

"Plastic" Solar Cells: Self-Assembly of Bulk Heterojunction Nanomaterials by Spontaneous Phase Separation

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As the global demand for low-cost renewable energy sources intensifies, interest in new routes for converting solar energy to electricity is rapidly increasing. Although photovoltaic cells have been commercially available for more than 50 years, only 0.1% of the total electricity generated in the United States comes directly from sunlight. The earliest commercial solar technology remains the basis for the most prevalent devices in current use, namely, highly-ordered crystalline, inorganic solar cells, commonly referred to as silicon cells.

Another class of solar cells that has recently inspired significant academic and industrial excitement is the bulk heterojunction (BHJ) "plastic" solar cell. Research by a rapidly growing community of scientists across the globe is generating a steady stream of new insights into the fundamental physics, the materials design and synthesis, the film processing and morphology, and the device science and architecture of BHJ technology. Future progress in the fabrication of high-performance BHJ cells will depend on our ability to combine aspects of synthetic and physical chemistry, condensed matter physics, and materials science.

In this Account, we use a combination of characterization tools to tie together recent advances in BHJ morphology characterization, device photophysics, and thin-film solution processing, illustrating how to identify the limiting factors in solar cell performance. We also highlight how new processing methods, which control both the BHJ phase separation and the internal order of the components, can be implemented to increase the power conversion efficiency (PCE).

The failure of many innovative materials to achieve high performance in BHJ solar cell devices has been blamed on "poor morphology" without significant characterization of either the structure of the phase-separated morphology or the nature of the charge carrier recombination. We demonstrate how properly controlling the "nanomorphology", which is critically dependent on minute experimental details at every step, from synthesis to device construction, provides a clear path to >10%PCE BHJ cells, which can be fabricated at a fraction of the cost of conventional solar cells.

Introduction

Enough energy arrives on the earth's surface every hour to power the entire human race for a year, yet despite the fact that solar photovoltaics have been commercially available for more than half a century, they account for less than a tenth of one percent of our electricity generation. Photovoltaics based on conjugated mate-



FIGURE 1. (A) Illustration of BHJ solar cell structure and components from the original 1995 publication. Reproduced with permission from ref 9. Copyright 1995 American Association for the Advancement of Science. (B) Schematic of the processes that must occur within the BHJ active layer for effective charge collection. Reproduced with permission from ref 5. Copyright 2008 Wiley-VCH Verlag GmbH & Co. KGaA.

rials solution-processed onto flexible plastic substrates represent a potential platform for continuous, large-scale printing of thin-film photovoltaics.^{1,2} Rapid development of the technology has led to growing interest in polymerbased solar cells in academic and industrial laboratories and has been the subject of multiple recent reviews.^{2–7} These devices are promising in terms of low-cost power generation and simplicity of fabrication, but are remarkably complex in terms of device physics and in the size of the parameter space for materials selection and device fabrication.⁸

The most common polymer solar cell structure is the bulk heterojunction (BHJ) device in which a polymeric electron donor and a fullerene-based electron acceptor are mixed in solution and cast into a thin film that is sandwiched between two electrodes. Due to the inherent symmetry of the BHJ active layer, the anode and cathode of the device must be defined by the nature of the electrodes.⁹ The first reported BHJ solar cell was published in 1995 and comprised a film of a poly(phenylene vinylene) (PPV) derivative blended with phenyl C₆₁-butyric acid methyl ester (PC₆₁BM), as shown in Figure 1A.⁹ Since that publication, the device architecture has changed only slightly, but improved understanding of the device operation, loss mechanisms, and limitations has enabled significant improvements in materials, processing, and characterization. These advances have been accompanied by progress in large area device fabrication via low-cost coating methods such as inkjet printing, doctor blade coating, slotdie coating, screen printing and rotogravure printing onto flexible plastic substrates.^{1,10} In addition, recent measurements of device operational lifetime and environmental stability indicate that the BHJ devices, even at the current level of development, will be viable for years of continuous use.^{11,12}

Unlike highly ordered crystalline inorganic solar cells, where photoexcitation yields a pair of free carriers, photons incident on the active layer of a polymer BHJ solar cell create excitons, that is, electron-hole pairs bound by their Coulomb attraction.⁶ In most pristine semiconducting polymers cast from solution, these excitons can diffuse less than 10-20 nm before decaying to the ground state.¹³ Subpicosecond photoinduced electron transfer from the polymer to the fullerene with nearly 100% quantum efficiency enables the formation of mobile carriers.⁹ Following exciton dissociation, however, there is evidence that the charges remain weakly bound at the interface before either recombining or separating into free carriers.^{14–16} The weakly bound carriers at the interface are referred to as being in a charge transfer (CT) state. Once formed, the holes are free to drift and diffuse within the polymer domains and the electrons are free to move within the fullerene domains. If the domain is isolated



FIGURE 2. Contour plot containing the theoretical solar cell PCE (contour lines) versus the donor polymer band gap and LUMO level for a BHJ device using $PC_{61}BM$. Reproduced with permission from ref 19. Copyright 2006 Wiley-VCH Verlag GmbH & Co. KGaA.

from the appropriate electrode or the carrier is too far from the electrode, it will eventually recombine at a polymer/fullerene interface. Thus, for the mobile carriers to contribute to the photocurrent, the domain in which they form must be in contact with the appropriate electrode. Because of this necessity for fully bicontinuous interpenetrating networks comprising the donor and acceptor materials and the weak intermolecular forces between the molecular partners, these devices are acutely sensitive to processing conditions.¹⁰ A schematic of the device operation is illustrated in Figure 1B.⁴

Solar power conversion efficiency (PCE) is dictated by the product of three electrical parameters: the device short circuit current (I_{sc}) , the open circuit voltage (V_{oc}) , and the fill factor (FF). The I_{sc} , or the device photocurrent at zero bias, is the product of the number of photons absorbed and the efficiency of free charge carrier generation and collection. The FF is, in part, a function of the efficiency of charge migration to the electrodes. The $V_{\rm oc}$ of the BHJ cell relates to the difference between the highest occupied molecular orbital (HOMO) of the electron donor and the lowest unoccupied molecular orbital (LUMO) of the electron acceptor.¹⁷ Note that the $V_{\rm oc}$ is usually reduced from the value predicted by subtracting the electron donor HOMO from the electron acceptor LUMO by approximately 0.3 V, presumably because of the energies associated with the molecular distortions involved in carrier formation.18,19

As presented in Figure 2, it is possible to calculate the theoretical efficiency for an electron donor blended with $PC_{61}BM$ based on the donor absorption and LUMO level and reasonable values for the device external quantum efficiency (EQE) and fill factor (65% each).¹⁹ The plot indicates that single layer devices in excess of 10% should be possible, given the correct molecular design and processing optimization.¹⁹ Moreover, it has been demonstrated that solution-processable tandem cells are possible and can potentially enable an additional 50% increase in efficiency by harvesting a broader fraction of the solar spectrum and by taking advantage of the increased voltage available for wide band gap materials.^{20,21}

Characterization of BHJ Solar Cells

Poly(3-hexylthiophene) (P3HT) is the most studied polymer in BHJ solar cell applications.⁷ Important qualities include good solubility in a variety of organic solvents, a high field effect hole mobility (> 10^{-2} cm²/(V s)) and a tendency to crystallize into ordered domains.²² The kinetics of the BHJ ordering are such that the degree of crystallization and polymer/fullerene phase separation can be tailored by altering the film casting conditions. The film morphology can then be further optimized through thermal annealing, which leads to better order within the P3HT and demixing of the blend.^{23,24} Other techniques, such as slow drying, solvent annealing, the use of processing additives, and aggregation in solution have also led to increased performance by allowing a degree of control over the polymer packing and polymer/fullerene phase separation during the film formation process.^{25–27} The relative ease with which P3HT/fullerene films can be optimized has resulted in a significant body of work on the relationships between processing, morphology, and performance.

The degree of phase separation is a critical parameter since large domains will prevent efficient charge separation and small domains will lead to a poorly connected network resulting in increased charge carrier recombination. Directly probing the phase separation between the polymer and the fullerene is difficult for highly optimized BHJ solar cell systems, however, because the domain sizes are on the order of tens of nanometers.²⁸ Furthermore, most studies attempting to image the phase separation concentrate on the surface of the film and investigations by X-ray photoelectron spectroscopy (XPS) and ellipsometry indicate vertical concentration gradients.^{29,30}

Recent studies have utilized a focused ion beam to "cut" cross sections through the BHJ film for characterization via atomic force microscopy (AFM) and transmission electron microscopy (TEM).^{31,32} Figure 3 contains a cross-sectional TEM image of a P3HT/PC₆₁BM blend film and a contrast-enhanced image of the BHJ morphology.³² Both cross-sectional AFM and TEM capture the continuous pathways of donor and acceptor domains.

By control of the polymer/fullerene phase separation, charge transport through the BHJ films can be optimized. One



FIGURE 3. Cross-sectional TEM of a BHJ solar cell with a contrastenhanced image to highlight the continuous domains of P3HT and $PC_{61}BM$. Reproduced with permission from ref 32. Copyright 2009 American Chemical Society.

of the most common charge transport characterization methods is the measurement of field effect mobility from thin film transistor (TFT) transconductance characteristics.³³ Recent work using bottom contact TFTs with aluminum electrodes indicates that BHJ solar cell active layers can be used to create ambipolar TFTs.³⁴ Fabrication of ambipolar transistors with various polymer/fullerene ratios to equalize the electron and hole mobilities yields a component ratio which correlates with the optimum ratio for solar cell device performance.³⁵ It is logical that equalizing charge transport though the BHJ film would increase performance by reducing space charge build up, but only recently has this been clearly demonstrated.³⁵ The use of ambipolar field effect transistors (FETs) to measure carrier mobilities in BHJ blends with different polymer/fullerene ratios can thus be used to compare different BHJ systems and to optimize the performance of new polymer/fullerene combinations.

Additional details on carrier generation and recombination in BHJ films can be explored by transient photoinduced absorption spectroscopy (TA). TA is a pump—probe technique where an ultrafast laser pulse is incident on the film and the photoinduced change in optical absorption is measured at various wavelengths as a function of time. Since different excited states within the film (excitons, mobile carriers after charge separation, etc.) have specific absorption profiles, their relative populations can be probed as a function of time following photoexcitation.

There has been uncertainty in the literature as to why solar cell PCEs have been highly variable for materials expected to yield high-performance devices based on optical absorption, mobility measurements, and component energy levels. Originally, it was thought that ultrafast exciton dissociation immediately yielded a free pair of mobile carriers.³⁶ TA data indicate that, for a variety of polymers, a charge transfer (CT) state or bound radical pair is formed at the interface and a sig-

nificant percentage of dissociated excitons recombine from the CT state in BHJ films rather than by subsequent mobile carrier recombination.^{14–16}

Analysis of transient absorption data from P3HT/PC₆₁BM BHJ films indicates that thermal annealing not only improves the carrier lifetime and mobility through improved morphology of the interpenetrating network but also increases the fraction of mobile carriers that emerge from the CT state.^{14,37} One possible explanation for this phenomenon is that the higher lying HOMO level in ordered polymer domains relative to the disordered polymer/fullerene interface serves as a driving force for hole migration away from the interface.¹⁴ Several other mechanisms for the decrease in geminate recombination with increased molecular order are possible; one alternate explanation is that ordered polymer chains contain fewer kinks and thus intersystem crossing from the CT state to a low-energy triplet state would be less probable.^{38,39} Combining the time-resolved evolution of excitations using TA with mobility measurements, morphology data, optical characterization, and device performance analysis enables the emergence of fundamental structure/property relationships in new materials systems.

Optimizing the Performance of New Materials: The Example of a Low Band Gap Polymer

Despite the dominance of P3HT in the literature, new materials are needed to achieve the required improvements in efficiency. P3HT lacks the broad absorption profile to collect a large fraction of the solar spectrum; moreover, the high lying LUMO of P3HT is more than 500 mV higher than it needs to be for electron transfer to the fullerene.¹⁹ An example of a new material that has recently been introduced as a candidate for higher performance solar cells is poly[(4,4-bis(2-ethylhexyl)-cyclopenta-[2,1-b;3,4-b']dithiophene)-2,6-diyl-alt-2,1,3-benzothiadiazole-4,7-diyl], PCPDTBT (structure shown in Figure 4A).⁴⁰ PCPDTBT is a "push-pull" copolymer, which uses alternating electron-withdrawing and electron-donating components to increase the double bond character between the units and thereby stabilize the guinoidal form of the polymer and decrease the band gap.^{3,41} This class of polymers is also susceptible to "tuning" of the HOMO and LUMO values since the HOMO value is largely derived from the electron-donating monomer and the LUMO is largely derived from the electron-withdrawing monomer.^{3,40} It should be noted that while the donor and acceptor monomers predominantly affect the HOMO and LUMO, respectively, mixing of the orbitals as well as chain planarity and



FIGURE 4. (A) Optical absorption spectra for PCPDTBT/PC₇₁BM blends cast from pristine chlorobenzene (black) and cast from chlorobenzene containing 2% by volume of various alkane dithiols (colored). The PCPDTBT structure is shown inset where the R represents an ethylhexyl group. (B) EQE specra of solar cells composed of $P3HT/PC_{61}BM$ before (dotted red line) and after (solid red line) thermal annealing and PCPDTBT/PC₇₁BM cast from chlorobenzene (dotted green line) and cast from chlorobenzene containing octanedithiol (solid green line). The AM 1.5G solar spectrum is shown in black for reference. Reproduced with permission from ref 43. Copyright 2007 Nature Publishing Group.

packing can alter the frontier orbitals from what might be predicted based on the monomers alone. PCPDTBT has approximately the same HOMO energy value as P3HT, and thus the same open circuit voltage is observed in BHJ solar cells. Because of the lower lying LUMO, PCPDTBT harvests light and generates photocurrent between 300 and 900 nm (compared with 300 to 650 nm for P3HT).⁴² While still not the ideal LUMO based on the theoretical value required for charge separation, PCPDTBT has a significantly greater potential for high-efficiency solar cells than does P3HT.⁴²

Measurements of the hole mobility for PCPDTBT indicate that it has a surprisingly high mobility (>10⁻³ cm²/(V s)) given that diffraction measurements indicate a poorly ordered morphology.^{42,43} Initial device results indicated that the *I*_{sc} obtained from the cells was low, implying poor collection of photogenerated carriers. Despite being a seemingly "better" material for BHJ solar cells, the highest performance cells that could be fabricated exhibited power conversion efficiencies below 4% compared with 5% for P3HT. This limit persisted despite attempts toward optimization via molecular weight, polymer/fullerene ratio, casting solvent, thermal annealing, and device architecture.

In response to the need to optimize the PCE of PCPDTBT devices, the use of processing additives was explored.⁴³ This approach was suggested by the significant improvements in the photoconductivity of P3HT-based BHJ blends processed with such additives.⁴⁴ Since the use of mixed solvents offers a fundamentally different route to polymer ordering and morphology control, the possibility existed that the use of processing additives might work with PCPDTBT where thermal annealing had failed. The increased versatility of the addi-

tives proved effective at optimizing the chain packing and phase separation in PCPDTBT solar cells.⁴³

The role of the processing additives was investigated by monitoring the UV and visible absorption spectra of nascent films as the solvents evaporated; because the aromatic organic solvents and the additives have absorption in the UV, the evaporation of each can be monitored with time.^{45,46} This experiment indicated that the additives function by slowing the evaporation of solvent from the nascent film and, perhaps more importantly, by changing the solvent quality during film formation from being dominated by the primary solvent (which must be a good solvent for both the polymer and the fullerene), to being dominated by the additive (which should be a relatively poor solvent for the polymer and a good solvent for the fullerene).^{46,47} This shift in solvent quality can be used to optimize the order within the polymer domains and the degree of polymer/fullerene phase separation.^{46,47} More critically, unlike other forms of processing optimization, additives can serve to form unique polymer structures and conformations that are not formed when only a good solvent is present, as has been shown to be the case for both PCPDTBT and poly(9,9-dioctylfluorene).^{45,46} Additionally, despite their extremely low vapor pressures, no detectable additive remains in the film after drying under vacuum.^{35,43}

The effect of using processing additives on BHJ films of PCPDTBT with PC₇₁BM is immediately apparent via a red shift in the absorption maximum from 760 to 800 nm, as presented in Figure 4A.⁴³ The additive used for processing the PCPDTBT solar cells was octane dithiol; this additive is a sufficiently good solvent for the fullerene and a poor solvent for the polymer that BHJ films dipped in additive are completely

depleted of fullerene and only a porous PCPDTBT film remains.⁴⁷ The solubility of the fullerene in the additive is critical to prevent macroscale crystallization of the fullerene.^{46,47} When devices were fabricated in which the 800 nm absorption peak was maximized, the solar cell current output nearly doubled. The EQE vs wavelength curve, shown in Figure 4B compared with a P3HT/PC₆₁BM solar cell and the solar spectrum, indicates that the current output of the device improves across all wavelengths, not only in the region near the absorption edge where the spectral features are better-defined and increased in magnitude by the additive processing. This increase in EQE implies an increase in the ability of the cell to generate and collect carriers independent of where the absorption event takes place.

New questions arose when the effects of the additives on PCPDTBT were investigated. Measurements of the carrier mobility of the BHJ films indicated that, despite the increase in the 800 nm absorption peak and improvements in the solar cell performance, the hole mobility did not increase.⁴³ Preliminary diffraction experiments also indicated that the film was amorphous when processed with or without additives. These results represent a departure from the results observed with P3HT, where additive processing increases long-range order within the polymer domains and increases carrier mobility.⁴⁴ Investigations into the effects of additive processing on the morphology of PCPDTBT BHJ blends by cross-sectional AFM indicate that the use of additives increases the scale of the phase separation as well as altering the polymer supramolecular structure.^{47,48} Some increases were observed in the electron mobility in bipolar FETs leading to slightly more balanced charge transport in films cast using the processing additives, but the changes were not sufficient to explain the increase in collected charge carriers.35,49

Detailed analysis of the transient absorption profile provided additional insight into the carrier formation and recombination dynamics in the PCPDTBT-based BHJ films.⁵⁰ The TA decay profiles indicated a significant decrease in carrier losses from the CT state for films processed with additives.^{50,51} Despite little observable long-range order and no change in hole mobility, films that contained the 800 nm peak much more efficiently generated mobile carriers from the CT state. Studies into the nature of the 800 nm peak revealed that it can only be formed when the number-average molecular weight of the polymer is greater than approximately 20 000.⁴⁶ If low molecular weight material is used in solar cells processed with additives, the effect of the additives on both absorption and device performance is negligible. Thus, the nanostructure associated with the 800 nm peak is neces-



FIGURE 5. (A) Molecular structure of PCDTBT where R is an *n*-octyl chain. (B) Structure of a trimetallic nitride endohedral fullerene recently used to increase the V_{oc} of a P3HT-based BHJ solar cell to more than 800 mV.

sary for achieving high performance. This fact explains both why the additive is necessary for high performance to be achieved and why high molecular weights are used in all high-performance PCPDTBT devices, but does not explain in what way the change in absorption is connected with the increase in performance. It remains unclear to what extent the absorption at 800 nm for PCPDTBT arises from a traditional "aggregate", with excitons delocalized across multiple polymer chains, or an effect similar to that observed in the β -phase of poly(9,9-dioctylfluorene), in which chain planarization in a poor solvent leads to increased intrachain exciton delocalization.⁵² The effect of additives in decreasing geminate recombination in BHJ films has been observed by multiple groups and additional work is needed to elucidate the nature of the PCPDTBT absorption band at 800 nm.^{51,53}

New Materials Systems

While the smaller band gap of PCPDTBT yields better light harvesting relative to P3HT, there is opportunity for significant improvement in PCE by increasing V_{oc} and EQE.¹⁹ Toward this goal, new materials systems are being designed to optimize the polymer and fullerene energy levels in order to increase device photovoltage. One new class of donor materials has been recently introduced that replaces the fused bithiophene in PCPDTBT with a carbazole derivative resulting the polymer poly[N-9'-heptadecanyl-2,7-carbazole-alt-5,5'-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole], PCDTBT (structure shown in Figure 5A).^{54–56} The low-lying HOMO of the carbazole results in a 50% increase in operating voltage compared with P3HT or PCPDTBT.^{54–56} The combination of the larger V_{0c} and a high quantum efficiency results in 6% PCE under AM1.5 irradiation even though the band gap is approximately the same as P3HT.⁵⁷ It is important in this context that carbazole-based copolymers from this class can be synthesized with significantly lower band gaps through the use of stronger acceptor units in the push-pull copolymer.

Another strategy for increasing photovoltage and thus the device performance is modification of the fullerene.^{9,58} While only small changes to the fullerene orbital energy levels can be realized via chemical modification of the fullerene, it has

been shown that the use of trimetallic nitride endohedral fullerenes can enable significant offsets in the fullerene LUMO levels.⁵⁹ One such material, using trilutetium nitride incarcerated in an 80 carbon fulleroid (structure shown in Figure 5B), has been modified with a phenyl butyric acid hexyl ester solubilizing group. When this material is blended with P3HT, one observes an increase in the V_{oc} of nearly 300 mV with no significant loss in I_{sc} . The potential of these fullerenes to enable performance increases across multiple established polymer systems is promising and future studies will determine the extent to which they can be effectively combined with low band gap materials.

Summary and Conclusion

The synthesis and optimization of new materials for BHJ solar cells will lead to significantly higher performance levels and the discovery of materials that maximize open circuit voltages will lead to increasingly efficient tandem solar cell devices, which can potentially enable power conversion efficiencies in excess of 15%.⁶⁰ It has also been shown that results from spin-casting can be readily transferred to more scalable film casting methods at least in the case of P3HT/PC₆₁BM devices.^{1,10} Moreover, by expansion of the selection of high-performance materials, characterization tools, and optimization techniques, the probability will increase that materials can be discovered that are capable of achieving high performance and long operational lifetimes when cast via large area continuous coating methods.

Since the first report of solution-processed photovoltaics based on blends of donor and acceptor molecules, significant progress has been made in the fundamental photophysics that underlies the devices, in the chemical synthesis of the components, in the film processing, and in the characterization tools that are necessary for the optimization of increasingly high-performance devices. Because the details of the materials synthesis and purification can so significantly affect the carrier dynamics and device performance, as can the details of the film processing and device fabrication, it is essential that all researchers involved in the fabrication and characterization of organic solar cells effectively communicate experimental details if the fundamental processing/structure/property relationships for these devices are to be elucidated and used to improve devices. A clear path exists to greater than 10% PCE for devices that may be fabricated at a fraction of the cost of conventional solar cells and the synthetic, photophysical, and film casting tools are in place to achieve that goal.

BIOGRAPHICAL INFORMATION

Jeffrey Peet is a doctoral candidate in Materials at the University of California at Santa Barbara (UCSB). He was raised in Chapel Hill, North Carolina, and received B.S. degrees in Materials Engineering and Textile Chemistry from North Carolina State University in 2004. He received a National Defense Science and Engineering Graduate Fellowship in 2005 and a Materials Research Society Graduate Student Award in 2008 for his work on enhancing performance in polymer solar cells using solvent additives. His current research interests include understanding the dynamics of active layer formation in solution-processed organic electronic devices and the fabrication of high-performance polymer photovoltaics.

Alan J. Heeger serves as a Professor of Physics and Professor of Materials at the University of California, Santa Barbara, and also heads a research group at the University's Center for Polymers and Organic Solids. He was awarded the Nobel Prize in Chemistry (2000) for his pioneering research in and the cofounding of the field of semiconducting and metallic polymers. His research efforts continue to focus on the science and technology of semiconducting and metallic polymers with emphasis on "plastic" solar cells. Heeger cofounded (with Howard Berke) Konarka Techonologies in 2001; he continues to serve as Chief Scientist. Konarka is commercializing low-cost plastic solar cells fabricated from bulk heterojunction materials fabricated via roll-to-roll manufacturing. Other current interests include studies of biospecific sensors for DNA and proteins.

Guillermo C. Bazan is a professor in the Departments of Materials and Chemistry & Biochemistry and is Co-Director of the Center for Polymers and Organic Solids at the University of California, Santa Barbara. He was born in Mendoza, Argentina, and was raised in Argentina, Belgium, and Canada. He obtained his B.Sc. in 1986 (Summa Cum Laude) from the University of Ottawa. His Ph.D. thesis was done with Professor Richard R. Schrock at MIT. After a postdoctoral appointment at Caltech with Professor John Bercaw, he began his independent career in 1992 at the University of Rochester. He moved to UCSB in 1998. His research interests concern the design, synthesis, photophysics, bulk properties, and applications of organic molecules with delocalized electronic structures and the design of homogeneous transition-metal catalysts for the controlled polymerization of olefins.

FOOTNOTES

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