Influence of Alkyl Substitution Pattern in Thiophene Copolymers on Composite Fullerene Solar Cell Performance

Barry C. Thompson, Bumjoon J. Kim, David F. Kavulak, Kevin Sivula, Clayton Mauldin, and Jean M. J. Fréchet*

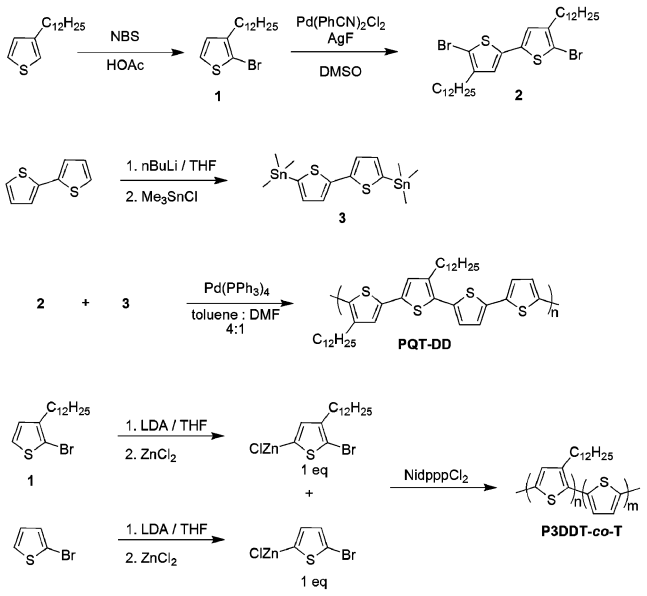
Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, and College of Chemistry, University of California, Berkeley, California 94720-1460

Received July 24, 2007
Revised Manuscript Received August 17, 2007

Polymer-fullerene based photovoltaic devices have attracted a great deal of attention based on the potential for realizing low-cost, solution-processable, and flexible solar cells.[1] Recently, power conversion efficiencies in excess of 5% have been reported for the poly(3-hexylthiophene)/[6,6]-phenyl-C_{61} butyric acid methyl ester (P3HT:PCBM) bulk heterojunction (BHJ) solar cell.[2] The successful combination of P3HT and PCBM is based on the ability of the two components to mix homogenously in a pristine cast film and then, under the influence of thermal or solvent annealing,[3,4] undergo a controlled phase segregation yielding a nanometer length scale bicontinuous network of highly ordered donor and acceptor phases, suitable for charge transport.[2] Much effort has been dedicated to the optimization of these devices, including a focus on developing a deeper understanding of the role of polythiophene structure on device performance.[5−10] The ability of regioregular (RR) P3HT to form crystalline phases with strong interchain and intrachain $\pi-\pi$ overlap is credited for the observed hole mobilites as high as 0.1 $cm^2\ V^{-1}\ s^{-1}$ measured in FETs[11] and for the enhanced visible light absorption properties of the polymer.[12] Polythiophene analogues that exhibit higher levels of crystallinity and higher hole mobilites than P3HT, such as the regiosymmetric polymers poly(3,3-didodecylquaterthiophene) (PQT-DD)[13,14] and poly(2,5-bis(3-tetradcylthiophen-2-yl)thieno[3,2-*b*]thiophene) (PBTTT),[15] have been studied for use in FETs, displaying mobilities from 0.18 to 0.6 $cm^2\ V^{-1}\ s^{-1}$. Such polymers achieve a greater overall degree of crystallinity than P3HT based on the length and distribution of alkyl side chains, which favors long-range three-dimensional ordering via $\pi-\pi$ stacking and side-chain interdigitation. While such polymers define the state-of-the-art in solution-processed FETs, their photovoltaic performance has not yet been reported, so it is unclear whether the enhanced inherent crystallinity will be beneficial to composite solar cells. As a means of investigating such highly ordered polymers and directly assessing the influence of a high degree of crystallinity on solar cell performance, here we examine two thiophene−alkylthiophene copolymers with identical molecular weight, composition, and electronic structure, which are composed of equal parts of 3-dodecylthiophene and unsubstituted thiophene. The first polymer is the perfectly alternating copolymer PQT-DD, described above, and the other is the random copolymer poly(3-dodecylthiophene-*co*-thiophene) (P3DDT-*co*-T). The effect of substituent sequence distribution on polymer crystallinity and solar cell performance in PCBM based BHJ devices is examined.

* Corresponding author. E-mail: frechet@berkeley.edu.

Scheme 1. Synthesis of Copolymers



Scheme 1 illustrates the synthetic routes used for the synthesis of PQT-DD and P3DDT-*co*-T. Here, dodecyl substituents were chosen to maintain solubility, while allowing for the incorporation of unsubstituted thiophene rings. The synthesis of PQT-DD was achieved via the Stille copolymerization of dibromo monomer **2** and distannyl monomer **3**, rather than the oxidative polymerization reported in the literature.[13] For P3DDT-*co*-T a random copolymerization of equimolar amounts of 2-bromo-3-dodecylthiophene and 2-bromothiophene was performed using a modified McCullough route.[16] On the basis of this synthetic route, P3DDT-*co*-T is expected to have a random sequence distribution but is expected to have predominantly head-to-tail linkages for any sequences of consecutively linked 3-dodecylthiophene repeat units. Analysis by NMR (see Supporting Information) is uninformative for establishing the precise sequence distribution in such a polymer; however, ^{1}H NMR does confirm the 1:1 ratio of monomer units in P3DDT-*co*-T. The molecular weights of PQT-DD and P3DDT-*co*-T were estimated via SEC to be 19 800 and 19 400 g/mol, respectively, with measured PDI values of 2.11 and 1.99, vs polystyrene standards. Thus, the two polymers are structurally equivalent, except for the sequence distribution of substituted and unsubstituted thiophene rings. Both polymers are less soluble than P3HT of a similar molecular weight, but both are soluble in chloroform, chlorobenzene, and dichlorobenzene. The similarity in the molecular weight and polydispersity of these two samples polymerized via different methods was achieved due to several different factors. First, the step growth nature of the Stille polymerization for PQT-DD combined with the inability of the fractionation procedure (see Supporting Information) to remove any appreciable amount of low molecular weight species due to the extremely low solubility of this polymer in hexanes led to a PDI of ∼2. The M_n of ∼20 kDa is similar to that reported for the equivalent polymer synthesized oxidatively and is probably due to the upper limit of polymer solubility in the reaction mixture.[13] For P3DDT-*co*-T, the M_n of ∼20 kDa is somewhat lower than that observed for P3HT polymerized under the same conditions,[5] as would be expected on the basis of the reduced solubility of P3DDT-*co*-T in THF relative to P3HT.

10.1021/ma071649s CCC: $37.00
Published on Web 09/12/2007

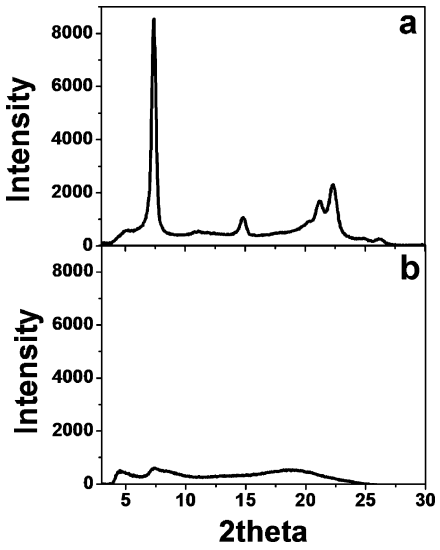


Figure 1. XRD for drop-cast films of PQT-DD (a) and P3DD-*co*-T (b). Films were annealed at 100 °C for 30 min prior to acquisition of data.

The PDI of ~2 for P3DDT-*co*-T is somewhat higher than the values of 1.4−1.7 observed using similar copolymerization techniques,[5,17] as expected again on the basis of the limited ability of hexanes to fractionate lower molecular weight species.

The electronic and structural properties of the polymers were investigated by UV−vis spectroscopy, electrochemistry, X-ray diffraction (XRD), and differential scanning calorimetry (DSC). The band structures and band energies of both PQT-DD and P3DDT-*co*-T are found to be equivalent (see Supporting Information), with optical band gaps estimated from thin film UV−vis to be ~2 eV. Thin film absorption coefficients of 7.6 $\times$ 10^4 and 5.4 $\times$ 10^4 cm^{-1} are measured for PQT-DD and P3DDT-*co*-T respectively, which compare favorably to P3HT (8.7 $\times$ 10^4 cm^{-1}).

Structural ordering within films of the two copolymers was examined by XRD (Figure 1) and transmission electron microscopy (TEM) (see Supporting Information). In both cases, polymer films were drop-cast from chloroform and annealed at 100 °C for 30 min prior to measurement, followed by slow cooling. It is clear, on the basis of XRD results and the fibrillar features observed only in PQT-DD by TEM, that PQT-DD is significantly more crystalline than P3DDT-*co*-T under these conditions, as would be expected on the basis of the precise, perfectly alternating nature of the PQT-DD primary structure relative to the random structure of P3DDT-*co*-T. The XRD pattern in Figure 1a represents the reflections from the interchain ordering (2θ = 5.2°, 10.5°), side-chain ordering (2θ = 7.4°, 14.8°, 22.3°), and $\pi-\pi$ stacking (2θ = 21.2°), giving a *d*-spacing of 1.70, 1.19, and 0.42 nm, respectively, which shows good agreement with the previous report.[18] Analysis by DSC further confirms the more ordered nature of PQT-DD, with no well-defined transitions observed for P3DDT-*co*-T (see Supporting Information).

In addition to the band structure of a donor polymer for photovoltaic devices, the other property of great inherent interest is the charge carrier mobility attainable in the polymer. For reference, P3HT is reported to have a hole mobility on the order of 10^{-3}−10^{-1} cm^2 V^{-1} s^{-1} measured in FETs, and PQT-DD has been shown to have a mobility as high as 0.18 cm^2 V^{-1} s^{-1} under the most optimal conditions.[14] In diagnostic FET measurements, PQT-DD was found give a reproducible mobility on the order of 10^{-2} cm^2 V^{-1} s^{-1}, which matches with reported

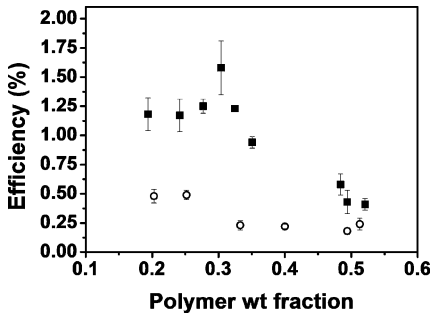


Figure 2. Relationship between power conversion efficiency and composition (plotted as polymer weight fraction) in polymer/PCBM solar cells. Closed squares (■) represent P3DDT-*co*-T blends cast from chloroform, and open circles (○) represent PQT-DD blends cast from chlorobenzene. Error bars indicate the 95% confidence interval of the average value. For optimal performance devices were not annealed.

average values of 0.07−0.12 cm^2 V^{-1} s^{-1}.[13] Measurement of FETs with P3DDT-*co*-T (see Supporting Information) showed a mobility of 10^{-3} cm^2 V^{-1} s^{-1}, reflecting the lower degree of order attainable in P3DDT-*co*-T, as evidenced by XRD. Perhaps a more representative measurement of charge carrier mobility, as relevant to solar cells, is the space charge limited current mobility (SCLC),[19] which measures the mobility perpendicular to the electrodes rather than parallel to the substrate and not under the influence of a gate bias, as in FETs. Typical values of SCLC mobility for P3HT are on the order of 10^{-4} cm^2 V^{-1} s^{-1}. For PQT-DD and P3DDT-*co*-T the SCLC mobilities were measured to be 2.7 $\times$ 10^{-4} and 2.8 $\times$ 10^{-4} cm^2 V^{-1} s^{-1}, respectively. The similarity in SCLC mobilities for these two polymers, which show such disparate abilities to order, is a surprising result, which also suggests a lower relevance to reported FET mobilities, when considering polymers for use in solar cells. The similar SCLC mobilites also suggest that despite the lack of observed long range order in P3DDT-*co*-T, locally ordered domains must exist in order to engender such a bulk mobility.

The performance of each of the two polymers in PCBM-based composite solar cells was independently optimized according to solvent choice, concentration, and composition. It was found that chlorobenzene gave the most efficient devices with PQT-DD and chloroform was most effective for P3DDT-*co*-T. Figure 2 is a comparison of the compositional dependence of power conversion efficiency for the two polymers in devices cast from their respective preferred solvents. Several important observations can be made about these results within the context of the most efficient P3HT:PCBM devices. First, for all weight ratios investigated, P3DDT-*co*-T outperformed PQT-DD. Second, the most efficient P3HT:PCBM devices are realized at approximately a 1:1 weight ratio of the two components due to the excellent miscibility of this pair. Here, neither polymer shows optimal performance in the 1:1 weight ratio range; instead, the best efficiencies are recorded for a 30:70 blend (polymer:PCBM) with P3DDT-*co*-T (η = 1.84%) and with a 25:75 blend with PQT-DD (η = 0.54%) (see Supporting Information for current voltage characteristics and parameters for solar cells). Therefore, the random and amorphous polymer outperforms its highly ordered analogue by a factor greater than 3. It should also be noted that any thermal annealing above 50 °C resulted in a significant decrease in device performance for both polymers at all weight ratios, and thus all reported results are for unannealed films.

A deeper insight into the compositional dependence of device performance can be gleaned by examination of the active layer morphology via transmission electron microscopy (TEM).

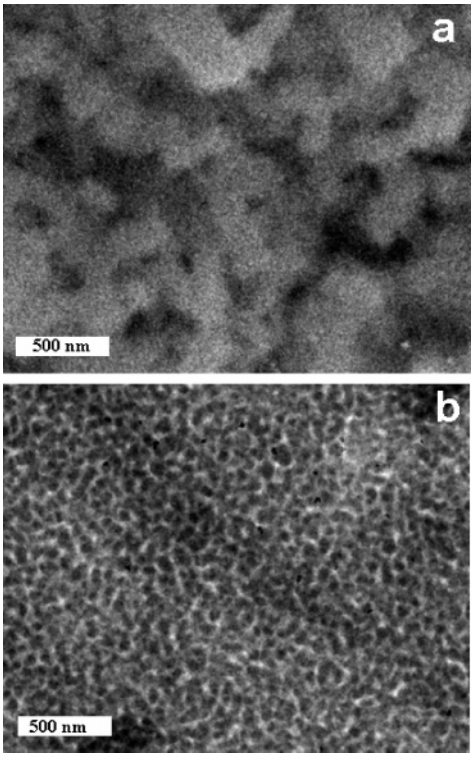


Figure 3. TEM images of a 25:75 blend of PQT-DD:PCBM (a) and a 30:70 blend of P3DDT-*co*-T:PCBM.

Figure 3 represents TEM images for both polymers in blends with PCBM at the optimal composition for device performance. It is clear that a major reason for the enhanced performance of P3DDT-*co*-T relative to PQT-DD is the ability of this random polymer to form a bicontinuous donor−acceptor network (Figure 3b), with domain sizes on the order of <50 nm. No such favorable morphology is observed for PQT-DD at any composition. For P3DDT-*co*-T at weight percentages of PCBM above 70%, phase segregation occurs on a much larger length scale (see Supporting Information), leading to diminishing device performance, while at weight percentages of PCBM less than 70%, homogeneous blends are observed, which lack the bicontinuous pathways necessary for charge extraction. Unlike the P3HT:PCBM blend system in which thermal annealing can be used to induce a controlled demixing of the two phases with concomitant intraphase ordering, any level of thermal annealing above 50 °C induces macrophase separation and marked decreases in device performance. Such behavior has been observed previously in dodecyl-substituted polythiophenes[9] and has been explained by the enhanced ability of PCBM molecules to diffuse within the polymer film, engendered by the significantly larger interchain spacing in the bulk polymer caused by the longer alkyl chains. Equivalently, the presence of longer alkyl chains may simply decrease the miscibility with the fullerene cage of PCBM. The effect is to render dodecyl-substituted poly(alkylthiophenes) unstable to large-scale phase segregation and renders them less effectively miscible with PCBM in general, as is reflected in the larger weight fraction of PCBM required for optimal performance in both copolymers described here. However, the ability to kinetically trap a favorable morphology with P3DDT-*co*-T but not with PQT-DD suggests that a greater inherent miscibility exists between the random copolymer and PCBM as opposed to the much more highly ordered PQT-DD, which is attributed to the greater tendency of PQT-DD to crystallize, favoring the exclusion of fullerene from the polymer phase. Conceptually similar results have been observed concerning the effect of the degree of regioregularity in P3HT.[5] In samples of P3HT with a higher degree of regioregularity, macrophase separation occurs on a much shorter time scale of annealing than for samples with a lower degree of regioregularity, suggesting that polymers capable of attaining a high degree of crystalline order engender macrophase separation. The previous results about the effect of regioregularity, taken with the present results, suggest that a certain degree of disorder in polythiophenes enhances their ability to effectively mix with the small molecule fullerene and favors the formation of bicontinuous networks with a nanometer length scale phase separation.

Of great interest is a comparison of the present polymers to P3HT, as P3HT contains the same overall alkyl content as PQT-DD and P3DDT-*co*-T but shows efficiencies of ∼5% in PCBM composite solar cells. The main difference of the present polymers relative to P3HT is expected to be the effect of alkyl chain length. As described above, longer alkyl chains lower the miscibility of poly(alkylthiophene)s with fullerenes.[9] Thus, P3HT inherently mixes better with PCBM than the dodecyl-substituted polymers presented here. The effect of polymer crystallization on phase separation is also significantly different for P3HT and PQT-DD, as PQT-DD crystallizes into a highly three-dimensionally ordered structure aided by side-chain interdigitation,[13] whereas P3HT is known to exhibit disordered, non-interdigitated side chains.[20] The mode of crystallization in P3HT thus favors a lower degree of three-dimensional ordering in the polymer crystal. The consequence is that P3HT favors the formation of a highly effective, intimately mixed morphology with PCBM, as has been reported.[2] For P3DDT-*co*-T, the disorder in the backbone is expected to overcome the strong driving force for the development of long-range order aided by interdigitation and render the polymer more miscible with PCBM than PQT-DD. Additional work will be required to fully correlate the effects of alkyl chain length, alkyl substituent distribution, and solid-state side-chain interdigitation with phase compatibility and solar cell performance in polythiophene−fullerene composite solar cells.

The work presented here points to several key concepts about polythiophene−fullerene bulk heterojunciton solar cells, which suggest a more general design principle for conjugated polymers intended for use in composite solar cells. First, the band structure of a polymer defines its electronic interaction with a fullerene acceptor, and this electronic band structure is primarily influenced by the chemical nature of the polymer backbone, rather than the solubilizing groups utilized to make it processable. However, the choice of solubilizing group and the attachment strategy are critical for determining the ability of the polymer to not only order for effective charge transport, but to effectively mix with the fullerene acceptor and present the possibility of generating a suitable bicontinuous morphology. Here it is illustrated that for two polythiophenes, which are compositionally and electronically equivalent and differ only in the sequence distribution of the alkyl solubilizing groups, the polymer with the random primary structure is superior to the polymer with the precisely defined primary structure, in the context of solar cell performance. It is suspected that the more than 3-fold increase in solar cell efficiency for P3DDT-*co*-T relative to PQT-DD is based on ability for the formation of bicontinuous structure in the random copolymer, brought about by the decreased tendency for crystallization. As a general conclusion toward the design and optimization of new polymers for photovoltaics, the comparison of P3HT, P3DDT-*co*-T, and PQT-DD illustrates an important point. While all three polymers

have very similar electronic structures and SCLC mobilities, the difference in peak achieved solar cell efficiencies varies over an entire order of magnitude, influenced by the placement and choice of solubilizing group and how such choices effect polymer crystallinity and miscibility with PCBM. Thus, optimization of new conjugated polymers goes beyond light absorption, energy levels, and mobility but ultimately must lie in a global structural optimization aimed at balancing electronic performance with polymer−fullerene miscibility.

Acknowledgment. The authors acknowledge financial support by the U.S. Department of Energy, Basic Energy Sciences, under Contract DE-AC03-76SF00098. B.C.T. thanks the American Chemical Society, Petroleum Research Fund, for an Alternative Energy Postdoctoral Fellowship.

Supporting Information Available: Synthetic procedures, polymer spectroscopic and electrochemical characterization, experimental methods, additional morphological characterization, and solar cell device data. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Gunes, S.; Neugebauer, H.; Sariciftci, N. S. *Chem. Rev.* **2007**, *107*, 1324−1338.
(2) Ma, W.; Yang, C.; Gong, X.; Lee, K.; Heeger, A. J. *Adv. Funct. Mater.* **2005**, *15*, 1617−1622.
(3) Li, G.; Shrotriya, V.; Huang, J.; Yao, Y.; Moriarity, T.; Emery, K.; Yang, Y. *Nat. Mater.* **2005**, *4*, 864−868.
(4) Mihailetchi, V. D.; Xie, H.; de Boer, B.; Popescu, L. M.; Hummelen, J. C.; Blom, P. W. M.; Koster, L. J. A. *Appl. Phys. Lett.* **2006**, *89*, 012107.
(5) Sivula, K.; Luscombe, C. K.; Thompson, B. C.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **2006**, *128*, 13988−13989.
(6) Kim, Y.; Cook, S.; Tuladhar, S. M.; Choulis, S. A.; Nelson, J.; Durrant, J. R.; Bradley, D. D. C.; Giles, M.; McCulloch, I.; Ha, C-S.; Ree, M. *Nat. Mater.* **2006**, *5*, 197−203.
(7) Schilinsky, P.; Asawapirom, U.; Scherf, U.; Biele, M.; Brabec, C. J. *Chem. Mater.* **2005**, *17*, 2175−2180.
(8) Hiorns, R. C.; de Bettignies, R.; Leroy, J.; Bailey, S.; Firon, M.; Sentein, C.; Khoukh, A.; Preud'homme, H.; Dagron-Lartigau, C. *Adv. Funct. Mater.* **2006**, *16*, 2263−2273.
(9) Nguyen, L. H.; Hoppe, H.; Erb, T.; Gunes, S.; Gobsch, G.; Sariciftci, N. S. *Adv. Funct. Mater.* **2007**, *17*, 1071−1078.
(10) Koppe, M.; Scharber, M.; Brabec, C.; Duffy, W.; Heeney, M.; McCulloch, I. *Adv. Funct. Mater.* **2007**, *17*, 1371−1376.
(11) Sirringhaus, H.; Brown, P. J.; Friend, R. H.; Nielsen, M. M.; Bechgaard, K.; Langeveld-Voss, B. M. W.; Spiering, A. J. H.; Janssen, R. A. J.; Meijer, E. W.; Herwig, P.; de Leeuw, D. M. *Nature (London)* **1999**, *401*, 685−688.
(12) Brown, P. J.; Thomas, D. S.; Kohler, A.; Wilson, J. S.; Kim, J-S.; Ramsdale, C. M.; Sirringhaus, H.; Friend, R. H. *Phys. Rev. B* **2003**, *67*, 064203.
(13) Ong, B. S.; Wu, Y.; Liu, P.; Gardner, S. *J. Am. Chem. Soc.* **2004**, *126*, 3378−3379.
(14) Wu, Y.; Liu, P.; Ong, B. S.; Srikumar, T.; Zhao, N.; Botton, G.; Zhu, S. *Appl. Phys. Lett.* **2005**, *86*, 142102.
(15) McCulloch, I.; Heeney, M.; Bailey, C.; Genevicius, K.; MacDonald, I.; Shkunov, M.; Sparrowe, D.; Tierney, S.; Wagner, R.; Zhang, W.; Chabinyc, M. L.; Kline, R. J.; McGehee, M. D.; Toney, M. F. *Nat. Mater.* **2006**, *5*, 328−333.
(16) Liu, J. S.; McCullough, R. D. *Macromolecules* **2002**, *35*, 9882−9889.
(17) Yu, J.; Holdcroft, S. *Macromolecules* **2000**, *33*, 5073−5079.
(18) Ong, B. S.; Wu, Y.; Liu, P.; Gardner, S. *Adv. Mater.* **2005**, *17*, 1141−1144.
(19) Goh, C.; Kline, R. J.; McGehee, M. D.; Kadnikova, E. N.; Fréchet, J. M. J. *Appl. Phys. Lett.* **2005**, *86*, 122110.
(20) Gurau, M. C.; Delongchamp, D. M.; Vogel, B. M.; Lin, E. K.; Fischer, D. A.; Sambasivan, S.; Richter, L. J. *Langmuir* **2007**, *23*, 834−842.

MA071649S