Bipolar Polymer Semiconductor Blends of C_{60}-End-Capped Poly(4-diphenylaminostyrene) and Poly(4-diphenylaminostyrene): One-Pot Synthesis and Charge-Transport Properties

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ABSTRACT: Three types of fullerene (C_{60})-end-capped poly(4-diphenylaminostyrene) (C_{60}–PDAS) and poly(4-diphenylaminostyrene) (PDAS) blends were prepared to investigate their potential as bipolar polymer semiconductors. The concentration of C_{60} in the C_{60}–PDAS/PDAS blends strongly affected the hole and electron drift mobility values; the hole drift mobility decreased with an increase in the C_{60} concentration. However, the electron drift mobility increased with an increase in the C_{60} concentration. The hole and electron drift mobility values were almost the same for the 1/2 C_{60}–PDAS/PDAS blend; therefore, this polymer blend was thought to be a bipolar polymer semiconductor. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 3433–3438, 2011

Key words: anionic polymerization; blends; charge transport; conducting polymers; fullerenes

INTRODUCTION

Among the triphenylamine derivatives, poly(4-diphenylaminostyrene) (PDAS) has generated considerable interest because of its growing potential as a stable and soluble hole-transport semiconducting polymer for optoelectronic applications.[1–11] For such applications, it is important to characterize the relationship between the polymer chain structure and properties. Therefore, a number of polymerization studies of 4-diphenylaminostyrene (DAS), the monomer of PDAS, have been carried out with anionic methods[1,3] and radical and living radical methods[1,2,4–11] to obtain PDAS with a well-defined and well-controlled polymer chain structure. However, in these previous studies, the controlled polymerization of DAS was quite difficult, even with living radical polymerization.

Recently, we attempted the anionic polymerization of DAS to obtain PDAS with a well-defined polymer chain structure.[12–15] As a result, the first successful example of the living anionic polymerization of DAS with the *tert*-butyllithium (*t*-BuLi)/*N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) system was discovered (Scheme 1),[12] and the stereoregularity of PDAS was also revealed.[12,14] Subsequently, we examined the grafting reaction of the poly(4-diphenylaminostyryl)lithium (PDASLi)/TMEDA system with a fullerene (C_{60}), and C_{60}-end-capped poly(4-diphenylaminostyrene) (C_{60}–PDAS), which consists of one PDAS molecule bonded to one C_{60} molecule at the polymer chain end, was successfully prepared (Scheme 2).[13]

With respect to C_{60}–PDAS, it was expected that the C_{60} molecule bound at the polymer chain end would have a strong effect on the charge-transport properties of PDAS because C_{60} itself has excellent hole and electron drift mobility.[16] Therefore, the possibility that C_{60}–PDAS as a bipolar polymer semiconductor could be used in organic field effect transistors and organic photovoltaic cells was examined.

In this article, we report bipolar polymer semiconductor blends of C_{60}–PDAS and PDAS. The one-pot synthesis and charge-transport properties of the blends are also described in detail.

EXPERIMENTAL

Materials

Toluene (≥99.8%) and TMEDA (≥99.5%) were refluxed over calcium hydride (95%) and then distilled under dry argon. C_{60} (99.5%) was washed with tetrahydrofuran (THF) and dried under reduced pressure. All other reagents were used as received unless otherwise stated. DAS was prepared via a

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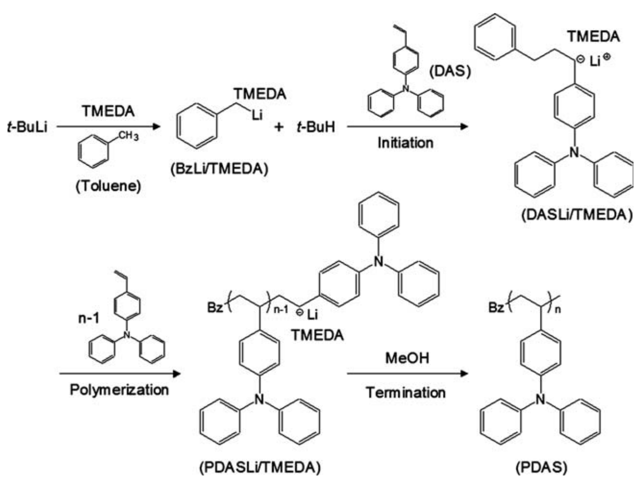


Scheme 1 Living anionic polymerization of DAS with the *t*-BuLi/TMEDA system.

standard Wittig reaction as previously reported.[12] All reagents were purchased from Aldrich.

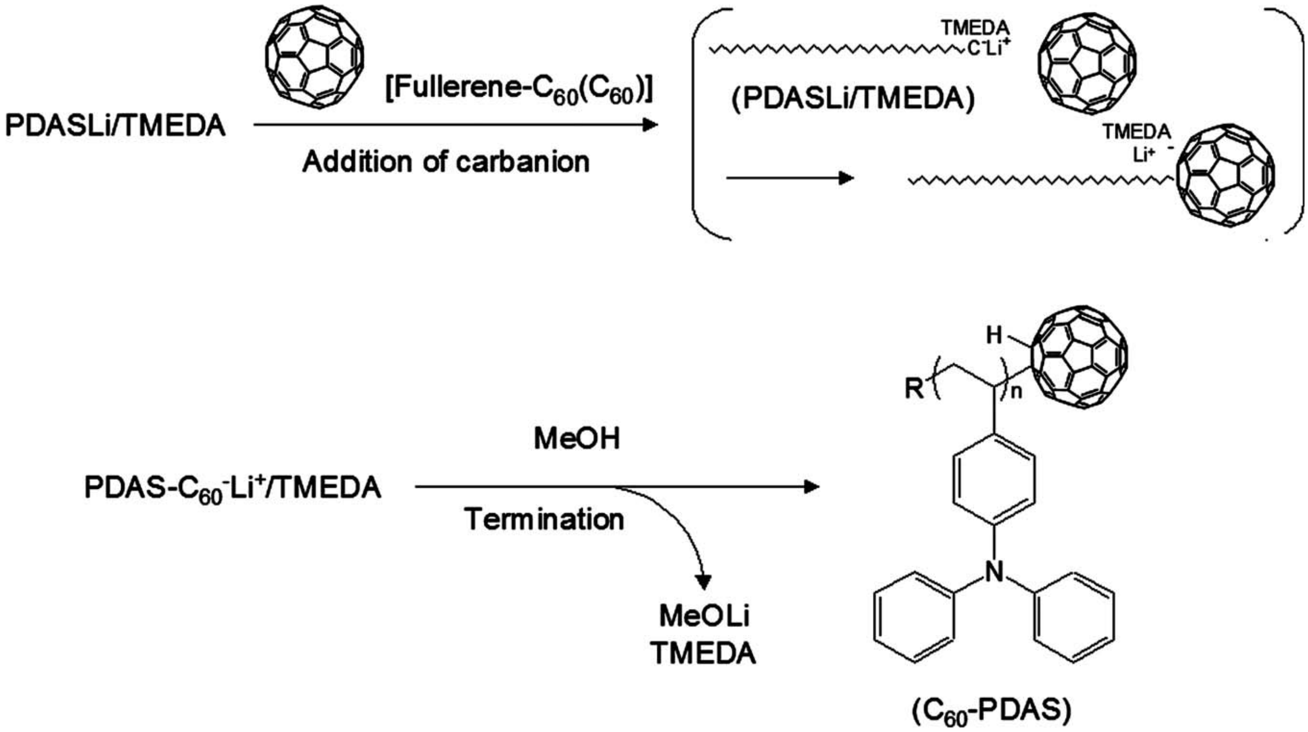
Preparation of the C_{60}–PDAS/PDAS blends

A well-dried 50-mL Schlenk tube was purged with dry argon, and then toluene (5.0 mL) was added at room temperature (ca. 25°C) with a syringe. *t*-BuLi (1.70 mol/L of pentane) was injected into this solution with a syringe. TMEDA (1.00/1.25 *t*-BuLi/TMEDA) was then added to the solution, and the mixture was stirred for 10 min to form the benzyllithium (BzLi)/TMEDA system. DAS (10.0 mL of a 0.185 mol/L solution in toluene) was added to the solution, and the reaction mixture was magnetically stirred for 2 h ($[DAS]_0/[Li]_0 = 7.4$); this resulted in the PDASLi/TMEDA system (Scheme 1).

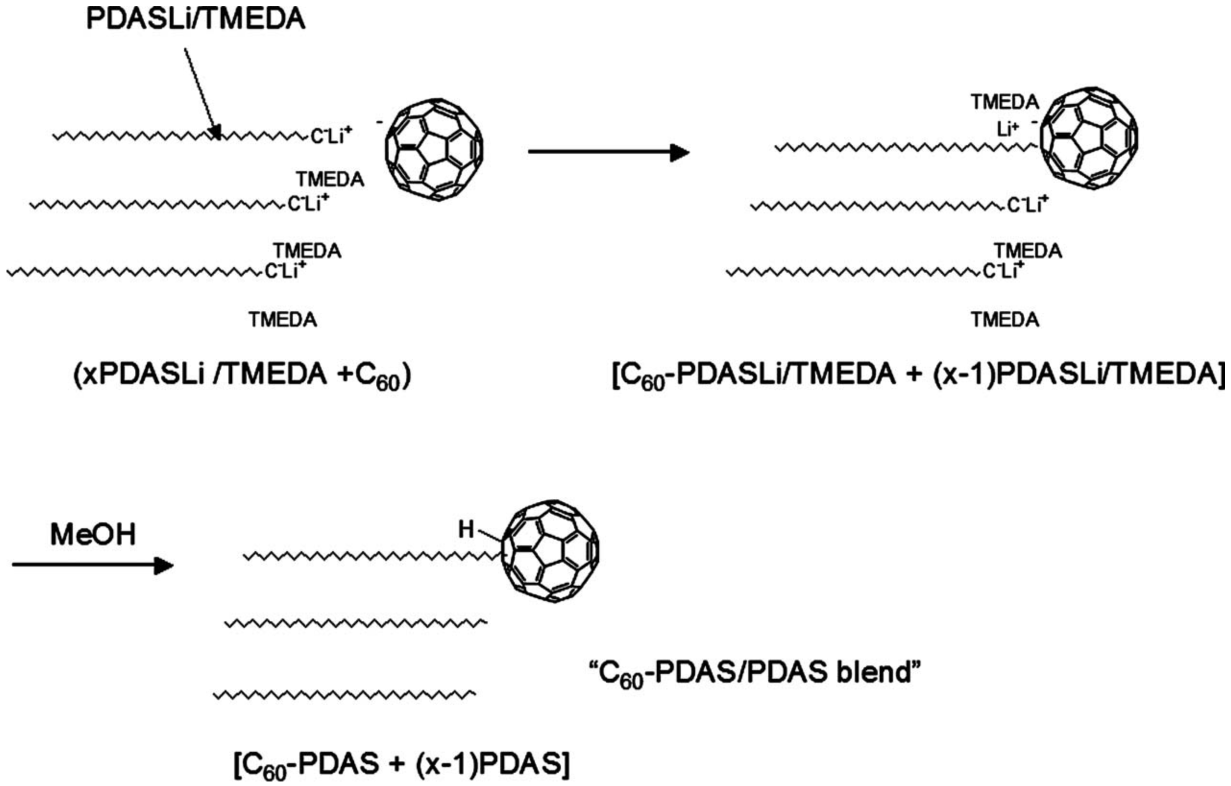
Subsequently, an excess amount of the PDASLi/TMEDA system was added to a toluene solution of C_{60} (30.0 mg of C_{60} per 20.0 mL of toluene) with a syringe (1/3–1/6 C_{60}/Li), and the reaction mixture was magnetically stirred at room temperature under dry argon for 24 h. Dry methanol (MeOH; ≥99.8%) was then added to the reaction mixture in an amount equimolar to the number of lithium atoms present to terminate the reaction. The reaction mixture was then poured into a large volume of MeOH (≥99.6%) to precipitate the polymer, which was then separated by filtration. The product was dried under reduced pressure at room temperature for 24 h to yield a brown, powdery substance (Scheme 3).

Measurements

The number-average molecular weight (M_n), weight-average molecular weight (M_w), and polydispersity index (PDI; i.e., M_w/M_n) were determined with a gel permeation chromatography apparatus equipped with a differential refractive-index detector and a Shimadzu Shim-pack GPC-80M column (column length = 300 mm, diameter = 8 mm, effective molecular weight range = 100–4,000,000) at 40°C (Shimazu, 1,Nishinokyo-Kuwabara-cho, Nakagyo-ku, Kyoto 604-8511, Japan). THF was used as the eluent at



Scheme 2 Synthesis of C_{60}–PDAS.



Scheme 3 One-pot synthesis of C_{60}–PDAS/PDAS blends.

a flow rate of 1.0 mL/min. A molecular weight calibration curve was obtained with polystyrene standards. Proton nuclear magnetic resonance (^{1}H-NMR) spectra of the polymers (ECA500, JEOL, 1-2 Musashino 3-chome Akishima, Tokyo 196-8558, Japan) were measured in deuterated chloroform at 500 MHz. The drift mobility was determined with a time-of-flight method with a device consisting of an aluminum/titanium phthalocyanine/polymer film/gold cell, a xenon flash lamp (L2359, Hamamatsu Photonics, 325-6 Sunayama-cho, Naka-ku, Hamamatsu City, Shizuoka 430-8587, Japan), and a digitizing oscilloscope (DSO630, Gould, 8333 Rockside Road, Valley View, Ohio (OH), 44125-6104, USA). The thickness of the polymer films was determined with a profilometer (Dektak II, Solan, 112 Robin Hill Rd, Goleta, CA 93117, USA).

RESULTS AND DISCUSSION

One-pot synthesis of the C_{60}–PDAS/PDAS blends

We have previously reported that in the reaction of an excess amount of the PDASLi/TMEDA system with C_{60}, only one PDASLi molecule selectively binds to one C_{60} molecule at the polymer chain end.[13] The addition of a second PDASLi molecule to C_{60} does not occur. As a result, C_{60}–PDAS/PDAS blends are formed in the reaction mixture (Scheme 3). That is, C_{60}–PDAS/PDAS blends can be obtained by a one-pot synthesis, and the molar ratio of C_{60}–PDAS to PDAS is controlled by the molar ratio of the PDASLi/TMEDA system to C_{60} in the reaction mixture. Therefore, three types of C_{60}–PDAS/PDAS blends were prepared with several molar ratios of the PDASLi/TMEDA system to C_{60} (1/6, 1/4, or 1/3 C_{60}/PDASLi). Pure PDAS was also prepared by living anionic polymerization for comparison. The results are summarized in Table I.

M_n for each original PDAS sample was approximately 2000 g/mol because of the nature of the living anionic polymerization of DAS with the BzLi/TMEDA system,[12] and the ratio of isotactic structures to syndiotactic structures in each polymer chain was approximately 7/3 (Fig. 1).[14] M_n for each reaction product (i.e., the C_{60}–PDAS/PDAS blend) was somewhat increased in comparison with the original PDAS, and this indicated the formation of C_{60}–PDAS in the polymer blends (1/5, 1/3, or 1/2 C_{60}–PDAS/PDAS). In addition, each product was completely soluble in THF, and this suggested 100% conversion from C_{60} to C_{60}–PDAS.[13] The concentrations of C_{60} in blends 1, 2, and 3 were 5.6, 8.2, and 11 wt %, respectively.

Drift mobility of the C_{60}–PDAS/PDAS blends

To examine the drift mobility of each C_{60}–PDAS/PDAS blend and pure PDAS, four different transparent

TABLE I
One-Pot Synthesis of C_{60}–PDAS/PDAS Blends

Sample	C_{60}/PDASLi (molar ratio)	Original PDAS(Li)[a] M_n (g/mol)	Original PDAS(Li)[a] PDI	Reaction product (C_{60}–PDAS/PDAS blend)[b] M_n (g/mol)	Reaction product (C_{60}–PDAS/PDAS blend)[b] PDI	C_{60}–PDAS/PDAS (molar ratio)	C_{60} concentration (wt %)[c]
Blend 1	1/6	1890	1.10	2250	1.30	1/5	5.6
Blend 2	1/4	1930	1.11	2410	1.22	1/3	8.2
Blend 3	1/3	1920	1.12	2460	1.20	1/2	11
PDAS	—	1980	1.10	—	—	—	0

[a] Polymerization was performed in toluene under dry argon at room temperature for 2.0 h ($[\mathrm{DAS}]_0/[\mathrm{Li}]_0 = 7.4$).

[b] The addition of the PDASLi/TMEDA system to C_{60} was performed in toluene under dry argon at room temperature for 24 h.

[c] $C_{60} = 720$; PDAS $= 7.4 \times 271$; C_{60}-PDAS/PDAS (= 1/5, 1/3, or 1/2) = PDAS/C_{60} (= 6, 4, or 3); C_{60} concentration = $720/720 + (7.4 \times 271) \times$ PDAS/C_{60} (mol/mol).

polymer films with thicknesses of the order of 1.0–3.0 μm were prepared by the bar-coating method with *o*-xylene solutions of each sample (0.03 g of the sample per 1.00 g of *o*-xylene).

The drift mobility values of the films of each C_{60}–PDAS/PDAS blend (blends 1–3) and pure PDAS were determined with a standard time-of-flight method and were calculated according to the following equation:

$$\text{Drift mobility} = L^2/t_T V$$

where L is the polymer film thickness, t_T is the transit time, and V is the applied voltage. The values of t_T were determined from plots of the logarithm of the current versus the logarithm of the time.

The logarithms of the hole drift mobility values for PDAS and blends 1–3 are plotted against the square root of the applied field [$(\mathrm{V/cm})^{1/2}$] in Figure 2. The results show that the concentration of C_{60} in the polymer films had a strong effect on the hole drift mobility of PDAS. The hole drift mobility of PDAS was of the order of 10^{-4}–10^{-5} cm^2/V s with a negative slope, whereas those for blends 1–3 were of the order of 10^{-4} cm^2/V s with a negative slope. A decrease in the hole drift mobility was observed with an increase in the C_{60} concentration in the polymer films (PDAS > blend 1 > blend 2 > blend 3).

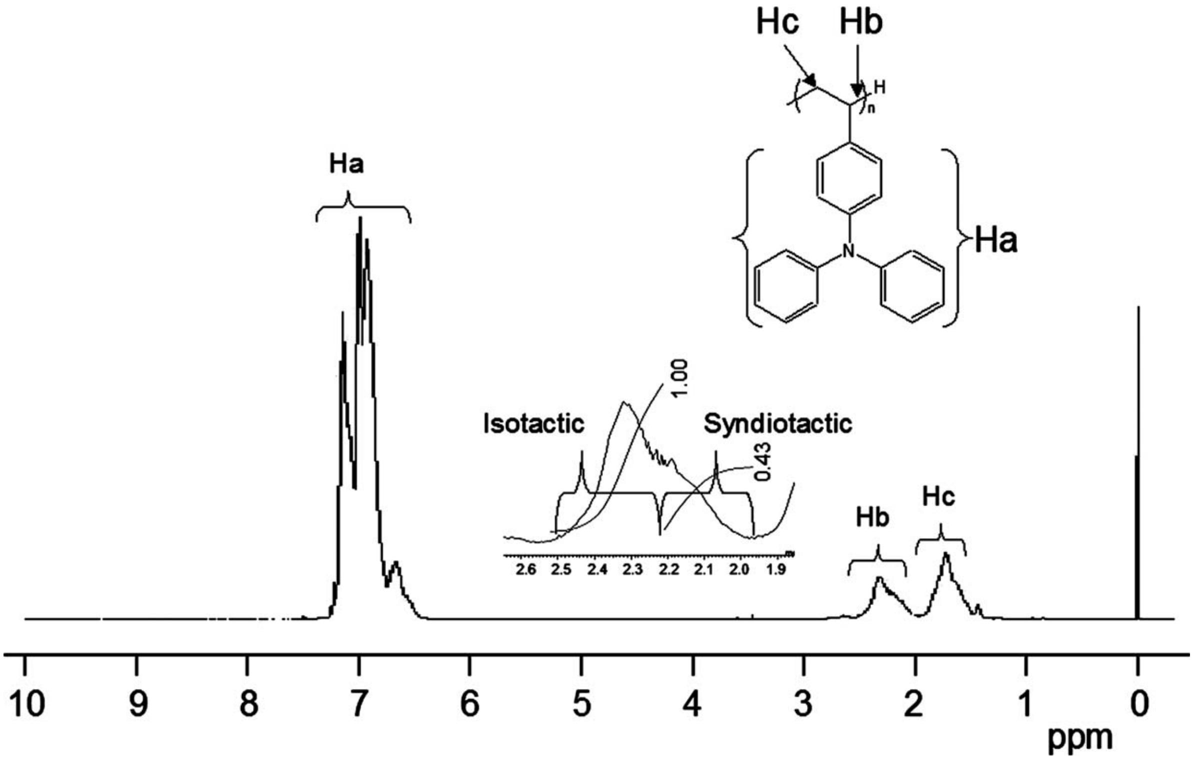


Figure 1 Typical ^{1}H-NMR spectrum of PDAS measured in a 3.0 wt % solution of deuterated chloroform at 50°C (M_n = 1980, PDI = 1.10).

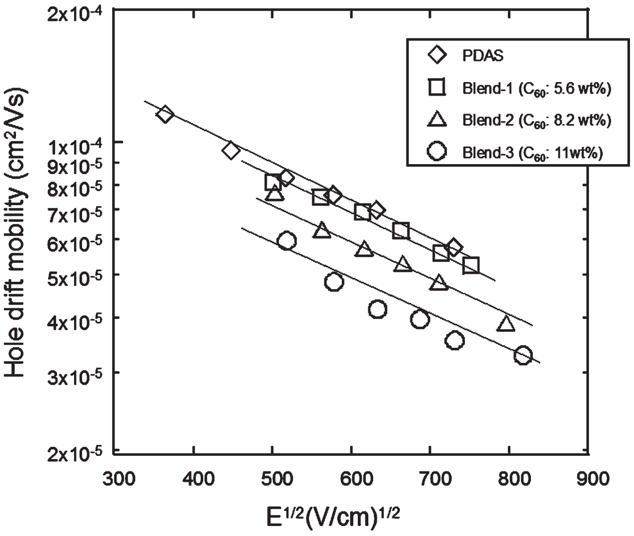


Figure 2 Dependence of the hole drift mobility on the square root of the applied field ($E^{1/2}$) for thin films of PDAS and C_{60}–PDAS/PDAS blends (blends 1–3).

Therefore, C_{60} in the polymer films seemed to prevent the hole drift mobility of PDAS.

rFigure 3 shows the electron drift mobility values for PDAS and blends 1–3 plotted against the square root of the applied field [$(V/cm)^{1/2}$]. Although the electron drift mobility values for PDAS and blends 1–3 were of the order of 10^{-5} cm^2/V s with a negative slope, an increase in the electron drift mobility was observed with an increase in the C_{60} concentration of the polymer films (PDAS < blend 1 < blend 2 < blend 3). Thus, C_{60} in the polymer films appeared to enhance the electron drift mobility of PDAS.

The results presented in Figures 2 and 3 suggest that the C_{60}–polymer networks provide a conduction path for electrons, whereas holes are transported through polymer-only paths, as reported for other polymers and C_{60} blends.[17–19] In addition, the hole and electron drift mobility values of C_{60}–PDAS/PDAS blends can be controlled by the concentration of C_{60}. That is, a C_{60}–PDAS/PDAS blend could potentially behave as a bipolar polymer semiconductor.

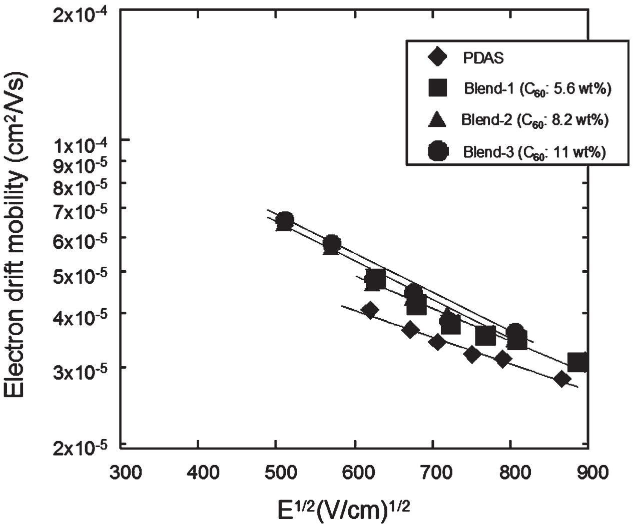


Figure 3 Dependence of the electron drift mobility on the square root of the applied field ($E^{1/2}$) for thin films of PDAS and C_{60}–PDAS/PDAS blends (blends 1–3).

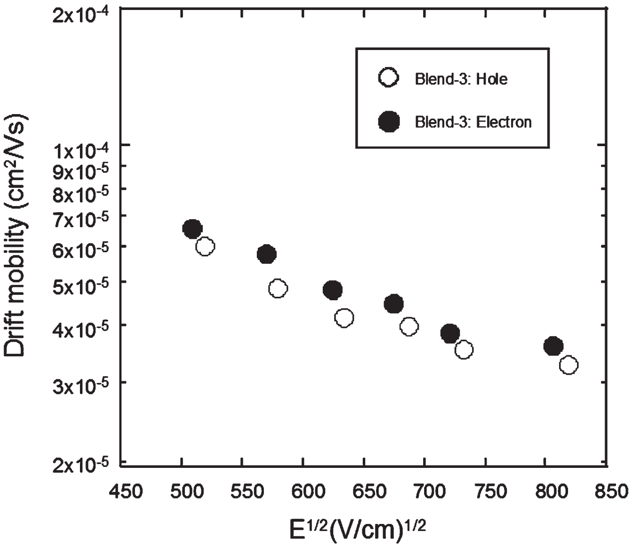


Figure 4 Dependence of the hole and electron drift mobility on the square root of the applied field ($E^{1/2}$) for thin films of C_{60}–PDAS/PDAS blend 3.

Subsequently, the hole and electron drift mobility values for each C_{60}–PDAS/PDAS blend were replotted against the square root of the applied field [$(V/cm)^{1/2}$]. Among the three polymer blends, the hole and electron drift mobility values for blend 3 were almost the same, and these were of the order of 10^{-5} cm^2/V s with a negative slope, as shown in Figure 4. Therefore, blend 3, which consisted of 1/2 C_{60}–PDAS/PDAS, was thought to behave as a bipolar polymer semiconductor.

CONCLUSIONS

The synthesis and charge-transport properties of C_{60}–PDAS/PDAS blends were examined in an attempt to obtain a bipolar polymer semiconductor. Three C_{60}–PDAS/PDAS blends were prepared by one-pot syntheses using living anionic polymerization. The M_n value of each original PDAS sample was approximately 2000 g/mol, and the ratio of isotactic structures to syndiotactic structures in each polymer chain was approximately 7/3. The hole and electron drift mobility values of the C_{60}–PDAS/PDAS blends could be controlled by the C_{60} concentration. A decrease in the hole drift mobility was observed with an increase in the C_{60} concentration, whereas an increase in the electron drift mobility was observed with an increase in the C_{60} concentration. The hole and electron drift mobility values for the 1/2 C_{60}–PDAS/PDAS blend containing 11 wt % C_{60} were almost the same; therefore, this polymer blend was thought to behave as a bipolar polymer semiconductor.

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