

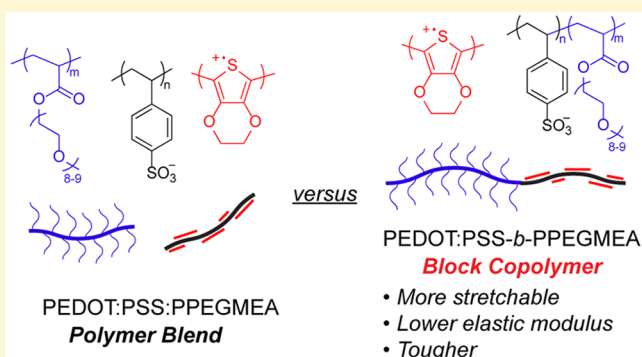
RAFT Polymerization of an Intrinsically Stretchable Water-Soluble Block Copolymer Scaffold for PEDOT

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Supporting Information

ABSTRACT: Despite the common association of π -conjugated polymers with flexible and stretchable electronics, these materials can be rigid and brittle unless they are designed otherwise. For example, low modulus, high extensibility, and high toughness are treated as prerequisites for integration with soft and biological structures. One of the most successful and commercially available organic electronic materials is the conductive and brittle polyelectrolyte complex poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS). To make this material stretchable, additives such as ionic liquids must be used. These additives may render the composite incompatible with biological tissue. In this work, we describe the synthesis of an intrinsically stretchable variant of the conductive polymer PEDOT:PSS that is free of additives. The approach involves the synthesis of a block copolymer comprising soft segments of poly(poly(ethylene glycol) methyl ether acrylate) (PPEGMEA) and hard segments of poly(styrenesulfonate) (PSS) using a reversible addition–fragmentation chain transfer (RAFT) polymerization. Subsequently, we used the newly synthesized ionic elastomer PSS-*b*-PPEGMEA as a matrix for the oxidative polymerization of EDOT. The resulting polyelectrolyte elastomer, PEDOT:PSS-*b*-PPEGMEA, can withstand elongations up to 128% and has a toughness up to 10.1 MJ m^{−3}. While the polyelectrolyte elastomer is not as conductive as the commercial material, the toughness and extensibility are each more than an order of magnitude higher. Moreover, the electrical conductivity of the polyelectrolyte elastomer exhibits minimal decrease with strain within the elastic regime. We then compared the block copolymer to physical blends of PEDOT:PSS and PPEGMEA. The blend material had a much lower failure strain of only 38% and a maximum toughness of 4.9 MJ m^{−3}. This approach thus emphasizes the importance of the covalent linking of the PSS and PPEGMEA blocks. Furthermore, we demonstrate that the conductivity of scratched films can be restored upon exposure to water.



INTRODUCTION

The advent of wearable and implantable electronics has driven the development of soft, stretchable, and skin-like semiconductors and conductors.^{1–6} Traditional inorganic materials such as silicon or metals are hard and brittle but can be incorporated in stretchable devices using wavy or serpentine layouts on elastomeric substrates. In contrast to approaches using inorganic materials, organics offer the advantages of oxide-free interfaces, ease of fabrication by printing, mixed modes of conductivity (ionic and electronic), molecular-scale conformability, tunability of color, bandgap, and selectivity in sensing.^{7–11} These organic materials can be designed to be intrinsically stretchable and biocompatible. While a large effort has been underway to improve the deformability of semiconducting polymers,⁷ a similar effort to produce intrinsically stretchable conducting polymers is lacking. The conductive polyelectrolyte complex poly(3,4-ethylenedioxythiophene):poly(4-styrenesulfonate) (PEDOT:PSS) is

brittle unless plasticized with additives that may leach into biological tissue.¹² This paper describes the synthesis of a stretchable block copolymer scaffold for conductive PEDOT.

Early work on stretchable organic conductors involved the use of graphite, carbon nanotubes, or graphene on or dispersed in an elastomer.^{13–17} These composites, however, rely on the formation of a percolated pathway—connectivity between the embedded structures—to transport charge. Moreover, the conductivity of such materials is often sensitive to strain. Intrinsically conductive polymers such as polyaniline and polypyrrole have also been incorporated into elastomers by blending or grafting.^{18–21} But again, a strategy that uses composite materials led to poor conductivity, high sensitivity to strain, or both. The most successful and studied conductive

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polymer is PEDOT:PSS, commercially available under the trade name of Clevios.^{22,23} To produce this material, EDOT is oxidatively polymerized in a matrix of PSS to form a dispersion in water. The PEDOT, once polymerized, is in its doped and positively charged state which is stabilized by the PSS polyanion. Conductivity around 1000 S cm^{-1} can be achieved by secondary doping with a high boiling solvent such as DMSO, sorbitol, or ethylene glycol. The polyelectrolyte complex PEDOT:PSS is composed of two brittle components: it can only be strained to 3–10% and has a high elastic modulus ($\sim 2 \text{ GPa}$).²⁴ These mechanical properties are in striking contrast with biological tissues, which are typically soft (elastic modulus $< 1 \text{ MPa}$) and stretchable (strain $\geq 50\%$).²⁵ This mismatch in mechanical properties renders its integration in conformable, wearable and implantable electronic devices difficult.^{26,27} Several approaches have been reported to improve the mechanical properties of PEDOT:PSS. Similar to other conductive polymers, PEDOT can be incorporated in elastomers. For example, PEDOT has been directly polymerized in water-insoluble elastomers such as polyurethane,^{28,29} hydrogels,³⁰ organogels,³¹ or aerogels³² or electropolymerized onto soft materials.³³ Meanwhile, most of the literature on stretchable PEDOT:PSS relies on the unmodified use of its commercially available form, for example, by patterning it over prestrained elastomers.³⁴ The direct blend of PEDOT:PSS with hydrophobic elastomers such as poly(dimethylsiloxane) (PDMS) cannot be achieved because of long-range phase separation. To circumvent this issue, Noh et al. mixed PEDOT:PSS with the amphiphilic diblock copolymer PDMS-*b*-PEO to improve its miscibility with PDMS leading to films that can accommodate 75% strain.³⁵ Most of these blending approaches require the use of organic solvents. Casting PEDOT-based films from organic solvents sacrifices the useful property of solvent orthogonality. That is, it is beneficial when producing multilayer devices to use PEDOT:PSS, which is ordinarily soluble in water, because it does not redissolve upon spin-coating or printing another polymer on top from an organic solvent. Because PEDOT:PSS is dispersed in water, however, it can be blended with water-soluble semicrystalline polymers such as poly(vinyl alcohol) (PVA), poly(ethylene glycol), or poly(ethylene oxide) (PEO) to increase the stretchability up to 55%.³⁶

Another strategy to improve the stretchability of PEDOT:PSS while maintaining its solubility in water involves the addition of small molecule additives. Zonyl, a fluorosurfactant, can be used as an additive to improve its adhesion to a hydrophobic elastomer (PDMS).^{12,37,38} The Zonyl-containing PEDOT:PSS coated on PDMS can be stretched up to a 188% (when the PDMS breaks) while retaining conductivity.³⁷ Another surfactant, Triton X-100, can act as a plasticizer for PEDOT:PSS, forming a conductive “dough”.³⁹ Recently, the groups of Lee⁴⁰ and Bao⁴¹ both showed that ionic liquids can improve both the conductivity and stretchability of PEDOT:PSS. This additive approach is not suitable for applications in wearable or implantable electronics where the electrode is in direct contact with the human body. The small molecules, which are often not biocompatible, could leach out of the film and not only deteriorate the properties of the material but are also toxic and have raised human health concerns.^{42–44}

While these approaches proved effective in improving the stretchability of PEDOT:PSS, the use of intrinsically stretchable, additive-free, and water-soluble PSS-based block

copolymers to achieve conductive elastomers has never been reported. Here, we synthesized a double hydrophilic block copolymer comprising “hard” PSS blocks linked by “soft” and biocompatible poly(poly(ethylene glycol) methyl ether acrylate) (PPEGMEA) blocks using a RAFT polymerization (Figure 1). The water-soluble, ionic elastomer PSS-*b*-

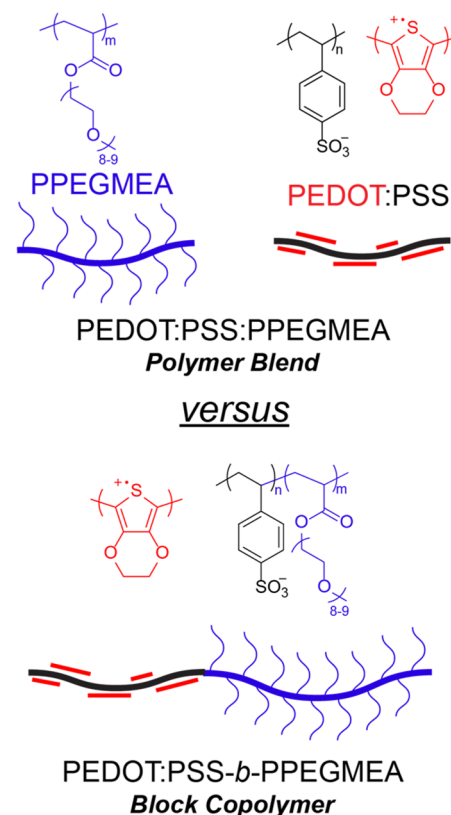


Figure 1. Schematic representation of the two strategies used here to obtain stretchable PEDOT:PSS using PPEGMEA as a soft polymer additive to PEDOT:PSS or in a block copolymer with PSS.

PPEGMEA was then used as a matrix for the oxidative polymerization of EDOT. The resulting polyelectrolyte elastomer could be stretched up to 128%, has a toughness up to 10.1 MJ m^{-3} , and the electrical resistance of the material showed low sensitivity to strain. This copolymer was compared to a physical blend of PEDOT:PSS with PPEGMEA which was weaker and could only be stretched up to 38%, highlighting the importance of a covalent linkage between PSS and PPEGMEA.

■ EXPERIMENTAL DESIGN

Choice of the Soft Block. Poly(poly(ethylene glycol) methyl ether acrylate) (PPEGMEA), with $M_n(\text{PEGMEA}) = 480 \text{ g mol}^{-1}$, was chosen as a soft block because it is water-soluble, biocompatible, and a liquid at room temperature.^{45,46} Moreover, its comb-like structure could increase the softness in elastomers by decreasing the glass transition temperature when compared to unsubstituted polymers.^{47–49} In the proposed PEDOT:PSS-*b*-PPEGMEA, we hypothesize that mechanical stress would be accommodated by the soft PPEGMEA block while the PEDOT:PSS polyelectrolyte complex would constitute the stiff block. As an acrylate-based monomer, PEGMEA can be easily integrated in block copolymers with styrenic derivatives using anionic or controlled radical

Table 1. Optimization of the RAFT Polymerization for the Synthesis of PSS, PPEGMEA, and PSS-*b*-PPEGMEA-*b*-PSS

entry	polymer	[M]:[RAFT]:[I]	reaction time	monomer conv ^a (%)	$M_{n,theor}^a$ (kg/mol)	$M_{n,exp}^b$ (kg/mol)	$M_{w,exp}^b$ (kg/mol)	\bar{D}
1	PSS ^c	300:1:0.1	15 h	95	59	55.5	76.8	1.4
2	triblock ^{c,d}	380:1:0.2	18 h	N.R.				
3	triblock ^{c,d}	300:1:0.4	5 h	88	184	52.8	102.5	1.9
4	triblock ^{c,d}	380:1:0.4	1 h	55	160	68.1	110.7	1.6
5	PSS- <i>b</i> -PPEGMEA ^e	N.A.	18 h	N.A.	83	38.1	68.5	1.8
6	PPEGMEA ^c	400:1:0.6	1 h	N.R.				
7	PPEGMEA ^f	50:1:0.14	8 h 30 min	86	21	6.8 (11.4 ^g)	14.6 (17.8 ^g)	2.1 (1.6 ^g)

^aObtained by ¹H NMR in D₂O. ^bObtained by size exclusion chromatography (SEC) in water buffer:methanol 70:30. ^cPolymerization in water using ACVA as a radical initiator. ^dThe RAFT agent is the PSS macro-RAFT from entry 1 and the monomer PEGMEA. ^eAminolysis of the PSS-*b*-PPEGMEA-*b*-PSS triblock at rt. ^fPolymerization in 1,4-dioxane using AIBN as a radical initiator. ^gObtained by SEC in CHCl₃.

polymerization such as a reversible addition–fragmentation chain transfer (RAFT) polymerization or an atom-transfer radical polymerization (ATRP). While a PSS-*b*-PPEGMEA has never been envisioned as a scaffold for PEDOT, it should be noted that a thermally cross-linked random copolymer of PSS and poly(ethylene glycol) methacrylate (up to 15 mol %) (P(SS-*co*-PEGMA)) was previously reported as a matrix for PEDOT.⁵⁰ The PEDOT:copolymer exhibited enhanced stability in water and organic solvents when compared to PEDOT:PSS, but the mechanical properties of the conductive material were not described in the study.

Choice of Block Copolymerization Approach. Poly(styrenesulfonate) is typically synthesized by sulfonation of polystyrene (PS). This postpolymerization approach uses harsh chemicals (sulfuric acid), organic solvents, does not lead to 100% sulfonation of the styrene, and often forms sulfone defects or cross-links in the polymer chain.⁵¹ Sulfonation of a PS-containing block copolymer—synthesized by anionic polymerization—has also been used for the preparation of PSS-based block copolymers. However, the sulfonation is not selective toward the phenyl group in the presence of nonaromatic double bonds. For example, Kim et al. showed that the sulfonation of the elastomer poly(styrene-*b*-butadiene-*b*-styrene) (SBS) led to the selective partial sulfonation of the alkene in the polybutadiene block. The resulting sulfonated SBS (sSBS) was subsequently used as a scaffold for PEDOT.⁵² The corresponding PEDOT:sSBS had a conductivity of 0.05 S cm^{−1} at 65% sulfonation, but the mechanical properties of the corresponding polymer were not reported. An alternative approach would be to polymerize sodium 4-styrenesulfonate (NaSS) directly. While anionic polymerizations are effective at forming block copolymers with a narrow distribution of molecular weight, it would prove difficult or impossible with hygroscopic monomers, such as NaSS and PEGMEA, due to the extreme sensitivity of the reaction to water. Alternatively, a RAFT polymerization would allow for the direct polymerization of hydrophilic monomers under aqueous conditions, and its quasi-living character permits the formation of block copolymers.^{53,54} The RAFT polymerization of PSS-*b*-PPEGMEA—with moderate degrees of polymerization—has previously been reported using a 4-cyanopentanoic acid dithiobenzoate (CPADB) chain transfer agent, proving the feasibility of the proposed synthetic pathway.⁵⁵

EXPERIMENTAL METHODS

Materials. Sodium 4-styrenesulfonate (NaSS), 4,4'-azobis(4-cyanovaleic acid) (ACVA), azobis(isobutyronitrile) (AIBN), and ethylenedioxythiophene (EDOT) were purchased from Sigma-Aldrich

and used without further purification. Poly(ethylene glycol methyl ether acrylate) (PEGMEA, $M_n = 480$ g mol^{−1}) was purchased from Sigma-Aldrich and filtered through a basic alumina column prior to polymerization. The RAFT chain transfer agent *S,S'*-bis(*R,R'*-dimethylacetic acid) trithiocarbonate (**1**) was synthesized according to a previously reported procedure.⁵⁶ Distilled water filtered using a Milli-Q purification system was used throughout.

RAFT Polymerization of PSS. NaSS (9.28 g, 45 mmol), *S,S'*-bis(*R,R'*-dimethylacetic acid) trithiocarbonate (**1**) (42 mg, 0.15 mmol), and ACVA (4.2 mg, 0.015 mmol) were dissolved in 45 mL of water, degassed using three evac–refill cycles, and blanketed with nitrogen. The reaction mixture was placed in an oil bath at 70 °C and left to react for 15 h. The reaction was stopped by rapid cooling and exposure to air. The PSS macro-chain-transfer agent was purified by precipitation in acetone and dried under vacuum to afford a yellow powder (8.8 g, 95% yield; SEC: $M_n = 55.5$ kDa, $M_w = 76.8$ kDa, $\bar{D} = 1.4$).

RAFT Polymerization of PSS-*b*-PPEGMEA-*b*-PSS. Procedure for Experiment in Table 1, Entry 4. The PSS macro-chain-transfer agent previously synthesized (1.86 g, 0.032 mmol), PEGMEA (5.3 mL, 12.0 mmol), and ACVA (3.5 mg, 0.013 mmol) were dissolved in 50 mL of water, degassed using three evac–refill cycles, and blanketed with nitrogen. The reaction mixture was placed in an oil bath at 70 °C and left to react for 1 h. The reaction was stopped by rapid cooling and exposure to air. The excess monomer was removed by five washings of the aqueous solution with chloroform. During these washings, the aqueous layer formed an emulsion which was destabilized between each wash by removal of the solvent under vacuum. The pure triblock was obtained as a pale yellow solid after evaporation of the water under vacuum at 50 °C (SEC: $M_n = 68.1$ kDa, $M_w = 110.7$ kDa, $\bar{D} = 1.6$).

RAFT Polymerization of PPEGMEA. Procedure for Experiment in Table 1, Entry 7. PEGMEA (1 g, 2.08 mmol), *S,S'*-bis(*R,R'*-dimethylacetic acid) trithiocarbonate (**1**) (11.7 mg, 0.042 mmol), and AIBN (1 mg, 0.006 mmol) were dissolved in 4 mL of 1,4-dioxane and degassed for 30 min under a nitrogen flow. The reaction was placed in an oil bath at 70 °C for 8.5 h and then stopped by rapid cooling and exposure to air. PPEGMEA was purified by precipitation in acetone at low temperature and then dried under vacuum to obtain a viscous yellow liquid. SEC in water buffer:methanol against PSS standards: $M_n = 6.8$ kDa, $M_w = 14.6$ kDa, $\bar{D} = 2.1$, SEC in chloroform against PS standards: $M_n = 11.4$ kDa, $M_w = 17.8$ kDa, $\bar{D} = 1.6$.

Preparation of PEDOT:PSS and PEDOT:PSS:PPEGMEA. PSS (from Table 1, entry 1) was dissolved in water (50 mg/mL) and stirred over an acidic resin (Dowex Marathon C hydrogen form) for 18 h at room temperature. The acidified PSS was filtered through a 1 μm filter. To 10 mL of this solution (PSS: 450 mg, 2.3 wt equiv), sodium persulfate (454 mg, 2.3 wt equiv), and iron trichloride (0.11 mL of 10 wt % solution) were added with an extra 29 mL of water. The reaction was stirred for 10 min before the addition of EDOT (194 mg, 1 wt equiv). The reaction was stirred vigorously at room temperature for 24 h. PEDOT:PSS was purified over 10 mL of acidic (Dowex Marathon C hydrogen form) and 7 mL of basic (Lewatit MP-62 free base) resins for 6 h and then filtered through a 10 μm filter.

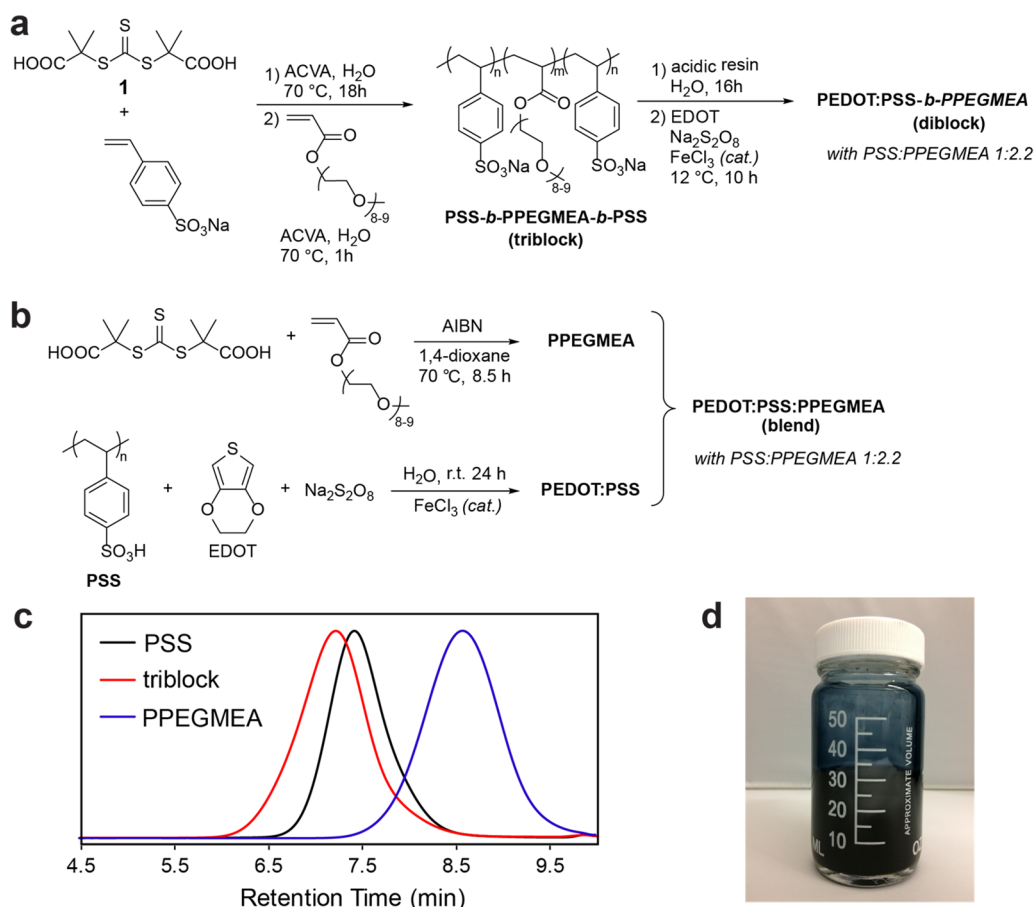


Figure 2. Synthesis of stretchable PEDOT:PSS using PPEGMEA. (a) RAFT polymerization of the PSS-*b*-PPEGMEA-*b*-PSS triblock copolymer and subsequent preparation of PEDOT:PSS-*b*-PPEGMEA. (b) Synthesis of PPEGMEA via RAFT polymerization and PEDOT:PSS by oxidative polymerization. The PEDOT:PSS:PPEGMEA polymer blend was obtained by the addition of PPEGMEA to the PEDOT:PSS solution. (c) Normalized size exclusion chromatograms of PSS, PSS-*b*-PPEGMEA-*b*-PSS triblock copolymer, and PPEGMEA in a methanol:water buffer solution. (d) Photograph of the PEDOT:PSS-*b*-PPEGMEA solution in water.

PEDOT:PSS:PPEGMEA was obtained by adding PPEGMEA (56 mg) to 5 mL of the PEDOT:PSS solution.

Preparation of PEDOT:PSS-*b*-PPEGMEA. PSS-*b*-PPEGMEA-*b*-PSS (from Table 1, entry 4) was dissolved in water (50 mg/mL) and stirred over an acidic resin (Dowex Marathon C hydrogen form) for 18 h at room temperature. The acidified PSS-*b*-PPEGMEA-*b*-PSS was filtered through a 10 μ m filter.

To 50 mL of this solution (PSS-*b*-PPEGMEA-*b*-PSS: 1 g, 1.3 wt equiv of PSS), sodium persulfate (809 mg, 3.5 wt equiv) and iron trichloride (6.7 mg, 3 wt %) were added with an extra 13 mL of water and cooled to 12 °C using a 1,4-dioxane/dry ice bath. The mixture was stirred for 10 min before the addition of EDOT (231 mg, 1 wt equiv). The reaction was stirred vigorously at 12 °C for 10 h. PEDOT:PSS was purified over 15 mL of acidic (Dowex Marathon C hydrogen form) and 9 mL of basic (Lewatit MP-62 free base) resins for 6 h at room temperature and then filtered through a 10 μ m filter.

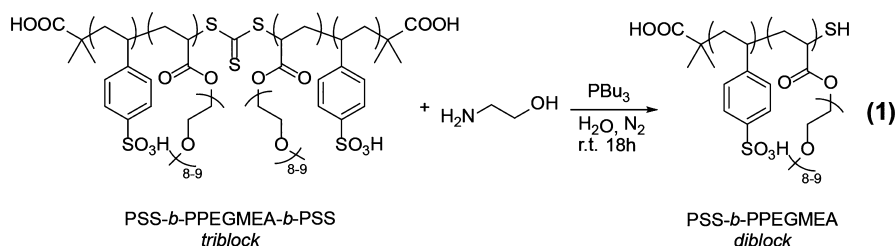
RESULTS AND DISCUSSION

RAFT Polymerization of PSS-*b*-PPEGMEA-*b*-PSS. The difunctional RAFT agent *S,S'*-bis(*R,R'*-dimethylacetic acid) trithiocarbonate (1) was chosen as a chain-transfer agent for its stability and solubility in water and the ability to form triblock copolymers in only two steps.⁵⁶ First, NaSS was polymerized using 4,4'-azobis(4-cyanovaleric acid) (ACVA) as a thermally activated radical initiator and with a [NaSS]:[RAFT]:[ACVA] ratio of 300:1:0.1. A low amount of initiator was used to minimize the number of dead chains (Figure 2a and Table 1,

entry 1). The polymerization proceeded for 18 h to afford a 95% conversion to PSS ($M_n = 55.5$ kDa) with a dispersity of 1.4. The relatively high dispersity obtained for a living polymerization is typical for high degrees of polymerization in RAFT.⁵⁷ While trithiocarbonates can be susceptible to hydrolysis, we observed a good correlation between the theoretical molecular weight and the one obtained from SEC. There was no decrease in molecular weight after precipitation in acetone (nor after stirring over acidic resin), indicating the persistence of the RAFT functionality at the center of the polymer.

Next, we used the synthesized PSS macro-chain-transfer agent to form the PSS-*b*-PPEGMEA-*b*-PSS triblock copolymer via chain extension (Figure 2a and Table 1, entry 2). Using a [PEGMEA]:[RAFT]:[ACVA] ratio of 400:1:0.2 did not produce any polymer. We hypothesized that the small concentration of inhibitor in the PEGMEA monomer was enough to prevent the radical initiation. Increasing the amount of initiator allowed the reaction to proceed to 88% conversion in 5 h (Table 1, entry 3). A large polydispersity was obtained for the triblock copolymer, however, and the SEC showed a shoulder at high molecular weights.

A similar shouldering has previously been observed for the RAFT polymerization of PEGMEA and was attributed to transfer to chain reactions—leading to branched structures—at conversions above 60%.⁵⁸ In order to obtain high molecular



weight and well-defined PPEGMEA center blocks, we increased the monomer loading and stopped the reaction at 55% conversion (Table 1, entry 4). In this instance, a monomodal trace with a dispersity of 1.6 was obtained. A shift in the SEC traces can be clearly observed, indicative of chain extension (Figure 2c). The number-average molecular weight, M_n , obtained for the triblock (68.1 kDa), however, is significantly lower than the theoretical value (160 kDa) partly due to the mismatch between the linear PSS standards used for the SEC calibration and the comb-like PPEGMEA polymer. The low molecular weight could also be attributed to the hydrolysis of the trithiocarbonate functional group at the center of the triblock copolymer which would lead to a PSS-*b*-PPEGMEA diblock copolymers of half the M_n . While the polymer still contains trithiocarbonate, as indicated by its yellow coloration, some could have hydrolyzed to the colorless thiol. Given the high molecular weight of the polymer, differentiating the diblock from the triblock would prove difficult by diffusion NMR (DOSY). Instead, we intentionally cleaved the trithiocarbonate by performing an aminolysis in water using ethanolamine (eq 1, Table 1, entry 5, and Figure S1).⁵⁹ The molecular weights obtained after aminolysis are close to half of the original triblock copolymer ($M_n = 38.1$ kDa), and the solution turned colorless. These results indicate that under conditions of aminolysis the triblock is cleaved to a PSS-*b*-PPEGMEA diblock copolymer, but that the trithiocarbonate was intact throughout the polymerization and after work-up.

RAFT Polymerization of PPEGMEA. For the synthesis of PPEGMEA, we first attempted to polymerize PEGMEA in water using ACVA as an initiator and the RAFT agent 1, but even at loadings of 1:0.6 of [RAFT]:[ACVA], the reaction did not proceed (Table 1, entry 6). We hypothesize this result could be due to the presence of inhibitor in PEGMEA, the poor solubility of the reagents in water, or both. In order to obtain well-defined PPEGMEA, we adapted a RAFT polymerization reported by Liu et al. with the RAFT agent 1 in 1,4-dioxane and using azobis(isobutyronitrile) (AIBN) as a radical initiator (Figure 2b and Table 1, entry 7).^{60,61} Under these conditions, we obtained PPEGMEA with a degree of polymerization of 43 ($M_{n,\text{theo}} = 21$ kDa). A high polydispersity and low molecular weights were obtained by aqueous SEC ($M_n = 6.8$ kDa, $D = 2.1$). We believe this result was from the poor suitability of the aqueous SEC system and its PSS standards with PPEGMEA. Indeed, by analyzing the polymer by SEC in chloroform, a narrower molecular weight distribution was obtained, but comparison with linear polystyrene standards still proved inappropriate ($M_n = 11.4$ kDa, $D = 1.6$). It should be noted that the behavior of PPEGMEA on the aqueous SEC system is consistent with the low molecular weights obtained for the triblock copolymer. Other attempts at obtaining higher molecular weights of PPEGMEA lead to highly polydisperse samples and were therefore not used in this study.

Oxidative Polymerization of PEDOT. In PEDOT:PSS, ethylenedioxythiophene (EDOT) is oxidatively polymerized in a PSS matrix whose function is to stabilize the p-doped cationic PEDOT and allow the dispersion of PEDOT in water by formation of a polyelectrolyte complex. Since the synthesized PSS-*b*-PPEGMEA-*b*-PSS is fully water-soluble, the same procedure as in PEDOT:PSS can be applied.⁶² First, the sodium-containing triblock was ion-exchanged over an acidic resin to remove the Na^+ ions.⁶³ After filtration, the sodium persulfate oxidant and the iron trichloride catalyst were added before the introduction of EDOT monomer. The solution was allowed to polymerize for 10 h, and the mixture turned dark blue as the reaction proceeded (Figures 2a,d). The reaction is stopped and the dispersion purified by the addition of acidic and basic resins. In the synthesized formulation, the weight ratio of PEDOT:PSS:PPEGMEA is 1:1.3:2.9. The integrity of the triblock copolymer could not be verified by SEC in the presence of PEDOT. Therefore, in order to test for hydrolysis of the trithiocarbonate, the triblock copolymer was exposed to the same conditions as for the oxidative polymerization without the addition of EDOT and analyzed by SEC. After the addition of $\text{Na}_2\text{S}_2\text{O}_8$ and FeCl_3 , the SEC trace showed that the triblock started degrading ($M_n = 44.6$ kDa, $D = 1.8$) and that after stirring over acidic and basic resin the polymer molecular weight was about half of its initial value ($M_n = 40.5$ kDa, $D = 1.8$) (see Supporting Information for SEC trace and experimental details). The molecular weight obtained is close to that of PSS-*b*-PPEGMEA obtained by aminolysis of PSS-*b*-PPEGMEA-*b*-PSS (Table 1, entry 5). We can conclude that the final molecular structure of the dispersion is PEDOT:PSS-*b*-PPEGMEA.

In order to compare the block copolymer of PSS-*b*-PPEGMEA with a physical blend of PSS and PPEGMEA, we chose to synthesize PEDOT:PSS from the PSS obtained by RAFT polymerization in Table 1, entry 1. Similar to the triblock, the trithiocarbonate chain transfer agent, at the center of PSS, hydrolyzes during the polymerization of EDOT which leads to PSS of the same molecular weight as in the block copolymer. After preparation of PEDOT:PSS, the aqueous solution was then mixed with PPEGMEA (Figure 2b and Table 1, entry 7) such that the weight ratio of PSS to PPEGMEA is the same as the block copolymer (1:2.2).

Conductivity. We first measured the conductivity of the synthesized PEDOT:PSS, PEDOT:PSS:PPEGMEA (blend), and PEDOT:PSS-*b*-PPEGMEA (block copolymer) (Figure 3). The conductivity of PEDOT:PSS is 7.4 S cm^{-1} , which is close to the commercially available Clevios without any dopant.⁶⁴ The addition of PPEGMEA in the same weight ratio as in the PEDOT:PSS-*b*-PPEGMEA leads to an increase in conductivity to 14.8 S cm^{-1} . Previous reports on the addition of PEO or PEG to PEDOT:PSS have shown the same enhancement.³⁶ In PEDOT:PSS-*b*-PPEGMEA, the conductivity is significantly decreased to 0.046 S cm^{-1} . Although the use of additives

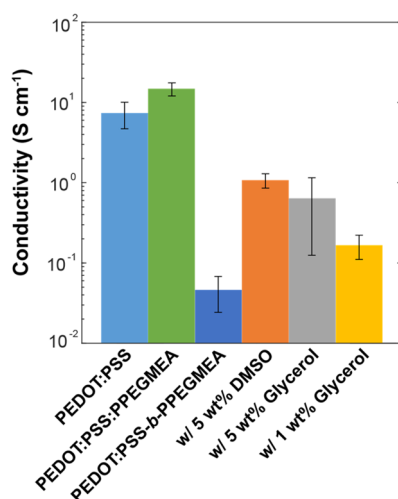


Figure 3. Conductivity of spin-coated thin films of PEDOT:PSS, PEDOT:PSS:PPEGMEA (blend), and PEDOT:PSS-*b*-PPEGMEA (block copolymer) neat and with 5 wt % DMSO as well as 5 and 1 wt % glycerol additives. The error bars represent the standard deviation from the average of three different samples.

should be avoided for biointegrated devices, we were interested in looking at the effect of commonly used secondary dopants to improve the conductivity. The use of such additives could be appropriate in applications such as deformable organic solar

cells, thin-film transistors, and light-emitting devices. We added 5 wt % DMSO as a secondary dopant, thereby improving the conductivity by a factor of 23 (1.1 S cm^{-1}).⁶⁵

While DMSO proved efficient, we were also interested in using a nontoxic additive, glycerol, for wearable and implantable applications.⁶⁶ The addition of 5 wt % glycerol to PEDOT:PSS-*b*-PPEGMEA enhanced the conductivity by a factor of 14 (0.63 S cm^{-1}) but led to heterogeneous films, likely due to the high boiling point of glycerol (290°C) which is not evaporated upon thermal annealing. The addition of 1 wt % glycerol increased the conductivity by a factor of 3.6 (0.17 S cm^{-1}) while maintaining the integrity of the film. Overall, lower conductivities were obtained for the block copolymer than the physical blend with or without secondary dopants. We believe that tuning the relative block size of PSS versus PPEGMEA and increasing the PEDOT loading in the matrix would lead to higher conductivities, although possibly at the expense of stretchability. Alternatively, not all applications of PEDOT:PSS require high conductivity. For example, low-conductivity PEDOT could be used in organic electrochemical transistors (OECTs), providing the materials have a good capacitance.⁶⁷ PEDOT:PSS-*b*-PPEGMEA could also be used in stretchable antistatic coatings,⁶⁸ charge injection layers in organic solar cells,⁶⁹ or strain sensors.¹²

Mechanical Properties. We examined the mechanical properties of the PEDOT:PSS and the effect of PPEGMEA in a physical blend (PEDOT:PSS:PPEGMEA) versus the sample

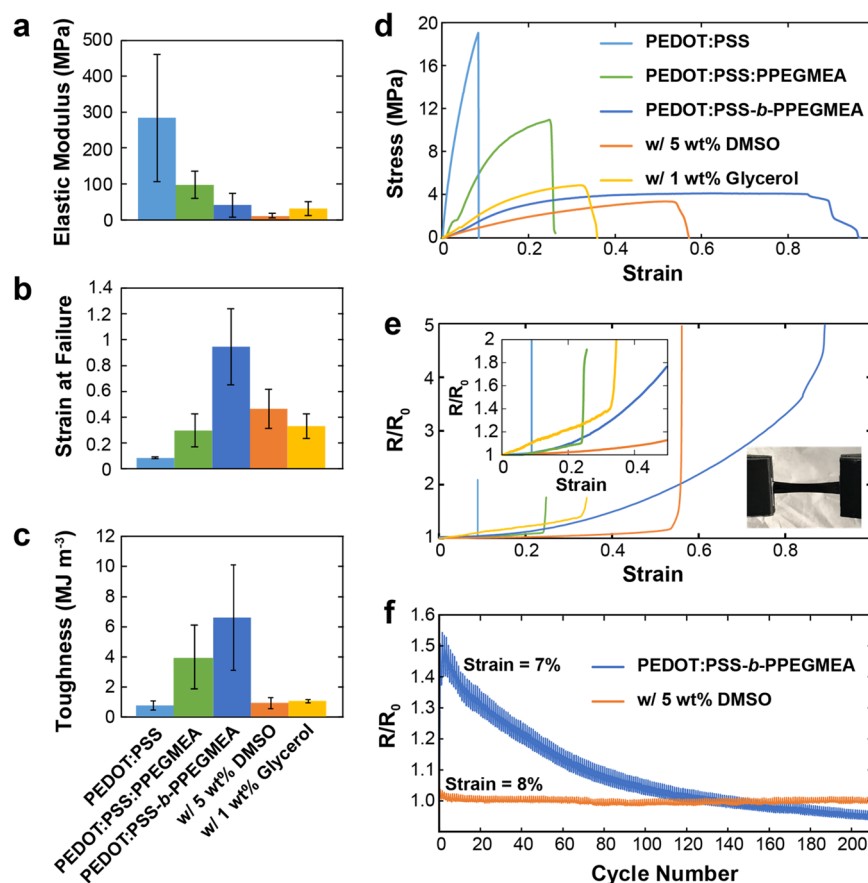


Figure 4. Mechanical properties of the PEDOT formulations as free-standing films. The error bars represent the standard deviation from the average of three different samples. (a) Elastic modulus. (b) Strain at failure. (c) Toughness. (d) Sample stress–strain curves. (e) Change in resistance (R/R_0) as a function of strain. Inset: picture of the stretched PEDOT:PSS-*b*-PPEGMEA taken during a tensile test. (f) Fatigue tests in the elastic regime of PEDOT:PSS-*b*-PPEGMEA neat or with 5 wt % DMSO.

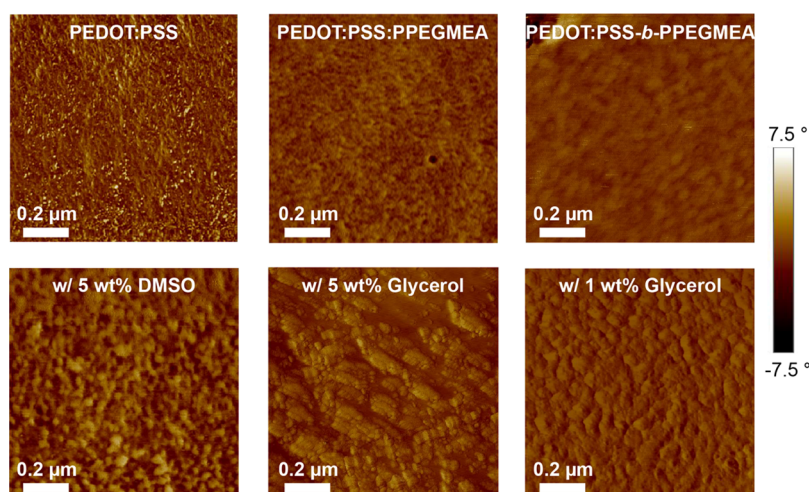


Figure 5. AFM phase images of spin-coated PEDOT thin films. Top: PEDOT:PSS, PEDOT:PSS:PPEGMEA and PEDOT:PSS-*b*-PPEGMEA. Bottom: PEDOT:PSS-*b*-PPEGMEA with 5 wt % DMSO, 5 wt % glycerol, and 1 wt % glycerol additives.

in which the PSS and PPEGMEA were covalently linked as a block copolymer, PEDOT:PSS-*b*-PPEGMEA (Figure 4). Films were casted on Teflon tape or PTFE sheets to obtain free-standing films which were subjected to a tensile test. As expected, the PEDOT:PSS films exhibited brittle behavior with an average elastic modulus (Young's modulus) of 284 MPa and strain at failure of 8.5%. In order to obtain robust and imperceptible electronic devices which can be directly worn on the skin or implanted in the body, they must be able to sustain strains up to $\geq 50\%$ and have an elastic modulus close to biological tissues (< 1 MPa) to reduce interfacial stresses. The addition of PPEGMEA in both the physical blend or the block copolymer lowers the Young's modulus of the conductive material to 97 and 41 MPa, respectively (Figure 4a). The maximum strain at failure obtained for the blend material was 38%, while the PEDOT:PSS-*b*-PPEGMEA could be strained up to 128% before failure (Figure 4b) (average strain at failure: 95%). Moreover, the diblock copolymer exhibited a higher toughness than the blend (6.6 vs 3.4 MJ m⁻³). (The toughness is the ability of the material to absorb energy before breaking and is measured by the area under the stress–strain curve.) A material exhibiting a high toughness which does not come at the expense of “softness” is highly desirable for wearable electronics. The addition of conductivity enhancers (DMSO and glycerol) to PEDOT:PSS-*b*-PPEGMEA reduced the Young's modulus but also the toughness (0.9–1 MJ m⁻³) (Figure 4c). Adding 5 wt % glycerol to PEDOT:PSS-*b*-PPEGMEA led to a film so weak that a free-standing film could not be obtained. With all additives, lower failure strains were obtained. The mechanical properties of the intrinsically stretchable PEDOT:PSS-*b*-PPEGMEA without additives outperformed the composite material PEDOT:PSS:PPEGMEA: lower elastic modulus, higher strain at failure, and greater toughness (Figure 4d).

We also measured the piezoresistance of the free-standing films (Figure 4e). PEDOT:PSS, PEDOT:PSS:PPEGMEA, and PEDOT:PSS-*b*-PPEGMEA films with 1 wt % glycerol break prematurely, leading to an open circuit. The gauge factor at 50% strain for the PEDOT:PSS-*b*-PPEGMEA without additives was 1.54 and 0.26 with 5 wt % DMSO. These low gauge factors signify that the conductivity of PEDOT:PSS-*b*-PPEGMEA is not strongly dependent on strain, indicating that

these materials could be used as interconnects in stretchable electronics.

Finally, we examined the change in resistance over multiple strain–release cycles for PEDOT:PSS-*b*-PPEGMEA neat and with 5 wt % DMSO (Figure 4f). The samples were strained within their respective elastic regimes to ensure there was no plastic deformation upon release. Interestingly, the resistance of the PEDOT:PSS-*b*-PPEGMEA sample initially increased in the first cycle but ultimately decreased over 210 cycles. Alternatively, the sample containing 5 wt % DMSO proved to be very stable over 210 cycles with little change in resistance.

Surface Morphology. In order to understand the correlation between conductivity and the mechanical properties, we looked for clues in the surface morphology by tapping-mode AFM (atomic force microscopy) height (Figure S2) and phase (Figure 5) and SEM (scanning electron microscopy) (Figure S3). While the AFM height images inform us about the topography of the film, more interesting information can be extracted from the phase images. In AFM phase images, a lower phase angle (dark area) is typically attributed to a polymeric material that is relatively softer than its surroundings whereas lighter areas correspond to harder regions.⁷⁰ In PEDOT:PSS, weakly connected grains and short fibrillar structures are observed; such features have previously been reported for PEDOT:PSS.⁷¹ The addition of PPEGMEA in a physical blend induces the disappearance of the fibrillar structures and forms irregular interconnected domains.

For the PEDOT:PSS-*b*-PPEGMEA images, the well-defined lighter islands can be attributed to the hard PEDOT:PSS domains which are surrounded by soft PPEGMEA. The relatively uniform distribution of the phase-separated domains is consistent with the block copolymer architecture whereas the PEDOT:PSS:PPEGMEA blend does not exhibit a well-defined morphology. The sequestration of the PEDOT:PSS hard domains in the insulating PPEGMEA could explain the relatively weak conductivity and is consistent with the improved stretchability. The addition of 5 wt % DMSO to PEDOT:PSS-*b*-PPEGMEA seems to break down these well-defined islands which show enhanced connectivity and higher conductivity. The 5 wt % glycerol sample shows irregular swelling of regions across the film indicative of dispersed solvent droplets, which may explain why free-standing films could not be obtained. With 1 wt % glycerol some domains are

swollen, but the PEDOT:PSS-*b*-PPEGMEA maintained a relatively regular morphology.

Water-Enabled Healing. PEDOT:PSS films of above 1 μm thickness have been recently shown to heal in the presence of water.⁷² While the mechanism of this healing process has not been fully investigated, Zhang et al. hypothesized that water swells the PSS domains and promotes diffusion of chains across the fractured interfaces. To test the water-enabled healing of PEDOT:PSS-*b*-PPEGMEA, we used a spin-coated thin film (~ 300 nm thickness) on glass. The film was cut using a razor blade across the entire sample (~ 50 μm gap), leading to an open circuit (Figure 6a). Water was subsequently added

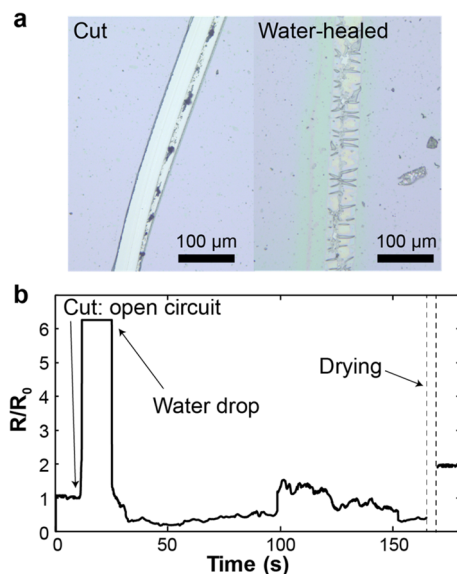


Figure 6. Water-enabled healing. (a) Optical microscope images of a PEDOT:PSS-*b*-PPEGMEA spin-coated thin film (~ 300 nm) damaged with a razor blade and after the addition of water and drying at 120 $^{\circ}\text{C}$ for 15 min. (b) Change in resistance before and after damage and water-enabled healing (drying step: 15 min at 120 $^{\circ}\text{C}$).

along the cut which induced an immediate recovery of the conductivity (Figure 6b).⁷³ To confirm the film was indeed healed, the drying process was accelerated by placing the sample on a hot plate at 120 $^{\circ}\text{C}$ for 15 min. The sample recovered approximately half of its initial conductivity. We defined the electrical healing efficiency as $\eta = R_0/R_{\text{healed}}$ to be 53%. While most of the cut was reconnected via the bridging of conductive regions, shown in Figure 6a, some areas of the film delaminated from the glass substrate upon drying or did not fully reconnect (Figure S4). The slightly different color around the gap is attributed to a thinning of the polymer film upon the addition of water.⁶⁷

CONCLUSION

We have shown that a block copolymer of PSS-*b*-PPEGMEA used as a scaffold for PEDOT showed enhanced mechanical properties over a blend of PEDOT:PSS with PPEGMEA. In particular, PEDOT:PSS-*b*-PPEGMEA exhibits higher failure strains, a lower elastic modulus, and a greater toughness. We believe this results from the well-defined morphology of the films, where conductive and stiff PEDOT:PSS domains are phase separated from soft PPEGMEA. Lastly, we have shown that stretchable PEDOT:PSS-*b*-PPEGMEA can be healed with water which could lead to new applications in wearable and

implantable organic electronic devices. In particular, this work proposes a new strategy for the design of stretchable and biocompatible conductive material using a block copolymer approach rather than additives.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.8b02040.

Additional experimental procedures; ^1H NMR traces of the polymers; AFM height images; SEM images; additional microscope images from the water-enabled healing experiments (PDF)

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Notes

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ABBREVIATIONS

RAFT, reversible addition–fragmentation chain transfer; PSS, poly(4-styrenesulfonate); PEDOT, poly(ethylenedioxythiophene), PPEGMEA poly(poly(ethylene glycol) methyl ether acrylate); ACVA, 4,4'-azobis(4-cyanovaleic acid); AIBN, azobis(isobutyronitrile).

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