years later, they applied a self-seeding method to prepare terminated thiol-poly(ethylene oxide) (HS-PEO) single crystals, which also enabled the asymmetric functionalization of AuNPs. AuNPs were immobilized using HS-PEO as a substrate, a method called “solid-state grafting” [25]. In the same year, it was reported that AuNPs were immobilized using HS-PEO as a substrate by combining the “solid-state grafting” and “grafting” methods. In the same year, it was reported that Janus AuNPs were functionalized with two different types of polymer chains on the other side of the AuNPs using HS-PEO as a substrate by combining the “solid-state grafting” and “grafting” methods [23]. The application of polymer single crystals as a substrate is advantageous because they have higher fluxes than self-assembled monomolecular membranes. The dissolution of the single crystals also leads to NPs with well-defined polymer patches (functional groups). This method will be able to serve as a general method for the synthesis of polymer-functionalized Janus NPs and is expected to lead to the controlled assembly of NPs and tunable optical and electronic properties.

A new method for the large-scale production of NP sheets with programmable patterns was investigated by Yuren Li's group in 2009. In the preparation of HS-PEO single crystals, nanoparticles were assembled in situ during the polymer crystallization process. This approach enables precise control over the three main features of the nanoparticle pattern on the single crystals: the NP spacing, the width and length of frames/chains, and the distance between frames/chains [26].

In 2010, Yuren Li's group and others demonstrated that polymer single crystals can be used as a versatile substrate for immobilizing NPs. By using PEO and PE-b-PEO as a single-crystal substrate, gold, magnetic, and semiconducting nanoparticles were immobilized on the surface of the polymer single crystal. The subsequent single-crystal dissolution generated different types of Janus nanoparticles and nanoparticle clusters of different polymers [28]. In the same year, Wang et al. faced the challenge of synthesizing Janus nanoparticles (JNPs) with diameters of less than 20 nm by using atom transfer radical polymerization to grow polymer brushes on polymer single crystal-immobilized gold nanoparticles (AuNPs) with diameters of 6 and 15 nm. By combining both the “grafting-to” and “grafting-from” approaches of polymer-functionalized Janus AuNPs, PEO-SH single crystals with HS groups on the surface were synthesized and then AuNPs were immobilized on top of them. The polymer brushes were grown on the AuNPs by applying an initiator on the top surface of the immobilized AuNPs [27].

In 2011, Yuren Li's group utilized the polymer single-crystal template approach to provide a new method for the synthesis of functional Janus nanoparticles. Polymer single crystals of bifunctional polymers were used as templates to which NPs were attached via covalent bonding with the thiol groups exposed on the surface of the single crystals. Covalent bonding was used to attach to this template, while asymmetric modifications and end-group functionalization were introduced to the NP surface [37]. The group introduced a facile method to synthesize amphiphilic Janus silica nanoparticles (SiNPs) with a two-compartment polymer in 2012 [30]. Single crystals of poly( $\epsilon$ -caprolactone) with alkoxysilane terminations (PCL-SiOR) were prepared using a self-seeding method, and silica nanoparticles were immobilized on the surface of the single crystals. The Janus particles of this method showed lower thermal transition temperatures and much narrower transition ranges [30].

In order to develop a low-cost and high-yield template for the synthesis of heterogeneous nanoparticles, Zhang Hui et al. from Yuren Li's group reported a new polymer single-crystal substrate method for directional self-assembly of heterogeneous nanoparticles. Polymer single crystals consisting of hydroxyl-terminated polycaprolactone (PCL-OH) with hydroxyl groups on the surface were formed using the self-seeding method. This approach is generally applicable to different nanoparticle systems as long as there are specific interactions between the first adsorbed nanoparticle and the single crystal as well as between the first and second adsorbed nanoparticles [29].

In the following two years, Yuren Li's group used the polymer single crystal substrate approach for the self-assembly of nano-motors [31][32]. This approach opens up great opportunities for miniaturization and mass production of future nano-motors as well as for other applications including sensors and directed transport. In 2014, Yuren Li's group provided a method to synthesize “dumbbell” nanoparticle dimers through one-step coupling of nanoparticles and quasi-two-dimensional polymer single crystals [33]. In subsequent work, the group reported a shape-controlled freestanding sheet

composed of nanoparticles generated using the PSCrYT method. Using the self-assembly technique, nanoparticle assemblies were obtained with nanoparticles and polymer single crystals as the basic building blocks [34].

In 2016, Tian Zhou et al. from Yuren Li's group combined the advantages of the traditional "grafting-to" and "grafting-from" methods of synthesizing polymer brushes to achieve the synthesis of polymer brushes with controlled structures and high grafting densities on planar surfaces [38]. For a given molar mass, the chain-folded structure can be precisely controlled by varying the crystallization temperature, which can ultimately be used to tune the grafting density of subsequent polymer brushes [38]. In 2017, Shan Mei et al. from Yuren Li's group used single-crystal templates to provide a directed assembly method to precisely assemble NPs into well-defined, independent frameworks [35]. The PEO single crystals were used as a template to direct the crystallization of the block copolymer (BCP) poly(ethylene oxide)-b-poly(4-vinylpyridine), which directs the AuNPs to form AuNP frameworks. The reported method may become a new approach to synthesize precisely assembled, free-standing cyclic NP chains and nanocycles.

In the following year, Yuren Li's group proposed a bottom-up method called "polymer single crystal assisted grafting method (PSCAGT)" to synthesize gradient polymer brushes with pre-designed and precisely controlled grafting density gradients and patterns [36]. By varying the incorporation rate of PEO<sub>114</sub>-OH, polymer brushes were successfully synthesized with pyramidal and smooth gradient structures with pyramidal micropatterns [36]. In 2020, Yuren Li's group reported a new method for synthesizing diblock copolymer brushes. The resulting diblock copolymer brushes showed a relatively high grafting density and also retained the original single-crystal morphology with high fidelity, providing a unique method for patterning polymer brushes [39].

The initial application of the polymer single-crystal template approach involved immobilizing nanoparticles to achieve patterning and asymmetric functionalization. Subsequently, the approach demonstrated capabilities in growing polymer brushes, modifying Janus NPs, and synthesizing small-sized Janus NPs on a substrate surface. Over time, it evolved into a cost-effective, high-yield template for heterogeneous nanoparticle synthesis and directed assembly of nanoparticles, facilitating diverse functionalities.

## 2.2. Photoresponsive Polymer Single Crystals

In 2000, Heeger [44][45][46], MacDiarmid [47][48][49], and Shirakawa [50][51][52] were awarded the Nobel Prize in Chemistry for the discovery and development of conductive polymers. It is common knowledge that plastics do not conduct electricity, so they can be used as insulating materials for wire cladding, socket switches, and so on. However, the discovery of electrically conductive polymers in the mid-1970s changed the long-held notion that polymers could only be insulators and led to the development of polymer materials with photo- and electro-activity.

In the past decades, conjugated polymers have been widely studied due to their excellent optoelectronic properties [53][54][55][56][57]. Compared with inorganic semiconductors, conjugated polymers have the advantages of being lightweight, corrosion resistant, environmentally stable, and cost effective [58][59][60][61][62]. Conductive polymers have become an alternative material for photovoltaic devices, e.g., conductive polymers have been successfully used in solar cells [63][64][65][66][67][68][69], light emitting diodes [70][71], chemical sensors [72], thin-film transistors [73][74][75][76], and field-effect transistors [77][78][79]. Compared with amorphous polymers, crystalline polymers with planarized main chains and close stacking of neighboring chains can greatly enhance the photovoltaic performance [80]. Single crystals normally show a better photovoltaic performance because of the perfect ordering of their molecular chains, the absence of grain boundaries, and good interfacial contacts [81][82][83][84][85][86][87][88][89][90].

In order to optimize the electrical properties, Kim et al. developed P3HT structures with strong  $\pi$ - $\pi$  interactions in the same direction [83]. A solvent-assisted crystallization method was developed by Ma et al. for the growth of high-quality regionally regular poly(3-butylthiophene) (rr-P3BT) single crystals.

Jeon proposed a method to control the morphology and size of conducting polymer nanostructures for their ordered growth. Using organic single crystals of monopotassium salt of 4-sulfobenzoic acid (KSBA) as a soluble template, KSBA precipitated as individual micro-sized crystals in an aqueous medium with a hexagonal plate-like shape. It was shown that the organic crystal surface-induced polymerization of the conductive polymer was able to replicate the shape of the organic monocrystal when the organic monocrystal was present in the polymerization medium. This method can be widely used in the fabrication of sensors, templates, catalyst carriers, and carbon material substitutes [82].

Xiao proposed another method to prepare poly(3-octylthiophene) (P3OT) needle-like single crystals by tetrahydrofuran steam annealing. This work demonstrated that the crystallization conditions can modulate the molecular orientation and help to further investigate the structure–property relationship of conducting polymers [88]. Xiao prepared P3HT and P3OT

by tetrahydrofuran steam annealing and controlling the solvent evaporation, respectively. When the films were annealed for 42 h, the P3HT single crystals were predominantly needle-like crystals with lengths of 20–60  $\mu\text{m}$  and diameters of 1–2.2  $\mu\text{m}$  [89]. The mobility of the P3HT single crystals was  $1.57 \times 10^{-3} \text{ cm}^2/\text{Vs}$  in the field effect transistor, where the current was parallel to the length axis of the single crystals. The mobility of P3OT single crystals was  $0.62 \text{ cm}^2/\text{Vs}$ . The shorter length of the alkyl side chains of P3HT compared to P3OT results in a higher mobility. This suggests that the alkyl side chains act as a barrier to carrier migration between poly(3-alkylthiophene) (P3AT)-like polymers [89].

Rahimi et al. used tetrahydrofuran as a solvent to prepare P3HT solutions at concentrations ranging from 0.1 mg/mL to 10 mg/mL, which were heated to 82 °C to completely dissolve the polymer. These solutions were then filtered using 0.45  $\mu\text{m}$  PTFE filters and the temperature of the solutions was controlled with an accuracy of 0.1 °C using a silicone oil bath thermostat. To obtain films from solutions containing single crystals, they had the substrates preheated to  $T_c$ , spin-cast 200  $\mu\text{L}$  of the solutions onto wafers, and then dried them in a vacuum oven for 1 h at room temperature, ultimately yielding P3HT macromonomers [90].

Nuraje prepared single crystals of poly(aniline) (PANI) by using the interfacial polymerization method. The resulting crystalline polymers showed conductivity switching times on the order of milliseconds between the insulating and conducting states [85]. Su prepared for the first time single-crystal poly(3,4-ethylenedioxythiophene) (PEDOT) nanoneedles that exhibited fast conductance switching using interfacial polymerization. By investigating the electronic conduction behavior of the single crystals, they found field-induced conductance switching within a response time of milliseconds [87].

Zenoozi used P3HT homopolymers and block copolymers to prepare single crystals and nanofibers in a range of solvents such as toluene, xylene, and anisole. It was found that when single crystals and nanofibers are developed from good solvents, the crystal structure becomes more ordered, yielding higher current densities [80]. Cho et al. developed single-crystal PEDOT nanowires with ultra-high electrical conductivity using liquid-bridge-mediated nanotransfer printing and gas-phase polymerization. The PEDOT nanowires had a tightly packed single-crystal structure with orthorhombic lattice units. Its electrical conductivity averaged 7619 S/cm and reached up to 8797 S/cm [81].

Wu et al. proposed a self-seeding method carried out in situ in solution to obtain highly ordered single crystals of P3HT. Precise control of the degree of supersaturation in space and time was achieved by forming a concentration gradient of poor solvents by vapor diffusion in the solution system. Eventually, the long needle-like crystals were formed after drastically reducing the nucleation density while maintaining a limited growth rate. The spectroscopic results showed that the obtained single crystals are capable of absorbing long wavelength light, which is promising for applications in the energy field [91].

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