Synthesis and Carrier Transport Properties of Triarylamine-based Amorphous Polymers for Organic Field-effect Transistors

Takeshi Yasuda,*[1,2] Takao Suzuki,[3] Mitsuru Takahashi,[3] and Tetsuo Tsutsui[4]
[1]*Exploratory Materials Research Laboratory for Energy and Environment, National Institute for Materials Science (NIMS),*
1-2-1 Sengen, Tsukuba 305-0047
[2]*PRESTO, Japan Science and Technology (JST) Agency, 5 Sanbancho, Chiyoda-ku, Tokyo 102-0075*
[3]*Tosoh Corporation, 4560 Kaisei-cho, Shunan 746-8501*
[4]*Institute for Materials Chemistry and Engineering, Kyushu University, 6-1 Kasugakoen, Kasuga 816-8580*

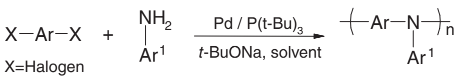
(Received August 13, 2009; CL-090750; E-mail: YASUDA.Takeshi@nims.go.jp)

Twenty-three kinds of triarylamine-based polymers, which are a new class of p-type semiconducting materials for organic field-effect transistors (OFETs), were synthesized by Pd-catalyzed amination of the corresponding aryldihalide and arylamine. All triarylamine-based polymers in this study exhibited p-channel behavior in OFETs, and field-effect hole mobilities ranged from 10^{-6} to $10^{-3}\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$.

Polycrystalline films of organic semiconductors have recently attracted considerable interest from the viewpoint of obtaining high carrier mobilities for organic field-effect transistors (OFETs).[1] Despite their lower carrier mobilities, amorphous organic thin films for OFETs are also interesting for several reasons.[2] First, morphological effects, which often lead to poor reproducibility of the performance of polycrystalline film OFETs, are not a major concern. Amorphous films without any grain boundaries lead to the spatial homogeneity of transport properties with high reproducibility of the data. Second, amorphous organic thin films can be fabricated by simple solution processes, such as spin-coating, screen printing, and inkjet printing.

In organic semiconductors that form amorphous films, triarylamine-based polymers are reported to be suitable materials for OFETs because they can be handled in air.[3] OFETs based on the semiconducting polymer and a low-*k* insulator remain stable and operate under ambient atmosphere with hole mobilities up to $10^{-2}\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$.[3] However, previous studies have examined only a few kinds of triarylamine-based polymers for OFETs.[3] Scheme 1 shows the general formula of a triarylamine-based polymer; by varying the π-conjugated main chain (Ar) or the pendant group (Ar^1), the highest occupied molecular orbital (HOMO) energy level and glass transition temperature can be influenced. The choice of the π-conjugated main chain or the pendant group is crucial for tuning the performance of OFETs. Therefore, in this study, we have designed and synthesized twenty-three kinds of triarylamine-based amorphous polymers (Figure 1), which are a new class of p-type semiconducting materials for OFETs, and investigated the performance of OFETs with the new polymers.

The polymers were synthesized by Pd-catalyzed amination of the corresponding aryldihalide and arylamine (Scheme 1).[4] By using this reaction, a wide range of triarylamine-based polymers was easily prepared with excellent yields under mild conditions. Among the polymers, only TSP-C11 and TSP-C21 were synthesized by using the Pd-catalyzed Suzuki coupling.[5] Polymer synthesis was controlled by using the end capping reagents introduced during the reaction to stop the polymer growth. The terminals of TSP-C11 and TSP-C21 were capped with biphenyl



$$X{-}Ar{-}X + \underset{Ar^1}{\overset{NH_2}{|}} \xrightarrow[t\text{-BuONa, solvent}]{Pd / P(t\text{-Bu})_3} \left(\underset{Ar^1}{\overset{}{Ar{-}N}}\right)_n \quad X{=}Halogen$$

Scheme 1. Synthesis of triarylamine-based polymers.

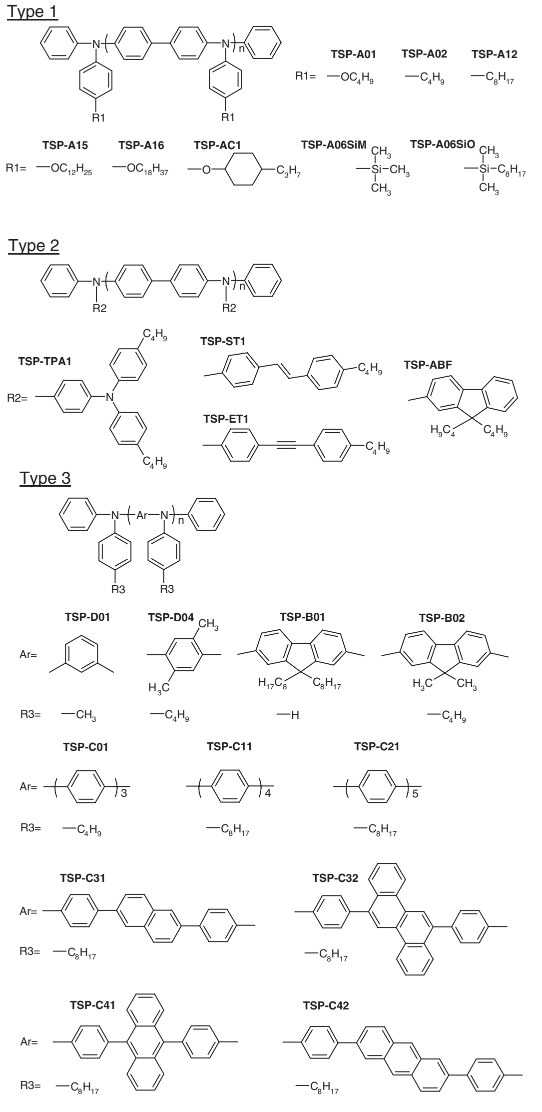


Figure 1. Molecular structure of triarylamine-based polymers.

groups, and the terminals of other polymers synthesized in this study were capped with phenyl groups.

The weight-average molecular weight (M_w) with the polydispersity index (M_w/M_n), the glass transition temperature, and HOMO energy levels were estimated and summarized as the physical and chemical properties of polymers.[5] We fabricated OFETs that had top-contact geometry.[6,7] All triarylamine-based polymers in this study exhibited p-channel behavior in OFETs, and field-effect hole mobilities ranged from 10^{-6} to $10^{-3}\,cm^2\,V^{-1}\,s^{-1}$. For example, OFETs based on the polymer with the chrysene unit in the conjugated main chain (TSP-C32) showed a field-effect hole mobility of $5.0 \times 10^{-6}\,cm^2\,V^{-1}\,s^{-1}$. On the other hand, the polymer with the biphenyl unit in the main chain (TSP-A12) exhibited a field-effect hole mobility of $8.0 \times 10^{-4}\,cm^2\,V^{-1}\,s^{-1}$.

To investigate the relationship between M_ws and the performance of OFETs, we prepared TSP-A02 with a M_w of 5500 and TSP-A02 with a M_w of 9400, and fabricated OFETs based on both materials. The field-effect hole mobility was $7.1 \times 10^{-4}\,cm^2\,V^{-1}\,s^{-1}$ for TSP-A02 ($M_w = 5500$) and $7.4 \times 10^{-4}\,cm^2\,V^{-1}\,s^{-1}$ for TSP-A02 ($M_w = 9400$). We did not expect a strong M_w influence on performances of OFETs that used materials listed in Table 1, which have M_ws in the 7300–24600 range.[5] Little difference in the mobilities was observed in OFETs based on type 1 and type 2 materials in Figure 1, which have different lengths of side alkyl chain or different pendant groups. The pendant groups did not change the OFET mobilities but changed the threshold voltages due to tuning of HOMO energy levels related to the hole injection barrier from Au source electrodes.[5]

Next, we investigated the relationship between the π-conjugated main chains (Ar in Scheme 1) of type 3 polymers (Figure 1) and the field-effect mobilities. Triarylamine-based polymers with short π-conjugation (TSP-D01 and -D04) or long π-conjugation (TSP-C01, -C11, and -C21) or bulky π-conjugated groups (TSP-C31, -C32, -C41, and -C42) had low field-effect mobilities compared to polymers with biphenyl units (TSP-A01 and -A12). Therefore, a suitable π-conjugation length and a suitable π-conjugated main chain size of a triarylamine-based polymer could improve the OFET performance. In order to form thin films of densely packed molecules, and then improve the OFET performance, a thermal treatment for some OFETs with triarylamine-based polymers was carried out at 100 °C under N_2 atmosphere for 12 h. After the treatment, the field-effect mobilities of OFETs using triarylamine-based polymers with bulky π-conjugated groups were much improved up to $1.6 \times 10^{-3}\,cm^2\,V^{-1}\,s^{-1}$.

In summary, we have demonstrated OFETs based on twenty-three kinds of triarylamine-based amorphous polymers, which are a new class of p-type semiconducting materials, and reported the relationship between the performance of OFETs and the molecular structure. These results provide a good strategy for molecular design of amorphous organic semiconductors for OFETs.

Table 1. OFET characteristics of organic semiconductors used in this study

Compound	FET hole mobility $/cm^2\,V^{-1}\,s^{-1}$	Threshold voltage /V	On/off current ratio
TSP-A01	5.3×10^{-4}	-15	6.7×10^3
TSP-A02	7.4×10^{-4}	-32	2.5×10^3
	(8.3×10^{-4})[a]	(-11)[a]	(3.7×10^3)[a]
TSP-A12	8.0×10^{-4}	-41	3.3×10^3
TSP-A15	7.8×10^{-4}	-22	2.2×10^3
TSP-A16	6.4×10^{-4}	-28	6.5×10^3
TSP-AC1	1.6×10^{-4}	-5	2.0×10^2
TSP-A06SiM	1.2×10^{-4}	-54	7.3×10^2
TSP-A06SiO	5.7×10^{-5}	-59	2.8×10^2
TSP-TPA1	2.0×10^{-4}	-15	1.5×10^3
TSP-ST1	5.6×10^{-5}	-45	3.2×10^2
TSP-ET1	5.0×10^{-4}	-35	1.6×10^3
TSP-ABF	2.0×10^{-4}	-45	8.1×10^2
	(4.6×10^{-4})[a]	(-19)[a]	(4.4×10^3)[a]
TSP-D01	6.4×10^{-6}	-52	3.0×10
TSP-D04	1.6×10^{-5}	$+3$	1.1×10^2
TSP-B01	2.3×10^{-4}	-18	8.0×10^2
TSP-B02	3.6×10^{-4}	-6	5.0×10^2
	(7.5×10^{-4})[a]	(-4)[a]	(7.5×10^3)[a]
TSP-C01	2.4×10^{-4}	-57	4.6×10^2
	(1.3×10^{-3})[a]	(-51)[a]	(5.6×10^3)[a]
TSP-C11	1.4×10^{-4}	-28	1.6×10^3
	(2.0×10^{-4})[a]	(-29)[a]	(2.4×10^3)[a]
TSP-C21	1.8×10^{-5}	-14	2.1×10^2
	(3.6×10^{-5})[a]	(-16)[a]	(4.1×10^2)[a]
TSP-C31	1.6×10^{-4}	-55	1.5×10^2
	(1.6×10^{-3})[a]	(-50)[a]	(1.2×10^3)[a]
TSP-C32	5.0×10^{-6}	-56	2.2×10
	(8.6×10^{-5})[a]	(-60)[a]	(2.8×10^2)[a]
TSP-C41	6.1×10^{-6}	-53	5.7×10
	(7.6×10^{-5})[a]	(-57)[a]	(3.6×10^2)[a]
TSP-C42[b]	2.5×10^{-4}	-46	1.1×10^3
	(6.4×10^{-4})[a]	(-44)[a]	(2.7×10^3)[a]

[a] After thermal treatment at 100 °C under N_2 atmosphere for 12 h. [b] Spin-coated from chlorobenzene solution.

References and Notes

1 K. Takimiya, Y. Kunugi, T. Otsubo, *Chem. Lett.* **2007**, *36*, 578; K. Kashiwagi, T. Yasuda, T. Tsutsui, *Chem. Lett.* **2007**, *36*, 1194; Y. Yamashita, *Chem. Lett.* **2009**, *38*, 870.

2 D. S. Chung, S. J. Lee, J. W. Park, D. B. Choi, D. H. Lee, J. W. Park, S. C. Shin, Y.-H. Kim, S.-K. Kwon, C. E. Park, *Chem. Mater.* **2008**, *20*, 3450; H. Kong, D. H. Lee, I.-N. Kang, E. Lim, Y. K. Jung, J.-H. Park, T. Ahn, M. H. Yi, C. E. Park, H.-K. Shim, *J. Mater. Chem.* **2008**, *18*, 1895.

3 J. Veres, S. D. Ogier, S. W. Leeming, D. C. Cupertino, S. M. Khaffaf, *Adv. Funct. Mater.* **2003**, *13*, 199; A. Das, R. Dost, T. Richardson, M. Grell, J. J. Morrison, M. L. Turner, *Adv. Mater.* **2007**, *19*, 4018; W. Zhang, J. Smith, R. Hamilton, M. Heeney, J. Kirkpatrick, K. Song, S. E. Watkins, T. Anthopoulos, I. McCulloch, *J. Am. Chem. Soc.* **2009**, *131*, 10814.

4 T. Yamamoto, M. Nishiyama, Y. Koie, *Tetrahedron Lett.* **1998**, *39*, 2367.

5 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

6 T. Yasuda, M. Saito, H. Nakamura, T. Tsutsui, *Chem. Phys. Lett.* **2008**, *452*, 110.

7 T. Yasuda, K. Fujita, H. Nakashima, T. Tsutsui, *Jpn. J. Appl. Phys.* **2003**, *42*, 6614.

Published on the web (Advance View) October 3, 2009; doi:10.1246/cl.2009.1040