CROSS TOKAI **Experimental Report** J-PARC	承認日 Date of Approval 2013/11/23 承認者 Approver Jun-ichi SUZUKI 提出日 Date of Report 2013/8/29
課題番号 Project No. 2012B0143 実験課題名 Title of experiment Nanoscale Phase Separation in Organic Solar Cells 実験責任者名 Name of principal investigator Prof. Ian R. Gentle 所属 Affiliation The University of Queensland, AUSTRALIA	装置責任者 Name of Instrument scientist Jun-ichi SUZUKI 装置名 Name of Instrument/（BL No.） BL15 TAIKAN 実施日 Date of Experiment 2013.02.14-18

試料、実験方法、利用の結果得られた主なデータ、考察、結論等を、記述して下さい。（適宜、図表添付のこと）
Please report your samples, experimental method and results, discussion and conclusions. Please add figures and tables for better explanation.

1. 試料 Name of sample(s) and chemical formula, or compositions including physical form.

The following materials were used during the experiment on TAIKAN, names and acronyms are given along with chemical formulae.

PCDTBT – poly[N-9''-hepta-decanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole] $(C_{43}H_{47}N_3S_3)_n(C_6H_5)_2$

PCPDTBT – poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b]dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)] $(C_{31}H_{38}N_2S_3)_n$

P3HT – poly(3-*n*-hexylthiophene) $(C_{10}H_{16}S)_n$

60-PCBM – [6,6]-phenyl C_{61} butyric acid methyl ester ($C_{72}H_{14}O_2$)

70-PCBM – [6,6]-phenyl C_{71} butyric acid methyl ester ($C_{82}H_{14}O_2$)

ICBA – indenyl C_{60} bis adduct ($C_{78}H_{16}$)

K12 – 2-[[7-(9,9-di-*n*-propyl-9H-fluoren-2-yl)benzo[c][1,2,5]thiadiazol-4-yl]methylene]malononitrile ($C_{29}H_{24}N_4S$)

YF25 – 2-[[7-(4,4-di-*n*-propyl-4H-silolo[3,2-b:4,5-b']dithien-2-yl)benzo[c][1,2,5]thiadiazol-4-yl]methylene]malononitrile ($C_{24}H_{20}N_4SiS_3$)

Thin films were deposited onto 12x12x0.2mm or 20x20x0.2mm silicon substrates in the following combinations to study their morphology as they would be in organic solar cells: P3HT:60-PCBM, P3HT:K12, P3HT:YF25, P3HT:ICBA, PCDTBT:ICBA, PCPDTBT:70-PCBM. The effect of thermal annealing and a processing additive 1,8-diiodooctane on the SANS spectra of the films was investigated on separately prepared films.

2. 実験方法及び結果（実験がうまくいかなかった場合、その理由を記述してください。）

Experimental method and results. If you failed to conduct experiment as planned, please describe reasons.

The samples deposited on silicon substrates were stacked (12 samples for spin-cast thin films) and enclosed inside aluminum foil. The scattering by the as-cast films was measured along with the scattering of uncoated silicon wafers and a glassy carbon standard material. The films cast without the processing additive DIO were then removed from the beamline and thermally annealed in a nitrogen-filled glovebox within the MLF to simulate the solar cell manufacturing process. The scattering of the annealed samples was then recorded.

Due to strong scattering by the Si wafers neutron wavelengths below 4 Å were neglected in the analysis of the data. This limited the accessible Q-range to around 0.01-0.2 $Å^{-1}$ and also lengthened the measurement time to acquire statistically meaningful data. Despite this setback we were able to test all but one of the samples brought to J-PARC in both the as-cast state and after a single anneal.

Sector averaging was performed by Dr Kazuki Ohishi prior to our departure from J-PARC and the data has since been converted into plots of differential scattering cross section *vs* Q-vector using the TAIKAN reduction software. Errors in the observed scattering intensities were calculated in house by combining the error in measured scattering film thickness with the error in observed scattering intensity.

The first aim of these experiments was to compare the scattering of a standard polymer:fullerene blend (P3HT:60-PCBM) with the scattering from blends of the same polymer with non-fullerene acceptors developed in our laboratory (K12 and YF25). The scattered intensity from both as cast and thermally annealed P3HT:60-PCBM films was recorded. The non-fullerene acceptors K12 and YF25 have been observed to spontaneously crystallise in thin films over time and these films were not thermally annealed but the scattered intensity was measured at 1 day, 3 days and 10 days after drop-casting to observe any changes occurring over time. Data were successfully collected with each of these systems and the scattered intensities for the P3HT:K12 and P3HT:YF25 blends are shown in Figure 1. Analysis of this data is ongoing.

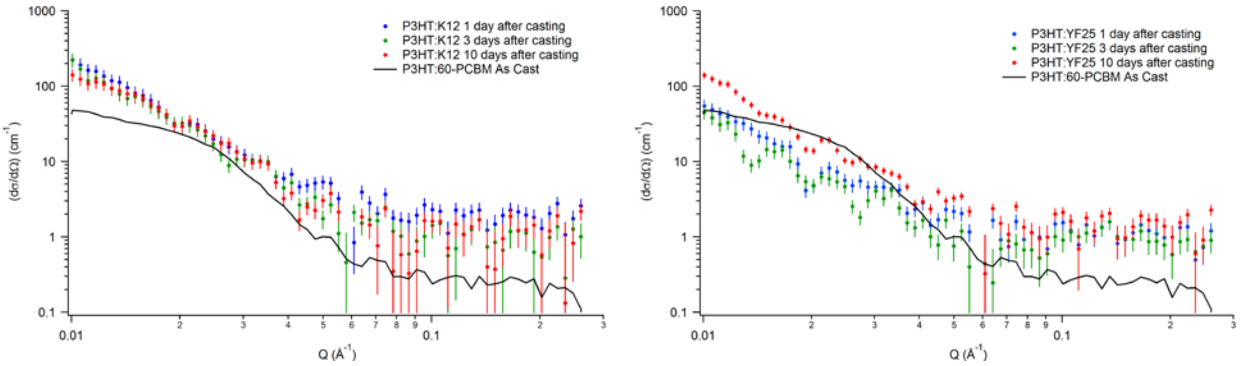

Figure 1 Differential scattering cross section *vs* Q plots for P3HT:K12 and P3HT:YF25 blends, as cast P3HT:60-PCBM plot included (black line) for comparison

2. 実験方法及び結果（つづき） Experimental method and results (continued)

The second aim of this work was to examine the influence of thermal annealing on the morphology of as cast bulk heterojunction P3HT:fullerene blends. Two fullerenes were examined: the standard 60-PCBM and a fullerene of increasing popularity in the field, ICBA.

It was observed that thermal annealing had a much greater effect on the scattered intensity for the P3HT:60-PCBM blends than the P3HT:ICBA blends. Modelling of the data is ongoing to determine the different fullerene clustering modes in the thin films.

The third aim of this work was to examine the influence of a processing additive 1,8-diiodooctane (DIO) commonly used to induce slow drying annealing on the scattering patterns of bulk heterojunction films. Two sets of films were investigated: the standard P3HT:60-PCBM system and blends of PCPDTBT:70-PCBM.

The DIO additive was found to have a minor influence on the observed scattering intensity of the P3HT:60-PCBM films and relatively weak scattering was observed from the PCPDTBT:70-PCBM films making comparison with the scattered intensities difficult. Analysis of the data is ongoing.