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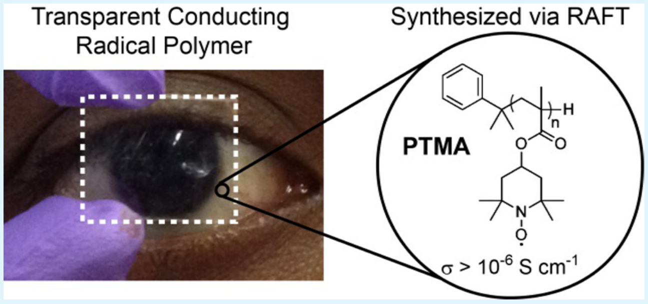
Controlled Radical Polymerization and Quantification of Solid State Electrical Conductivities of Macromolecules Bearing Pendant Stable Radical Groups

Lizbeth Rostro, Aditya G. Baradwaj, and Bryan W. Boudouris*

480 Stadium Mall Drive, School of Chemical Engineering, Purdue University, West Lafayette, Indiana 47907, United States

Supporting Information

ABSTRACT: Macromolecules with aliphatic backbones that bear pendant stable radical groups (i.e., radical polymers) have attracted much attention in applications where a supporting electrolyte is capable of aiding charge transport in solution; however, the utilization of these materials in solid state applications has been limited. Here, we synthesize a model radical polymer, poly(2,2,6,6-tetramethylpiperidinyloxy methacrylate) (PTMA), through a controlled reversible addition−fragmentation chain transfer (RAFT) mediated polymerization mechanism to generate well-defined and easily-tunable functional polymers. These completely amorphous, electronically-active polymers demonstrate relatively high glass transition temperatures (T_g ~170 °C) and, because of the aliphatic nature of the backbone of the radical polymers, are almost completely transparent in the visible region of the electromagnetic spectrum. Additionally, we quantify the conductivity of PTMA (~1×10^{-6} S cm^{-1}) and find it to be on par with pristine π-conjugated polymers such as poly(phenylene vinylenes) (PPVs) and poly(3-alkylthiophenes) (P3ATs). Furthermore, we demonstrate that the addition of small molecules bearing stable radical groups provides for more solid state charge hopping sites without altering the chemical nature of radical polymers; this, in turn, allows for an increase in the conductivity of PTMA relative to neat PTMA thin films while still retaining the same high degree of optical transparency and device stability. Because of the synthetic flexibility and easily-controlled doping mechanisms (that do not alter the PTMA chemistry), radical polymers present themselves as promising and tunable materials for transparent solid-state plastic electronic applications.



KEYWORDS: *radical polymers, controlled radical polymerization, solid-state charge transport, nonconjugated transparent conductors, molecular doping*

INTRODUCTION

Functional macromolecules have garnered increasing attention in fields ranging from organic electronics to biotechnology due to their potential to offer a chemically-tunable, mechanically-robust solution for applications traditionally dominated by inorganic materials.[1−4] In particular, semiconducting polymers based on π-conjugated, and often semicrystalline, macromolecules have emerged for a number of device types including organic field-effect transistors (OFETs),[5−7] organic light-emitting devices (OLEDs),[8,9] organic photovoltaic (OPV) devices,[10−12] and thermoelectric units.[13,14] The large strides that have occurred through the development of novel optoelectronically-active materials have allowed for the growth of polymer-based electronic devices such that they are becoming cost-competitive with their inorganic counterparts.[15−17] However, almost all of the protocols utilized for the syntheses of these π-conjugated macromolecules (save the Grignard metathesis (GRIM)[18−20] method) rely on schemes that lead to polymers with poorly controlled molecular weights, molecular weight distributions, and end group functionalities.[21−24] Also, many of these polymerization schemes are incompatible with different monomer chemistries; therefore, designing copolymers becomes synthetically challenging. Furthermore, many π-conjugated polymerization mechanisms are metal-catalyzed, using species that are difficult to remove from the final polymer product.[20,25] These metal impurities, in turn, have been shown to impact organic electronic device performance negatively and to reduce device lifetimes.[26,27] As such, changing the paradigm from charge-transporting polymers that require macromolecular architectures that include a conjugated backbone could alter the landscape of organic electronic materials in terms of molecular design flexibility, optoelectronic activity, and device stability. These improvements, could allow for the emergence of the widespread production of organic electronic devices.

Macromolecular species bearing radical moieties (i.e., polyradicals) have been studied in many research fields, and have found a large amount of interest in the realm of high-spin

Received: August 4, 2013
Accepted: September 17, 2013
Published: September 17, 2013

organic molecules for magnetic applications.[28−31] However, these magnetically-active materials generally are composed of highly conjugated polymers that are not necessarily trivial to synthesize. Conversely, radical polymers are macromolecules with aliphatic backbones where a stable radical group is pendant on the side chain of many (if not all) of the repeat units of the polymer chain, and they are synthesized using well-established and easily-managed protocols (e.g., controlled radical and anionic polymerizations).[32−39] As opposed to polyradicals, where the lone electron is stabilized by delocalization of π-conjugated electrons along the backbone of the polymer, the organic radicals of radical polymers are stabilized along the side chain of the macromolecules by implementing groups that have a high delocalization of electrons or bulky substituents.[38] This related, but distinctly different, class of macromolecules that is radical polymers offers the promise of high solid state charge transport without the synthetic or nanostructural issues that can plague polyradicals and conjugated macromolecules.[40] Furthermore, because these radicals are stabilized, they are robust when exposed to ambient conditions or implemented in devices.[36,40] In fact, these functional macromolecules have been used commonly in the development of flexible batteries.[38] When implemented into batteries, the radical polymers pass charge between an anionic or cationic species to an uncharged stable radical using an oxidation-reduction (redox) mechanism in the presence of a supporting electrolyte.[33,36,37,40−43] In these wet-cell types of systems, the rather efficient redox gradient mechanism allows for relatively high heterogeneous charge transfer rate constants to exist ($k_{CT} \approx 0.1$ cm s^{-1}).[44] However, due to the battery-driven nature of the work, the transport ability of radical polymers in the solid state has not been quantified to this point.

Here, we synthesize a model radical polymer, poly(2,2,6,6-tetramethylpiperidinyloxy methacrylate) (PTMA), using a metal-free reversible addition−fragmentation chain transfer (RAFT) mechanism to generate radical polymers with well-controlled, predictable molecular weights and narrow molecular weight distributions ($Đ$ = 1.2). These polymers are readily soluble in common organic solvents, and they are completely amorphous with relatively high glass transition temperatures ($T_g \approx 170$ °C). This is consistent with non-conjugated, atactic polymers with bulky side groups.[45,46] Furthermore, we utilize ultraviolet-visible (UV−vis) light spectroscopy to demonstrate that conversion of the protected repeat unit to the functional stable radical repeat unit is not complete (conversion ~70%) for the first time. This incomplete conversion was observed to be independent of molecular weight, and suggests that the commonly-used deprotection studies presented previously may require alteration. Despite this incomplete conversion, solid state conductivity values of pristine PTMA thin films were ~1×10^{-6} S cm^{-1}; this is on par with common pristine (i.e., not doped) π-conjugated polymer semiconductors like poly(3-hexylthiophene) (P3HT).[47−49] Furthermore, the conductivity of PTMA is enhanced with the addition of small molecule stable radicals. In contrast to molecular doping (which usually alters the local chemical environment) in conjugated polymers, this phenomenon indicates that at a higher concentration of radical sites the conductivity increases by more than a factor of two simply by providing more hopping sites for the charges. As such, this work demonstrates the ability of non-conjugated radical polymers to be utilized as a new class of highly-tunable, highly-transparent conducting macromolecules; therefore, this establishes that radical polymers could be of utility in a variety of solid-state organic electronic applications.

RESULTS AND DISCUSSION

Although PTMA has been synthesized using controlled radical polymerization techniques previously,[37,50−52] this is the first detailed example of utilizing a RAFT polymerization mechanism to generate PTMA. In this manner, we have developed a methodology to produce radical polymers with controlled molecular weights that does not require the use of metal catalysts, which can be difficult to remove from the final polymer product. As such, we are confident that the observed optoelectronic properties of the polymers are intrinsic in nature, and they are not due to unintentional doping from reaction impurities. The synthetic methodology is shown in Scheme 1; here, the first step of the procedure involved the polymerization of the 2,2,6,6-tetramethyl-4-piperidinyl methacrylate (TMPM) monomer to generate poly(2,2,6,6-tetramethyl-4-piperidinyl methacrylate) (PTMPM-RAFT). Because a RAFT polymerization scheme was utilized, the molecular weights of the polymers could be tuned to a predetermined value in the range of 5 kg mol^{-1} and 24 kg mol^{-1}, as measured by size exclusion chromatography (SEC) against polystyrene (PS) standards (Table 1). We note that end group integration of the PTMPM-RAFT polymer using ^{1}H NMR spectroscopy confirmed the SEC-determined molecular weights (see Figure S1 in the Supporting Information). Furthermore, dispersity ($Đ$) values of the polymers were found to be 1.2, as measured against PS standards (Table 1), highlighting the controlled nature of the polymerization. This ability to grow well-defined radical polymer precursors with a macroinitiating end group easily could lead to the fabrication of electronically-active block polymers with dual functionalities (e.g., hole and electron-transporting domains), which can prove challenging if conjugated polymers are used.[53−55] Therefore, radical polymers

Scheme 1. Synthesis of Poly(2,2,6,6-tetramethylpiperidinyloxy methacrylate) (PTMA) via a RAFT-Mediated Polymerization Mechanism

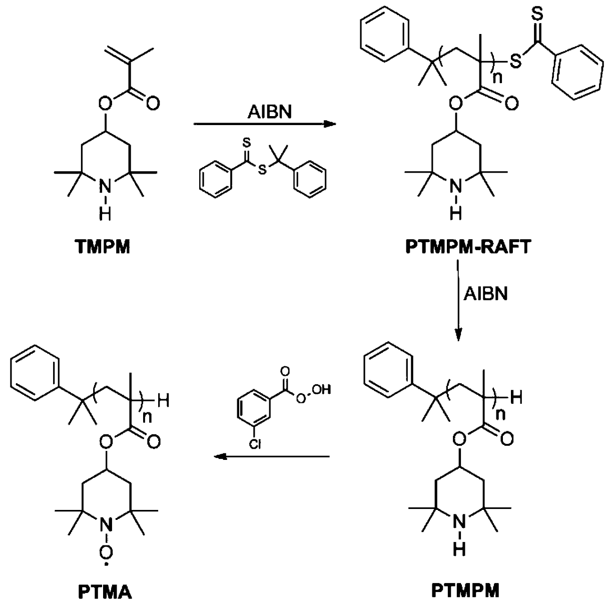


Table 1. PTMA(X) are the Labels for the Different Macromolecules Studied within Where the X Represents the Molecular Weight (in kg mol^{-1}) of the Given Polymer, As Shown in the Second Column of the Table

sample	M_n[a] (kg mol^{-1})	Đ[a]	T_g-PTMPM[b] (°C)	T_g-PTMA[b] (°C)	radical conversion[c] (%)	σ[d] (S cm^{-1})
PTMA(5)	4.7	1.2	112	153	71	$1.2 \pm 0.1 \times 10^{-8}$
PTMA(10)	9.5	1.2	102	164	65	$1.1 \pm 0.2 \times 10^{-6}$
PTMA(19)	19	1.2	105	179	66	$6.2 \pm 0.5 \times 10^{-7}$
PTMA(24)	24	1.2	102	185	73	$2.1 \pm 0.2 \times 10^{-7}$

[a] As determined by size exclusion chromatography (SEC), versus polystyrene (PS) standards. [b] Glass transition temperatures were determined by differential scanning calorimetry (DSC) on the second heating scan. These data were acquired after removal of the thermal history, and the scan rate was 10 °C min^{-1}. Note that no melting temperature was observed in any of the samples as these materials are completely amorphous. [c] As determined using UV−vis spectroscopy. [d] As determined by current−voltage response data using an applied bias between −10 V to +10 V and a 100 μm channel length; the number shown is the average value over multiple samples. The upper and lower bounds shown for the conductivities indicate one standard deviation from the average value.

could be of utility in generating large quantities of electronically active polymers with intricate molecular architectures.

Because of the reactivity of the thiocarbonylthio end group, direct oxidation of the PTMPM-RAFT polymers to form the PTMA radical polymers generated gel-like products, which were insoluble in common organic solvents. In order to circumvent this undesired side reaction, excess amounts of 2,2′-azobisisobutyronitrile (AIBN) were added to a solution of PTMPM-RAFT, and these solutions were heated overnight at elevated temperatures to remove the chain transfer terminus.[56,57] This reaction proceeded readily and the conversions of the PTMPM-RAFT end groups were monitored using ^{1}H NMR spectroscopy (see Figure S2 in the Supporting Information). Once this conversion to PTMPM was performed, the protected end group could be oxidized in a straightforward manner with *meta*-chloroperbenzoic acid (*m*CPBA) at room temperature to generate the PTMA radical polymer.[50,58] Note that this reaction scheme allows for the completely metal-free synthesis of PTMA, and that the molecular weight and the molecular weight distributions of the final products are the same as the initially-polymerized PTMPM-RAFT (i.e., no coupling occurred during the end group conversion and deprotection steps). As such, this synthetic strategy presents itself as a robust platform by which other radical homopolymer, copolymer, and block polymer derivatives can be synthesized in short order.

After confirmation of the removal of the chain transfer end group, the conversion of PTMPM to PTMA was quantified by measuring the ultraviolet−visible light absorbance of the material pre- and post-oxidation. First, the molar absorptivity of the radical pendant group was determined utilizing the radical-bearing small molecule analog (chemical structure inset into Figure 1a), (4-hydroxy-2,2,6,6-tetramethyl-piperidinyl)-oxidanyl (TEMPO−OH), whose concentration could be controlled readily in solution. In agreement with the literature, the molar absorptivity of this small molecule was found to be 11.4 M^{-1} cm^{-1} at λ = 458 nm (Figure 1a)[59] using a simple Beer's Law regression.[60] By utilizing this value, the concentration of radicals present in PTMA-containing solutions could be calculated in a straightforward manner. This was done by dissolving a known amount of PTMA (with a known molecular weight) into a chloroform solution after oxidation of the PTMPM to PTMA. As shown in Figure 1b, the conversion of PTMPM to PTMA was not complete. In fact, the percent conversion of protected pendant groups to the radical groups is only 69 ± 4%. To the best of our knowledge, this is the first quantitative report of the conversion of radical groups, and these data suggest that a better oxidizing agent or better oxidation conditions could prove extremely useful in generating PTMA molecules with complete radical conversion; this should increase charge transport ability of the functional polymers (vide infra). The glass transition of both PTMPM and PTMA were obtained and found to agree well with previous studies (see Figure S3 in the Supporting Information).[51] The materials were confirmed to be completely amorphous, and we note that these relatively high flow temperatures allow for the potential utilization of PTMA in a wide range of organic electronic applications where high temperature operation is potentially desired (e.g., organic photovoltaic and thermoelectric devices).

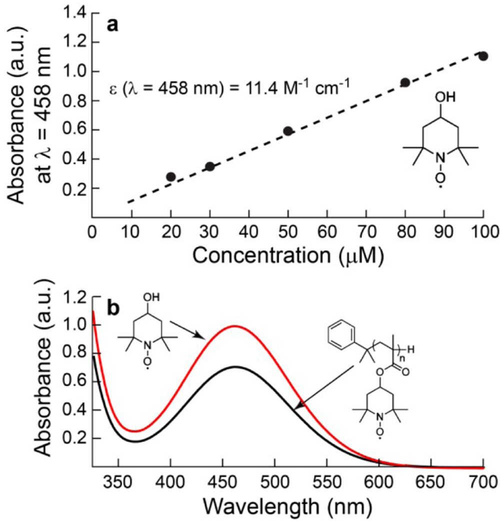


Figure 1. (a) Absorbance of the small molecule, TEMPO−OH (the chemical structure is inset in the figure), in chloroform, which is the small molecule analog to the pendant groups of PTMA. The measured molar absorptivity of this molecule was used to determine the concentration of pendant radicals in PTMA solutions. The dashed line is a linear regression fit to the data points. (b) UV−vis absorbance spectra of PTMA(10) (black curve) in chloroform at a concentration of 30 mg mL^{-1}. The red curve of b is the absorption spectrum of small molecule TEMPO−OH that would indicate 100% conversion of the protected pendant groups.

Despite the relatively modest conversion of protected pendant groups to radical groups, the radical polymers conduct charge well when cast into solid state thin films. In a manner akin to the Highest Occupied and Lowest Unoccupied Molecular Orbital (HOMO and LUMO) energy levels in π-conjugated organic semiconductors, radical polymers have a singly occupied molecular orbital (SOMO) of the lone radical electron, and this level is the guiding factor in determining charge transport in radical polymers.[61] In electrolyte-supported solutions, and in preliminary solid state devices,[39] PTMA is known to be a hole-conducting (p-type) radical polymer. This corresponds well with the fact that the SOMO energy level of PTMA has been estimated to be 5.3 eV removed from vacuum.[38] Here, the conductivity values of the hole-conducting properties of the PTMA samples were quantified fully in the solid state for the first time, and they were found to be similar to those of semicrystalline π-conjugated polymers despite the lack of crystallinity in the radical polymer thin films.

As shown in Figure 2, there exists a minimum molecular weight requirement in order to achieve a relatively high conductivity value for the PTMA radical polymers. This appears to originate from the poor film-forming properties of the lower molecular weight PTMA sample relative to the high molecular weight samples. Furthermore, this highlights the need to utilize radical-containing polymers in place of radical-bearing small molecules (e.g., neat TEMPO−OH), as these materials do not form continuous films capable of transporting charge well. Beyond the critical molecular weight, we find little dependence on the conductivity of the PTMA thin films. Note that this conductivity of $\sim 1 \times 10^{-6}$ S cm^{-1} is greater than the conductivity values ($\sim 1 \times 10^{-8}$ S cm^{-1}) for many neat (i.e., undoped) π-conjugated polymers (e.g., poly(phenylene vinylenes) (PPVs)) and comparable to the conductivity values (1×10^{-6} S cm^{-1}) of neat poly(3-hexylthiophene) (P3HT) thin films.[46,47] It is important to stress that the conductivity of conjugated polymers can be increased greatly through the incorporation of molecular dopants,[62] with one of the most well-studied examples of this being the doping of poly(3,4-ethylene dioxythiophene) with poly(styrene sulfonate) (PEDOT:PSS).[63−65] This allows these doped conjugated polymers to be used in a suite of organic electronic applications (e.g., OPV, OLED, and TE devices). However, the conductivity values for pristine radical polymers reported here serve as a baseline value for charge conductivities in pristine radical polymer films. It is anticipated that intra- and intermolecular organic dopants can be used to increase the conductivity (and, thus, the range of potential device applications) of radical polymers in a manner similar to that observed in π-conjugated polymers.

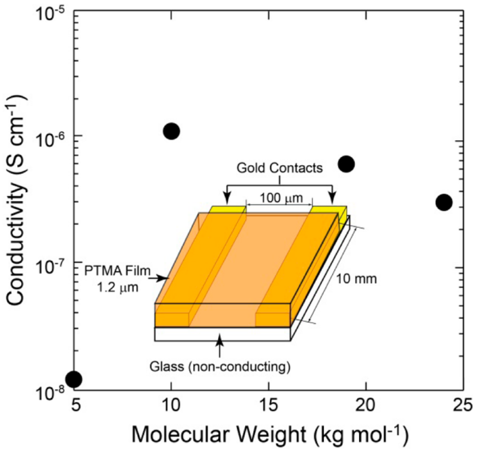


Figure 2. Conductivity of PTMA as a function of molecular weight. The solid-state conductivity was determined to be $\sim 1 \times 10^{-6}$ S cm^{-1} for sufficiently-high PTMA molecular weights. The sharp increase in conductivity is attributed to the film formation properties of low molecular weight PTMA polymers. Note that the data points shown are the average conductivity values for 6 samples. The standard deviations around the averages are smaller than the sizes of the data points. The device schematic used for these studies is inset into the figure.

To increase the amount of hopping sites available for charge transfer, small amounts of TEMPO−OH were added to the pristine PTMA thin films. By providing more sites (or, alternatively, shorter distances between hopping sites, on average), the conductivity of the neat PTMA thin films increased by more than a factor of two ($\sigma_{\max} = 4 \times 10^{-6}$ S cm^{-1}), as shown in Figure 3a. In contrast to many molecular dopants used in conjugated polymer systems, these intentional dopants do not alter the chemistry of the PTMA conducting polymer; as such, these dopants should not cause the polymer to be unstable in nature over the course of time. The fact that a percolating network of small molecule charge hopping sites did lead to the increase in conductivity was confirmed by the fact that the TEMPO−OH molecules were well-mixed (*i.e.*, not macrophase separated). Specifically, atomic force microscopy (AFM) images depict flat, homogenous topologies of the PTMA-TEMPO−OH blended films (see Figure S5 in the Supporting Information). Additionally, the optical transparency of the films (Figure 3b), even at relatively high loadings of TEMPO−OH, indicate the lack of small molecule macrophase

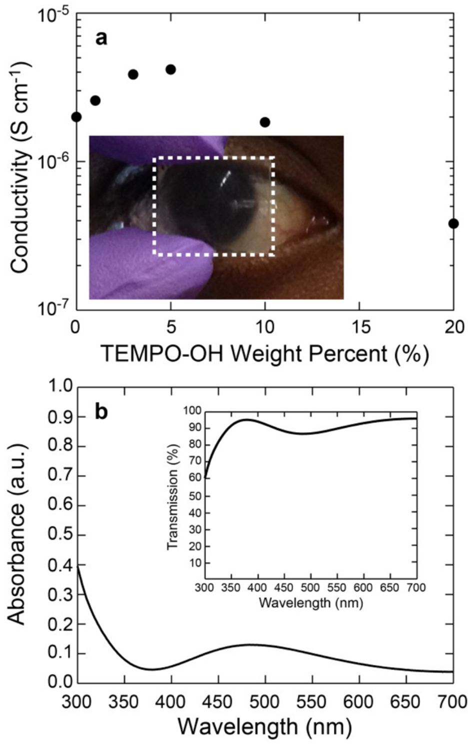


Figure 3. (a) Conductivity of PTMA(10) films doped with varying amounts of TEMPO−OH. A maximum in the conductivity of the films is observed at intermediate loadings of the small molecule radical. Specifically, the conductivity more than doubles with only 5% (by weight) TEMPO−OH relative to the pristine PTMA thin films due to the increased presence of radical sites capable of transporting charge. The inset shows an optical image of the 5% (by weight) TEMPO−OH-loaded PTMA thin film. The PTMA thin film is highlighted with a dashed line for clarity. Note that the human eye beneath the PTMA (on glass) substrate is readily visible even for a ~ 1.2 μm thick film. (b) Absorbance and transmission spectrum of the PTMA thin film doped with TEMPO−OH shown in the inset of a.

separation. As such, the increase in the conductivity of the thin films is consistent with the fact that providing a shorter hopping distance allows for better short-range transport of charge. This type of charge hopping is in accord with the idea that the film is highly disordered, and these results are in agreement with similar transport processes seen in highly disordered conjugated polymer thin films.[5,10,15] As with the low-molecular-weight PTMA sample, the decrease in conductivity with increasing TEMPO−OH loading beyond 5% (by weight), is due to the poor film formation properties of the highly-doped PTMA samples. Importantly, we note the relatively high optical transparency of these non-conjugated macromolecules. As demonstrated in the inset of Figure 3a, even a 1.2 μm thick PTMA film containing 5% (by weight) TEMPO−OH is transparent to the eye. This is confirmed by the data of Figure 3b, which show a transparency of this 1.2 μm thick PTMA film at >85% at all wavelengths greater than 300 nm; furthermore, the transparency approaches 100% (even at a large film thickness) for many wavelengths of light in the visible region. In contrast, this thick of a film containing the commonly-used conductor, poly(3,4-ethylene dioxythiophene) doped with poly(styrene sulfonate) (PEDOT:PSS), which is praised for its transparency in ∼20−30 nm thick films, would be a dark blue, opaque film if cast at thicknesses greater than 1 μm. Therefore, the ability to dope the PTMA thin films systematically with molecular dopants allows for the generation of nearly optically transparent thin films with tunable, stable electron transport properties, and this provides a useful handle by which to increase the overall conductivity of radical polymer-based thin films.

CONCLUSIONS

Well-defined PTMA radical polymers were synthesized using a metal-free, RAFT-mediated polymerization scheme. Importantly, this polymerization mechanism is compatible with the synthesis of random and multiblock copolymers, which could lead to complicated, yet useful, macromolecular architectures not achievable using common conjugated polymer synthesis mechanisms. The PTMA polymers demonstrated relatively high glass transition temperatures and the transmission of a micrometer-thick polymer film approached 100% in a large range of the visible spectrum, even when a small molecule dopant was included in the film. We attribute this low absorption coefficient to the lack of conjugation along the backbones of the PTMA chains. Despite this lack of π-conjugation or crystallinity in the functional macromolecules, the PTMA radical polymers were capable of transporting charge at the same level as non-doped P3HT thin films. Specifically, we find that the conductivity of PTMA in between adjacent gold contacts is $\sim 1 \times 10^{-6}$ S cm^{-1}, and it has a small molecular weight dependence across the range of molecular weights used in this work. This dependence is attributed to the relatively poor film-forming properties of the lowest molecular weight PTMA sample studied. Furthermore, the conductivity of the radical polymers can be increased readily through blending the radical polymers with of small molecule radical additives, which serve as intentional dopants. Therefore, PTMA thin films have demonstrated the ability to conduct charge relatively well in the solid state while remaining nearly completely transparent in the visible spectrum. These properties could make them of great import to future organic electronic applications.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Detailed synthetic procedure, ^{1}H NMR data of TMPM, PTMPM-RAFT, and PTMPM, differential scanning calorimetry (DSC) data of PTMPM and PTMA samples, atomic force microscopy (AFM) images, and representative current−voltage data for PTMA devices. This material is available for free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: boudouris@purdue.edu.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We gratefully acknowledge financial support from the Air Force Office of Scientific Research through the Young Investigator Program (AFOSR YIP, Grant FA9550-12-1-0243, Program Manager: Dr. Charles Lee). L.R. appreciatively acknowledges the National Science Foundation for a graduate fellowship (Grant DGE-13333468).

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