

Development of Next Generation Organic Solar Cell

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Organic photovoltaic, OPV, cells have been attracted much attention for next generation solar cells. OPV is based on the same technology as polymer light-emitting diodes, PLED, which has been developed intensively for TV application at Sumitomo Chemical Co., Ltd. Many PLED-related materials and device fabrication processes can accelerate the development of OPV technology. Although very high efficiency of 6.5% has already been achieved, the efficiency of more than 10% is necessary for the commercialization of OPV. In order to achieve this goal, a new class of low band gap polymer has successfully been prepared together with morphology controlling methods of an active layer of OPV. In this paper, we report the present status of OPV research at Sumitomo Chemical Co., Ltd. as well as worldwide research.

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Introduction

With the recent increase in awareness of the problems of measures for global warming and the exhausting of natural resources, solar cells have attracted worldwide attention as the trump card for solving these problems. Moving forward, they are predicted to be a significant global market exceeding 10 trillion yen in 2020, but we need a scenario for dissemination that makes the costs for power generation using solar cells lower than commercial power costs. However, the cost of generating power using current solar cells is more expensive than commercial power generation, and the current situation is one where dissemination is happening because of government subsidies. The mainstream solar cells are currently inorganic solar cells like those made of silicon. Since they are manufactured by high temperature and vacuum processes and have a large number of associated parts, cost reductions have been slow. Furthermore, since the modules are very heavy,

dissemination to homes has been limited because of installation costs and limits on the houses where installation is possible.

Thin film organic photovoltaics (abbreviated OPV in the following) are a new generation of solar cells for overcoming these disadvantages of inorganic solar cells. As is shown in **Fig. 1**, OPVs are similar to the polymer light-emitting diodes (PLEDs) that Sumitomo Chemical has put effort into developing in terms of the structure of the device, but the direction of operation is reversed. PLEDs generate light from electricity, but OPVs are devices that extract electricity with exposure to the sun. The main materials for these devices are conjugated polymers. Since high temperature manufacturing processes are not used, plastic substrates can be used, and a common feature is the ease of making them flexible.

Furthermore, if the features of manufacturing by application and printing are used, a roll to roll processing can be employed as a manufacturing method. Large

cost reductions are then possible using continuous production. In addition, since the flexible OPVs are light, they can easily be installed on houses, and we expect that they can be supplied at a low cost. Advanced molecular design technology and synthesis technology are necessary for manufacturing the conjugated polymers used in OPVs, and raw material makers like Sumitomo Chemical can easily make use of their strengths. Furthermore, this is a field where Sumitomo Chemical, which leads the world in PLED material design technology and device manufacturing technology, can easily make use of its technical expertise. In fact, we are the first worldwide to be successful with an efficiency exceeding 6% in a single device,¹⁾ and we can brag about development at the highest level.

However, when we look at things from the standpoint of making OPVs practical, we are still at the research and development level compared with silicon solar cells, which are the main current now. Improvements in both efficiency and durability are necessary. Not only Sumitomo Chemical, but also the rest of the world is getting more active in studying these improvements aimed at making OPVs practical. In this article, we will report on the (1) features of OPVs, (2) trends in development worldwide and (3) current status of OPV development at Sumitomo Chemical.

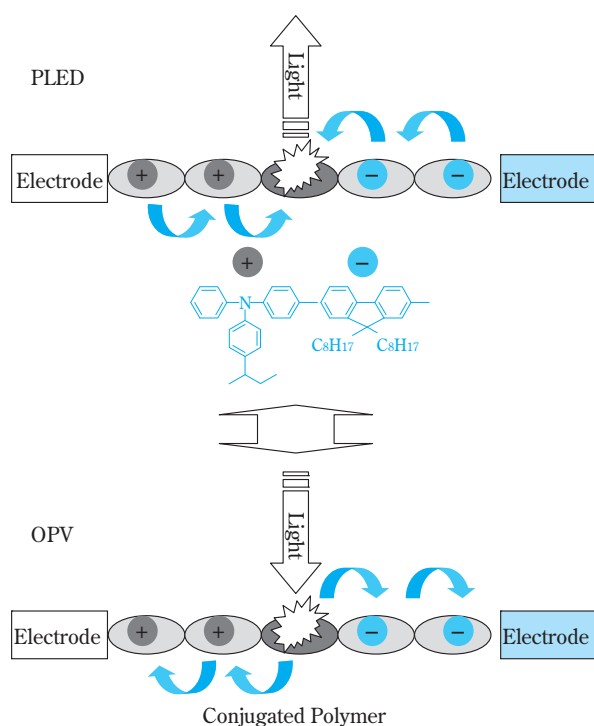


Fig. 1 Similarity in device structures and materials

Current Situation in Photovoltaic Power Generation

1. Photovoltaic power generation expected to be trump card for solving environment problems

Abnormal weather conditions, increases in the level of the oceans and other problems caused by global warming are intensifying. The problems of global warming are being taken up as problems for society as a whole. CO₂ and other greenhouse gases are said to be one of the causes of the global warming problem. Work on reducing CO₂ has started worldwide. Recently, international targets for reducing greenhouse gases were determined at COP15, and Cool Earth 50 for halving the emissions of greenhouse gases worldwide by 2050 was proposed for the Post-Kyoto Protocol. Furthermore, even though this is presupposed on the Japanese government and other countries agreeing, CO₂ reductions have become an extremely important topic with the setting a target of a 25% reduction from the 1990 greenhouse gas levels by 2020 and the like.

Under these circumstances, photovoltaic power generation is a green energy source that converts sunlight directly into electrical energy and does not produce CO₂. It is one of the technologies that is receiving attention as a trump card in CO₂ reduction. The solar energy that reaches the Earth is immense at 176 trillion kJ/sec,²⁾ and just an hour of solar energy could cover the world's annual energy consumption (11.10 billion tons (equivalent in oil) in 2007).

However, sunlight has a broad spectrum ranging from ultraviolet rays to infrared rays, and there are factors, such as limitations to the wavelengths that can be converted into electricity, the energy density being low (1 kW/m² at the mid latitudes) and variability in the amount of power generated because of night and day as well as weather, that have prevented dissemination. For example, to generate the 2 to 3 kWh that is the power used by a standard household, a surface area of 20 to 30 m² would be necessary with a conversion efficiency of 10%. The key to dissemination of photovoltaics is high efficiency and low cost.

2. Types and features of solar cells

Fig. 2 shows the types of solar cells that are currently on the market or being developed. There is a profusion of solar cells now, but the main current among them at present is silicon solar cells. There are thin film and crystalline silicon solar cells, and crystalline ones

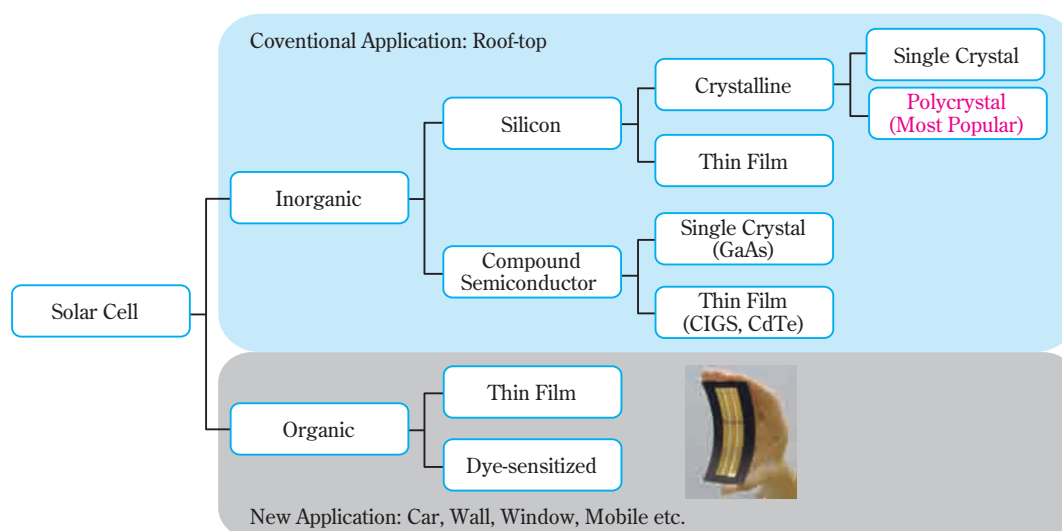


Fig. 2 The classification of materials for solar cells

include single crystal and polycrystal types. High purity silicon must be used as the raw material for crystalline solar cells, and high temperature processes are necessary in the production process for the raw materials and ingots. Thin-film solar cells are manufactured by plasma CVD using silane gas. The thickness required for thin film solar cells is several microns, less than one-tenth of that for crystalline solar cells, but they have lower efficiency than crystalline solar cells.

Practical applications of thin film solar cells that make use of compound semiconductors such as copper indium gallium selenide (CIGS) and CdTe have come about to eliminate these deficiencies. However, little progress has been made on cost reduction for these inorganic solar cells because high temperature and vacuum processes are used, and there is also the use of materials for which there are limited resources.

On the other hand, dye-sensitized and thin film organic solar cells have been developed. Dye-sensitized solar cells are devices where a dye is absorbed into porous titanium oxide. They convert the energy of light that is absorbed by the dye into electrical energy. There have been reports of efficiency exceeding 10%.³⁾ However, there are problems with liquids leaking since an iodine solution is used, so they have still not become practical. Thin film organic solar cells are roughly divided into small molecule and polymer types depending on the p-type material used. Light is converted into electricity by using both p-type and n-type materials in a mixture or in laminations. The trend has been for development of polymer materials to be more active than that for smaller molecules, and improvement in the effi-

ciency of polymer systems is moving forward. In addition, a fullerene derivative (PCBM), which is an n-type material, is mixed in by solution in polymer systems, and a feature of these is being able to manufacture the solar cells by application or printing. High-temperature processes are unnecessary, and it is easy to use a plastic substrate to make them flexible. Since cost reductions are possible using a roll to roll process, these are attracting attention as being the closest thing for the next generation of solar cells. Development of uses in mobile equipment, vehicles, etc., making use of features not available in conventional solar cells, such as light weight and flexibility, are being investigated.

3. Scenario for dissemination of solar cells and market

The key to widespread dissemination of solar power generation is the reduction of generating costs. The New Energy and Industrial Technology Development Organization (NEDO) has planned for a dissemination scenario known as PV2030+ (Fig. 3).⁴⁾ In this scenario, mass dissemination is achieved by lowering the cost of solar power generation to the equivalent of home electrical utility rates, commercial electrical utility rates and general-purpose electrical utility rates. Organic photovoltaics are a new generation of solar cells for overcoming these disadvantages of inorganic solar cells.

Under these circumstances, the potential need for solar power generation is great, and as is shown in Fig. 4, there are expectations of rapid growth with the scale of the market exceeding 80 GW and ¥10 trillion by 2020.⁵⁾

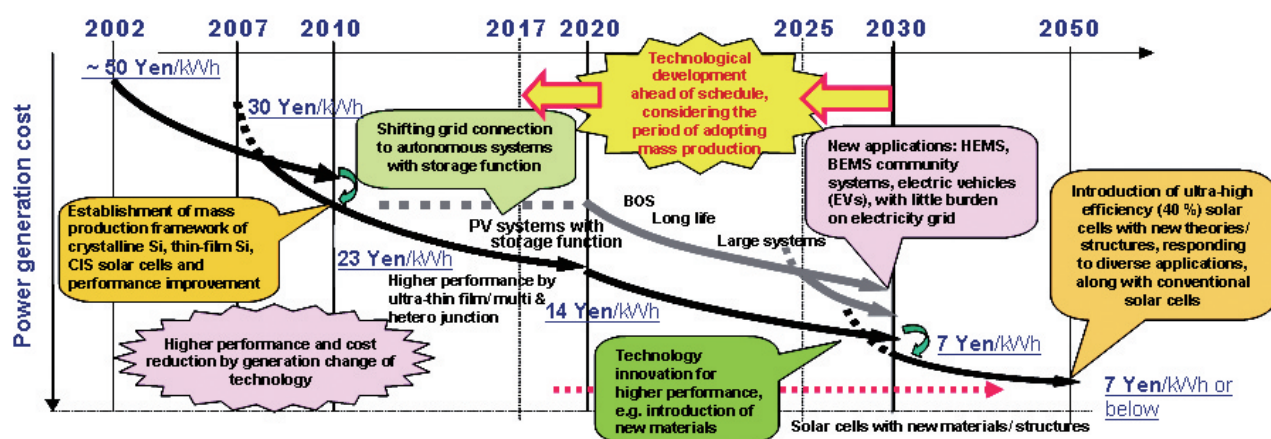


Fig. 3 PV2030+ scenario for future growth of PV power generation ⁴⁾

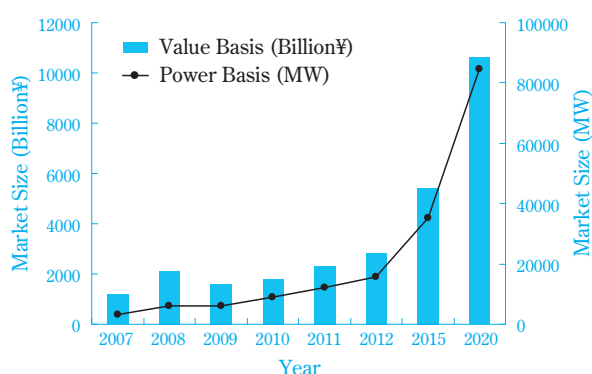


Fig. 4 Market size of solar cells
[Data from reference 5)]

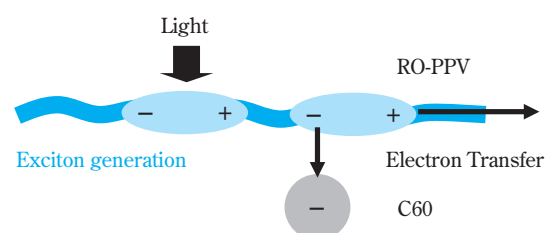
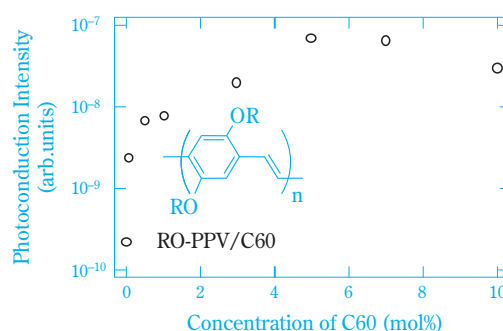


Fig. 5 Photoconduction in the blend of PPV and C60 and schematic illustration of the mechanism of generation of photocurrent

Trends in the Development of Thin Film Organic Photovoltaics

1. History

Calvin et al. discovered in 1958 that shining light on organic materials such as magnesium porphyrin caused an electrical current to arise. Unceasing efforts were put in to applications of this in solar cells, but nothing with a high efficiency was discovered. Before the development of organic LEDs by Kodak's Tang in 1986, the highest efficiency reported for solar cells with laminations of organic layers was approximately 1%. With the advent of organic LEDs, the interest in solar cells that use organic materials increased worldwide.⁶⁾

On the other hand, in 1992, Osaka University's Yoshino discovered that a photocurrent could be obtained with good efficiency by mixing polythiophene or polyphenylene (jointly with Sumitomo Chemical), which are known to be electrically conductive polymers, with fullerene (C60).⁷⁾ As is shown in Fig. 5, this

phenomenon is explained by electrons moving to the C60 after the conjugated polymer is excited by illumination with light. Holes (positive charges) move into the polymer chain, and the electrons move into the C60, creating an efficient photoelectric charge separation. With this discovery, development of solar cells using conjugated polymers began.⁸⁾ With the development of fullerene derivatives that are soluble in solvents in 1995, the efficiency was increased and reached approximately 3%.⁹⁾

2. Thin Film Organic Photovoltaics

Conjugated polymers have pi electrons and are typically p-type materials. Their bandgap (range of light ab-

sorption) is in the visible range. As is shown in **Fig. 6**, if an n-type material like C60 is present near the polymer, the electrons move to the n-type material after excitation by exposure to light as described above. Normally, the electrons that have moved and the remaining holes recombine and cannot be extracted as electricity. However, when an electric field is formed in the film or when the movement of the electrons and holes is quick, the electrons and holes are separated and an electric current may be extracted to the outside. Furthermore, the excitons for the organic material can only move approximately 10 nm in the solid film.¹⁰⁾ When they cannot reach the location connected to the n-type material, they return to the ground state via fluorescence or a nonradiative process and are not converted into a photocurrent. The main difference between inorganic materials and organic materials is the diffusion length of excitons. The diffusion length with silicon and the like is large (on the order of microns), and photoelectric charge separation occurs efficiently with excitons moving to the p/n junction interface. When the p-type material and n-type material are laminated in organic materials, there are few excitons, and the efficiency is kept low. OPVs where n-type material is mixed into the polymer are called the bulk hetero junction type, but these have the microphase separation structure for the p-type polymer domain and the n-type fullerene domain shown in **Fig. 6**. In other words, this means that a large number of p/n junction interfaces are formed, and the excitons can reach a p/n junction interface efficiently. Photoelectric charge separation occurs with good efficiency.

This bulk hetero type photoelectric conversion layer is normally formed by applying a solvent in which a

polymer and n-type material are dissolved by a method like spin coating.

The output characteristics of solar cells are shown in **Fig. 7**. In the dark, they exhibit the current rectification action of diodes. If light shines on them, the photocurrent is added to the dark current.

Maximum power generation is achieved when the area of the rectangle touching the inside of the characteristic curve for the current and voltage during illumination is maximized. Let the current when the voltage is 0 be the short-circuit current (J_{sc}) and the voltage when the current is 0 be the open circuit voltage (V_{oc}). If the ratio of the product of the current and the voltage given for the rectangle that is in contact and the product

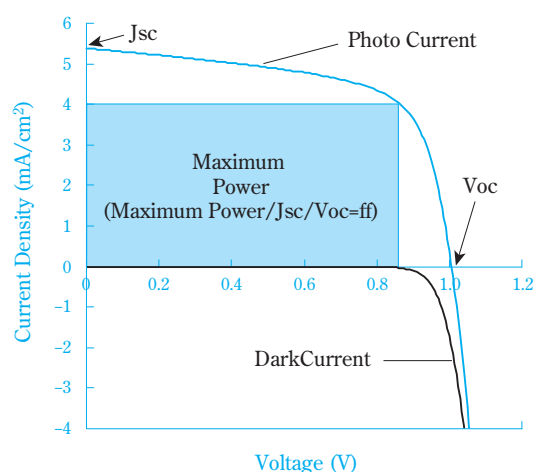


Fig. 7 The I-V curve in dark and under illumination and the parameters of solar cell

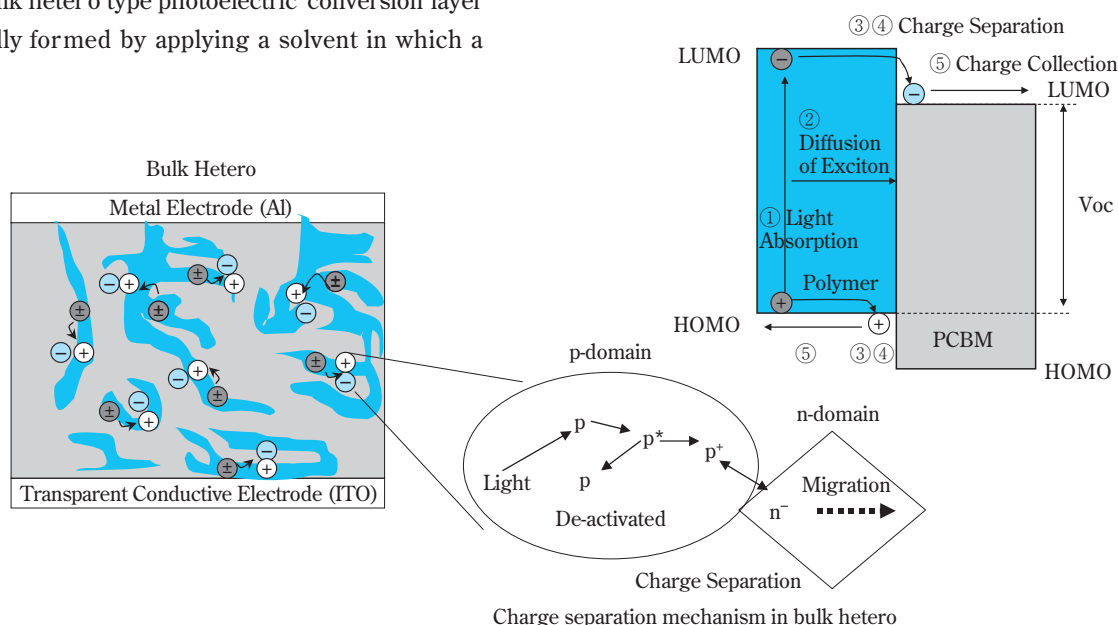


Fig. 6 Device structure and working mechanism of bulk hetero type OPV

of J_{sc} and V_{oc} are expressed by the fill factor (f_f), the power generating efficiency is given by:

$$\eta \text{ (generating efficiency)} = \frac{J_{sc} \text{ (short circuit current density)} \times V_{oc} \text{ (open circuit voltage)} \times f_f \text{ (fill factor)}}{\text{energy of incident light}} \quad (\text{Eq. 1})$$

Typically, a light source with an intensity of 100 mW/cm^2 that approximates the spectrum of sunlight is used as illumination for the incident light.

Moreover, since J_{sc} simply shows the efficiency of converting light to electrons and V_{oc} is related to the differential in energy for the p-type material and n-type material, they are useful as parameters when considering improving the characteristics from the standpoint of materials.

3. Current status and problems with organic thin film photovoltaics

The following is a more detailed description of the OPV photoelectric charge separation process shown in Fig. 6.

- (1) Organic molecules in the photoelectric conversion layer absorb light and excitons are generated
- (2) The excitons diffuse to the p/n junction interface
- (3) The excitons reaching the p/n junction interface are divided into ion pairs
- (4) Charges separate into free carriers (electrons and holes)
- (5) Free carriers migrate to electrodes after charge separation¹¹⁾

Considering this OPV power generation mechanism, we can obtain guidance for further increases in efficiency based on Eq. 1. To improve J_{sc} :

- i. Increasing amount of light absorption
- ii. Improving the efficiency of photoelectric charge separation
- iii. Preventing recombination of electric charges that have been separated

can be considered. For i, it is important to increase the range of absorption. For ii and iii, it is important to optimize the phase separation structure and realize higher mobility of carriers.

First, we will describe the current trends in development for i. As is shown in Fig. 8, the absorption threshold for poly-3-hexylthiophene (P3HT), which is a typical polymer that has been investigated up to now, is approximately 650 nm, but there is a wavelength range exceeding 2000 nm in the spectrum of sunlight. Large

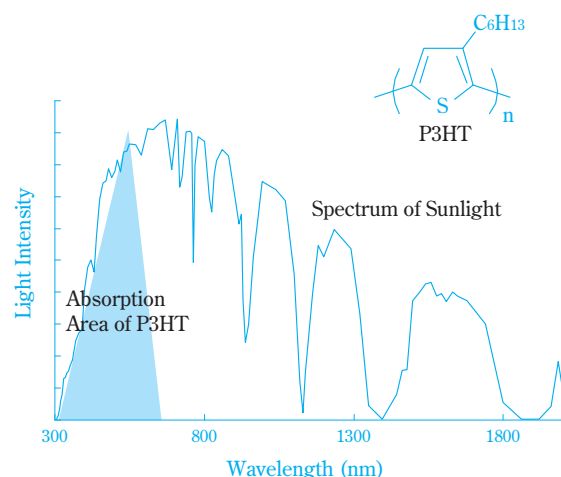


Fig. 8 Spectrum of sunlight and the absorption area of P3HT

amount of the sunlight is discarded without being absorbed. A recent trend is the active development of polymer materials that absorb more sunlight and absorb light in ranges of wavelengths where high efficiency can be expected.

Furthermore, for ii, there have been thorough investigations into controlling morphology using application solvents and additives according to the polymer since there is an optimal phase separation structure with a balance of photoelectric charge separation and ease of migration for free carriers after charge separation. In addition, for iii, increasing the flatness and the extent of conjugation between units constituting the polymer to improve the hole mobility of polymer have been investigated.

Furthermore, as is shown in Fig. 6, V_{oc} depends on the difference in the energy level for the highest occupied molecular orbital (HOMO) of the p-type material and the energy level of the lowest unoccupied molecular orbital (LUMO) of the n-type material. Therefore, to improve V_{oc} :

- iv. Development of polymers with low HOMO
- v. Development of fullerene derivatives with high LUMO

are effective. For iv, the HOMO level can be adjusted and a high V_{oc} achieved by introducing electron accepting and electron donating substituents into the conjugated polymer.

The fill factor is related to the internal resistance of the solar cell and the shunt resistance. Therefore, to improve the fill factor:

- vi. Developing materials with high mobility so the internal resistance is low

- vii. Reducing the number of film defects and increasing the purity of materials so that the parallel resistance for the equivalent circuit for the device is increased are effective.

Rapid improvements in efficiency have been achieved recently by controlling these factors well, making use of the characteristic that the polymers can be designed freely with conjugated polymers.

4. Example of p-type conjugated polymer development

A typical example of the most advanced, high performance, long wavelength absorbing conjugated polymers being investigated worldwide is shown in Fig. 9. Historically, development of materials has started with polythiophene derivatives and polyphenylene derivatives, but currently, a variety of materials are being used.

In terms of molecular design for long wavelength absorbing conjugated polymers, most carry out polymerization that alternates acceptor units and donor units. These reduce the bandgap (difference in HOMO and LUMO), and are effective in achieving a longer absorption wavelength. Furthermore, many units for which high mobility can be expected, such as those used in organic transistor materials are being used, and mobility is being improved so as to be effective for photoelectric charge separation. Among these conjugated polymers, there have been reports of achieving longer absorption wavelengths in the neighborhood of 900 nm. However, when films were simply grown with polymer P1 having a transannular structure with a methylene group over a thiophene ring, the efficiency was held to approximately 2%. However, with the addition of several

percent octanedithiol or diiodooctane, it reached 5.5%.¹²⁾ This was explained as being because it was possible to optimally grow phase separation structures. There has been a report of the world's highest level of efficiency of 6.5% in tandem cells using these polymers.¹³⁾ With this success as an impetus, similar polymers having transannular bithiophene units like those shown in P2 and P3 have been proposed one after another, and they have been reported to have efficiencies of 5.1% and 2.18%, respectively.^{14), 15)}

Among these materials, there have been reports of 7.4% by effectively carrying out control of mobility, phase separation and HOMO in P4 and P5.^{16), 17)}

In terms of the fluorene polymers that are often used as units that are dissolvable in solvents, longer wavelengths up to the neighborhood of 650 nm in the absorption threshold and an efficiency of 4.5% have been reported with ones that have a thiophene-benzothiadiazole-thiophene unit (RBT) like P6.¹⁸⁾ With polymer P7, which has a backbone similar to RBT, an absorption threshold in the neighborhood of 640 nm and an efficiency of 5.5% have been reported. This efficiency was achieved by changing the ratio of the solvent mixture of chloroform and chlorobenzene and optimizing the phase separation structure.¹⁹⁾

Status of Thin Film Organic Photovoltaics at Sumitomo Chemical

1. History of development of thin film organic photovoltaics at Sumitomo Chemical

Fig. 10 shows the history of development of conjugated polymer materials at Sumitomo Chemical. OPVs

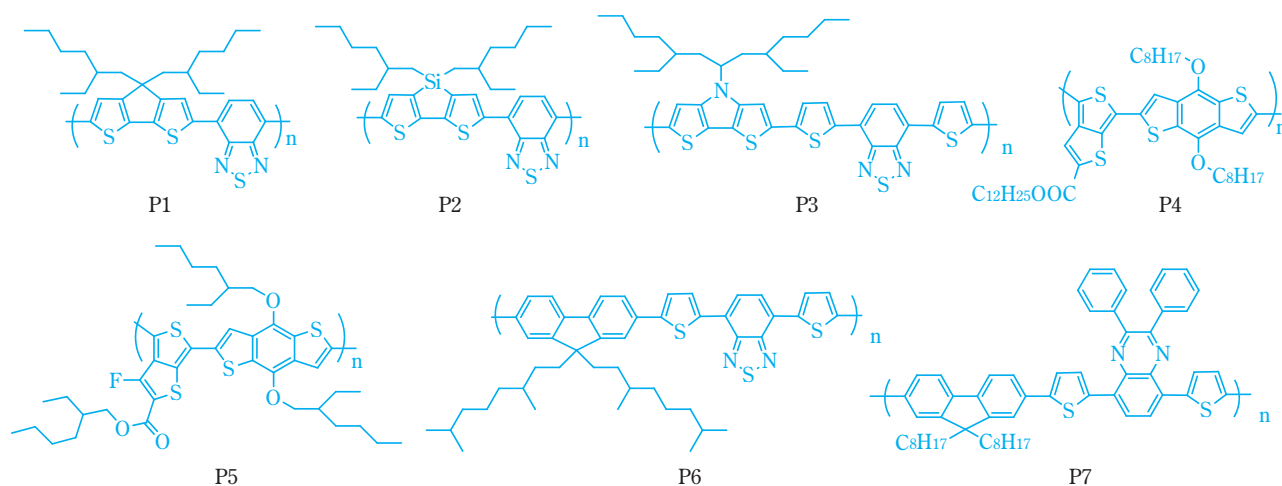


Fig. 9 Examples of highly efficient p-type polymers

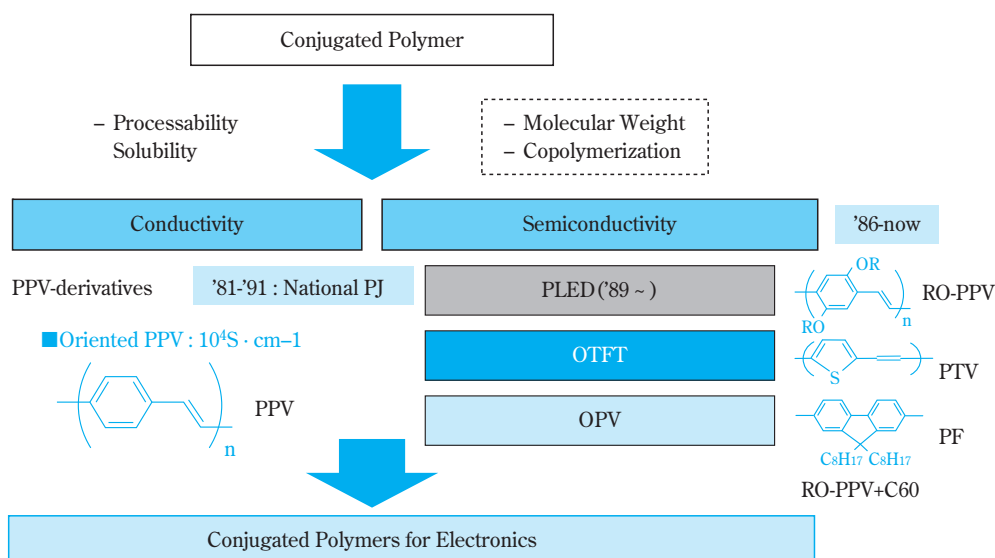


Fig. 10 History of development of conjugated polymer at Sumitomo Chemical

have evolved from research and development on conductive polymers as have PLEDs. Development was started on conductive polymers in 1981, but since up to that time conjugated polymers were insoluble in solvents, development was carried out placing importance on their forming properties. Since the polyphenylene vinylene that was developed could be molded in a film, its semiconductor characteristics were a field other than conductivity that was interesting. Investigations into applications in photoelectric fields also started since it could be molded into a film. Out of this, organic LEDs, organic transistors and photoelectric conversion devices were discovered. From this history it can also be said that PLED and OPV materials have the same technical foundations. PLED materials are materials that show a strong fluorescence in visible light, but polymer OPV materials are materials that exhibit absorption from visible light to the infrared range. Therefore, a different molecular design is necessary for the structure of the monomers that are used, but there is a great deal of commonality in the polymerization methods and production of devices. A great deal of technology, such as knowledge about the correlation between the functions being fostered in PLED material development and molecular design, techniques for uniform formation of organic films and techniques for synthesizing highly pure polymer materials, has accumulated, and this is also a driving force in the development of high-performance OPVs at Sumitomo Chemical.

Based on this technology, Sumitomo Chemical has been the first worldwide to be successful in exceeding

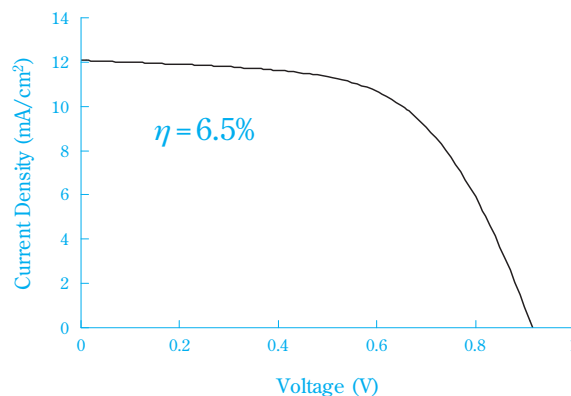


Fig. 11 The result of efficiency of OPV measured at Sumitomo Chemical

6% (Sumitomo Chemical measurements, **Fig. 11**). In addition, precise measurements of efficiency were made jointly with the National Institute of Advanced Industrial Science and Technology (AIST), and an efficiency close to this has been confirmed.

Currently, along with radically reassessing materials to achieve efficiencies of 10% or greater, which are the target for practicality, we are carefully examining J_{sc} and V_{oc} as they relate to efficiency, fill factor and material structure, and the relationship between purity and microphase separation structure. We are carrying out investigations into increased efficiency based on this knowledge and the results of analyzing the mechanisms. Furthermore, to get an early grasp on the problems for making practical OPVs, we are carrying out investigations into production processes while making use of knowledge regarding PLED device development.

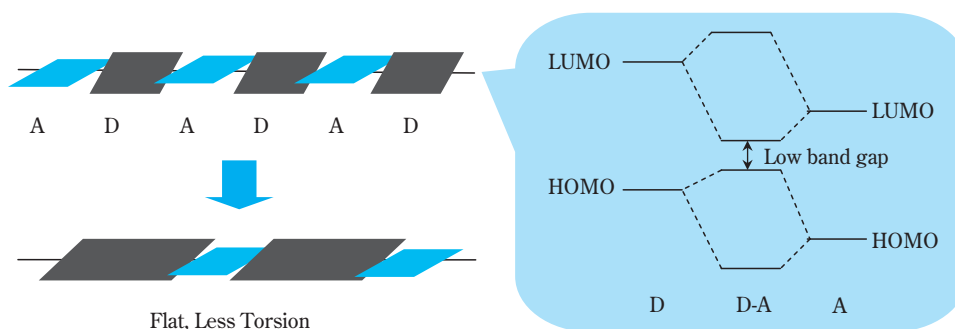


Fig. 12 The schematic illustration of molecular design of low band gap polymers

2. Status of material development

As is shown in **Fig. 12**, the basic molecular designs of materials that absorb long wavelengths are designs carried out to reduce the bandgap by combining donor units and acceptor units and give a high degree of flatness with a further control of the twisting of molecular chains. Molecules with greater flatness have stronger interactions between molecules, and we can expect higher mobility.

New materials under development through these investigations have reached an absorption threshold of 900 nm. They can absorb a wider range of sunlight, and the efficiency is expected to exceed 20%. Moving forward, we are thinking in terms of reaching an efficiency that exceeds 10% since by improving J_{sc} through the morphology control that will be discussed in the following, improving V_{oc} by controlling HOMO and LUMO using backbone modifications and investigating improvements in fill factor by increasing mobility.

3. Status of developments in morphology control

It is important not only to increase in the amount of light absorbed for increasing the efficiency but also to efficiently bring about photoelectric charge separation and charge transport. Since the average distance for free movement of excitons is approximately 10 nm, the p/n interface must be formed at approximately the same size. We have observed the morphology using a transmission electron microscope (TEM) to establish a method for controlling the formation of this microphase separation structure.

We investigated a method for processing TEM images and digitizing interface length as a method for quantifying the phase separation structure. The results are shown in **Fig. 13**. We found that there was a clear correlation between this interface length and efficiency, and we found that there was an optimal point

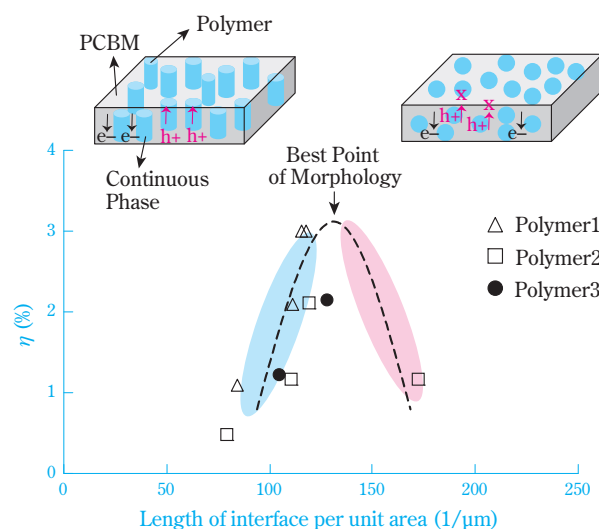


Fig. 13 Relation between morphology and efficiency

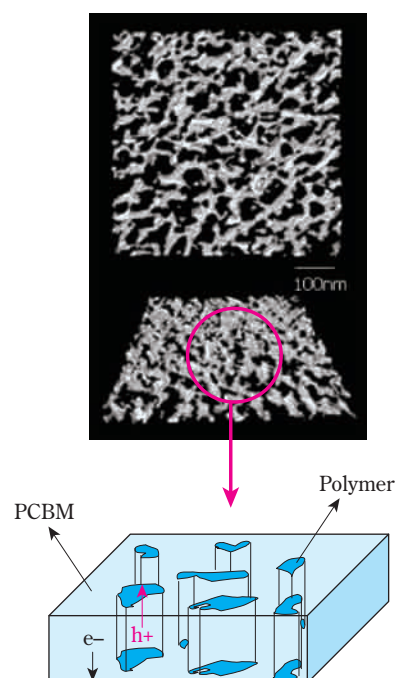


Fig. 14 TEM Tomography of OPV active layer

for interface length. The formation of the interface is insufficient when the interface length is too short, so the charge separation efficiency is poor. The interface formation is sufficient when the interface length is too large, but it is thought that the free carrier movement deteriorates because of insufficient formation of the continuous phase. **Fig. 14** shows a TEM morphology image of observations in the neighborhood of the optimal point for interface length. As predicted, we found that an island structure of microphase separation is seen, and continuous phases for each of the domains are formed in the direction of the film thickness. An ideal morphology is formed. We think that interface length is suitable as an indicator of morphology.

Next, we investigated the establishment of a morphology control method using interface length. Since the microphase separation structure is thought to be related to the solubility of the polymers that are p-type material and the n-type material (PCBM) in solvents, we investigated the relationship between the solvents having various solubility parameters (SP value) and interface length. We found that the closer the SP value of the solvent used was to PCBM, the smaller the phase separation structure was and the longer the interface length. This was estimated to be the primary cause of precipitation of the p-type molecules from the solution. In this manner, we were able to establish a method for controlling the morphology using solvents having various SP values.

As a result of investigating low band gap polymers and morphology control methods as described above, we achieved the world's highest values for a single device with J_{sc} at 16 mA/cm^2 and an efficiency of approximately 7%.

4. Assurance of reliability

Besides the conversion efficiency, assurance of reliability is also important for making OPVs practical. As a step toward this, we have begun measurements of life with outdoor exposure and continuous exposure to light indoors using solar simulators with systems that make use of typical p-type polymers PCBM (**Fig. 15**). The horizontal axis is total light intensity. There are different results for the rate of reduction in efficiency indoors and outdoors, and after one month of outdoor exposure we couldn't find that there is a clear reduction in efficiency. On the other hand, in the tests of continuous exposure indoors, we found reductions in efficiency due to a reduction in J_{sc} in particular. We measured the infrared absorption spectrum to examine the chemical changes in the material due to exposure to light, but we saw no changes that could be detected. Therefore, we presumed that the causes of deterioration were differences in the phase separation structure and changes in the electrode interfaces. The investigation has just gotten started, but the current value flowing is on about the same order as PLEDs, and it is presumed that most of the deterioration mechanisms are similar in that they pass through the excited state. Therefore, we think that we can quickly improve reliability if we make use of our knowledge of PLEDs.

One of the important problems for assuring reliability is that a method for predicting the life of OPVs has not been established. Since it is assumed that the methods used with silicon solar cells for the materials and power generation principles used cannot be applied as it is to OPVs, it is important to identify the deterioration modes peculiar to OPVs and establish new methods for predicting their life. We plan to accumulate data under various conditions, such as device structure, elucidate

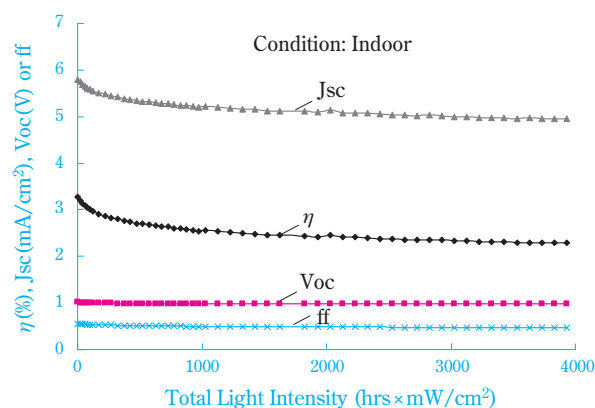
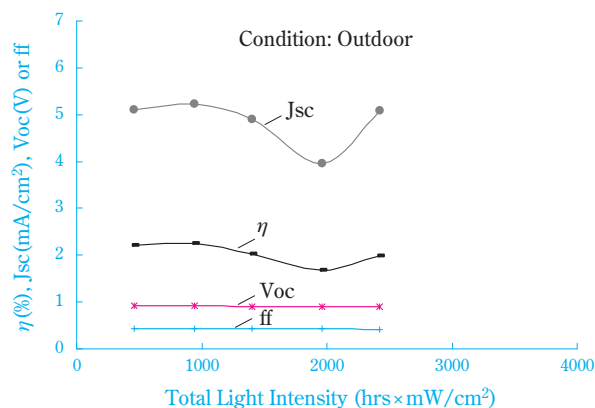


Fig. 15 Comparison of stability under between indoor and outdoor condition

the mechanism of deterioration, establish a life prediction method by comparing the life in outdoor exposure and accelerated indoor testing and increase a life based on these.

Future Outlook

Silicon solar cells are widely disseminated, but the energy produced by power generation using solar cells is only 0.1% or less of energy consumed. With the increase in concern for environmental problems, there are further expectations for the dissemination of solar cells, but a breakthrough is necessary for replacing current power generating systems. OPVs are thought to hold the possibilities for an important breakthrough in the field of solar cells. In addition to improving efficiency and assuring reliability, a key is developing roll-to-roll processes. We are planning to achieve these and make an early entry into the market.

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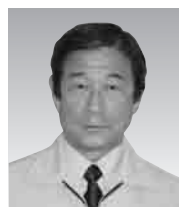
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