REVIEW ARTICLE

Non-conjugated Polymers Containing Side-chain Groups as Potential Materials for Organic Light-emitting Diodes

Y. Shirota [a] and H. Kageyama [b]

Affiliations:

[a]   Osaka University, Osaka, Japan

[b]   Department of Electrical and Electronics Engineering, Faculty of Engineering, University of the Ryukyus, 1 Senbaru, Nishihara, Okinawa 903-0213, Japan

Corresponding Authors: Y. Shirota, E-mail: shirota@chem.eng.osaka-u.ac.jp;
H. Kageyama, E-mail: kageyama@tec.u-ryukyu.ac.jp

Abstract:

There have been extensive studies on organic light-emitting diodes (OLEDs) in view of both fundamental science and technological applications for full-color, flat-panel displays and lighting. Both small molecular materials and polymers have been studied for use as materials in OLEDs. This short review article focuses on non-conjugated polymers with side chain groups as potential materials for OLEDs. Concrete examples of non-conjugated pendant polymers that function as hole-transporting, electron-transporting, emitting, and host materials and the performance of devices using these materials are introduced from the recent literature.

Keywords: Organic Light-emitting Diode, Polymer with Side-chain Group, Hole-transporting Polymer, Electron-transporting Polymer, Emitting Polymer, Host Polymer for Emissive Dopant

1. Introduction

Since the pioneering works on organic light-emitting diodes (OLEDs) toward their practical use were reported,[1,2] OLEDs or organic electroluminescent devices have attracted a great deal of attention in view of both fundamental science and technological applications for full-color, flat-panel displays and lighting.[3,4] OLEDs have now been practically used in smartphones and televisions.

Electroluminescence (EL) originates from the exciton of an emissive material, i.e., the electronically excited-state of an emissive molecule, produced by the recombination of holes and electrons injected from the two respective electrodes. OLEDs are classified into fluorescence- and phosphorescence-based devices. As the statistical probability ratio of the generation of the triplet exciton to the singlet exciton is 3:1, the luminous efficiency of phosphorescence-based OLEDs is in principle three times

higher than that of fluorescence-based OLEDs. Since the finding of room-temperature phosphorescent emission for transition metal-complexes, e.g., platinum and iridium complexes,[5,6] high-performance phosphorescent OLEDs have been developed and put to practical use. A nearly 100 % internal EL quantum efficiency has been realized by the use of the iridium complex.[7-9] Very recently, high-performance fluorescence-based OLEDs utilizing thermally activated delayed fluorescence (TADF) generated by the thermal up-conversion from the triplet exciton to the singlet exciton have been developed.[10-12]

Both small molecular materials and polymers have been used as materials for OLEDs. Generally, materials for use in OLEDs should form uniform, smooth films by either thermal deposition in vacuum or by solution processing. They should be thermally and morphologically stable. While thin films of small molecular materials for OLEDs have usually been fabricated by a thermal deposition method, polymer thin films have been fabricated by solution processing. Polymers can provide ideally all solution-processed OLEDs;[13] however, a problem involved in the solution processing of polymers is that the fabrication of layered structures is not easy because the solvent employed for the fabrication of the second layer dissolves the first layer already formed.

OLEDs usually consist of multilayers such as hole-transport, electron-transport, and emitting layers. Therefore, materials with several functions such as charge injection, charge transport, charge blocking, and light emission are required. Highly emissive small molecules with no film-forming ability can also be used by being doped in host materials that function as the recombination center. Accordingly, host materials for emissive dopants are also required. Fluorescent dopants which have often been used in OLEDs include green-emitting dimethylquinacridone (DMQA), yellow-emitting rubrene, and

red-emitting 4-dicyanomethylene-2-methyl-6-[2-(2,3,6,7-tetrahydro-1H,5H-benzo[ij] quinolizin-9-yl)ethenyl]-4H-pyran (DCM2). Room-temperature phosphorescent transition-metal complexes such as platinum, iridium, and osmium complexes constitute phosphorescent dopants. The performance of OLEDs depends upon materials playing specialized roles in each layer.

There have been extensive studies on OLEDs using both small molecular materials and polymers, in particular, π-conjugated polymers. This short review article focuses on non-conjugated polymers with pendant groups as potential candidates for OLED materials. They form uniform, smooth amorphous films by solution processing. Layered structures in OLEDs in the literature are often composed of the layers of a polymer and small molecular materials fabricated by the solution processing and thermal deposition in vacuum, respectively. Concrete examples of non-conjugated pendant polymers that function as hole-transporting, electron-transporting, emitting, and host materials in OLEDs and the performance of devices using these materials are introduced from the recent literature.

2. Hole-transporting Polymers

Hole-transporting materials should meet the following requirements. They should have proper highest occupied molecular orbital (HOMO) energy levels to accept hole carriers from the anode through the hole-injection layer. The injected hole carriers, i.e., cation-radical species of hole-transporting materials, should be stable. In other words, the anodic oxidation processes of hole-transporting materials should be reversible. They should have hole-transporting ability along with the electron-blocking character.

Hole-transporting, non-conjugated polymers containing pendant groups are exemplified by a vinyl polymer containing a N,N'-bis(3-

methylphenyl)-N,N'-diphenyl-[1,1'-biphenyl]-4,4'-diamine (TPD) moiety as a pendant group, poly{4-(m-tolyl-m-fluorophenyl-amino)-4'-(m-fluorophenyl-p-vinyl-phenylamino)biphenyl} (P3),[14,15] and vinyl polymers containing triarylamine moieties as pendant groups, poly{4-vinyl-4'-[bis(4'-tert-butylbiphenyl-4-yl)amino]biphenyl} (PVBAB) and poly{4-vinyl-4'-[N,N-bis(9,9-dimethylfluoren-2-yl)amino]biphenyl} (PVFAB) with high glass-transition temperatures of 229 °C and 204 °C (Figure 1).[16] The HOMO energy level of P3 is −5.56 eV with respect to the vacuum level.[14] Both PVBAB and PVFAB have HOMO energy levels of ca. −5.6 eV as estimated from their oxidation potentials.[16] A device, ITO / P3 (40 nm) / quinacridone-doped Alq_3 (60 nm) / LiF (0.8 nm) / Al (150 nm), exhibited green EL originating from quinacridone with a maximum luminance of 30,000 cdm^{-2}.[14,15] Multilayer OLEDs using poly(4-styrene sulfonate)-doped poly(3,4-ethylene-dioxythiophene) (PEDOT:PSS) as the hole-injection layer, the vinyl polymers as the hole-transport layer, quinacridone-doped Alq_3 as the emitting layer, and Alq_3 as the electron-transporting layer, ITO / PEDOT:PSS (50 − 55 nm) / PVBAB or PVFAB (50 nm) / quinacridone-doped Alq_3 (30 nm) / Alq_3 (20 nm) / LiF / Al, showed maximum luminances of 95,000 and 91,000 cdm^{-2} (at an applied voltage of 10.5 and 11.5V, respectively) and luminous and external quantum efficiencies of 3.9 lmW^{-1} and 1.9% at a luminance of 300 cdm^{-2} for both polymers.[16] A novel vinyl polymer containing the moiety of a part of 4,4',4"-tris(3-methylphenylphenylamino)triphenyl-amine (m-MTDATA) as pendant groups, poly[4-(bis{4-[bis(4-tert-buthyphenyl)amino]-phenyl}amino)biphenyl-4'-ylethylene] (PVDAPhAB) (Figure 1), has been developed for potential use as the hole-injection layer.[17] The polymer has a high glass-transition temperature of 220 °C and a HOMO energy level of ca. −5.2 eV as estimated from its oxidation potential. A multilayer device using PVDAPhAB as a hole- injection layer, N,N'-di(1-naphthyl) -N,N'-diphenyl-[1,1'-biphenyl]-4,4'-diamine (α-NPD) as the hole-transport layer, and Alq_3 as the electron-transporting, emitting layer functioning as a host for emissive quinacridone, ITO / PVDAPhAB (30 nm) / α-NPD (20 nm) / quinacridone-doped Alq_3 (30 nm) / Alq_3 (20 nm) / LiF / Al, exhibited performance with a turn-on voltage of 2.7 V, a maximum luminance of 90,500 cdm^{-2} at 9.6 V, a luminous efficiency of 3.4 lmW^{-1} and an external quantum efficiency of 1.6 %.[17] Other reported non-conjugated polymers that serve as potential hole-injection layers include triarylamine siloxane[18] and poly(methyl-silsesquioxane)-poly(N,N-di-4-methylphenyl-aminostyrene).[19]

3. Electron-transporting Polymers

Electron-transporting materials should meet the following requirements. They should possess proper lowest unoccupied molecular orbital (LUMO) energy levels to accept electron carriers injected from the cathode through the electron-injection layer. Injected electron carriers, i.e., the anion-radical species of electron-transporting materials, should be stable. In other words, their cathodic reduction processes should be reversible. They should have electron-transporting ability along with the hole-blocking character.
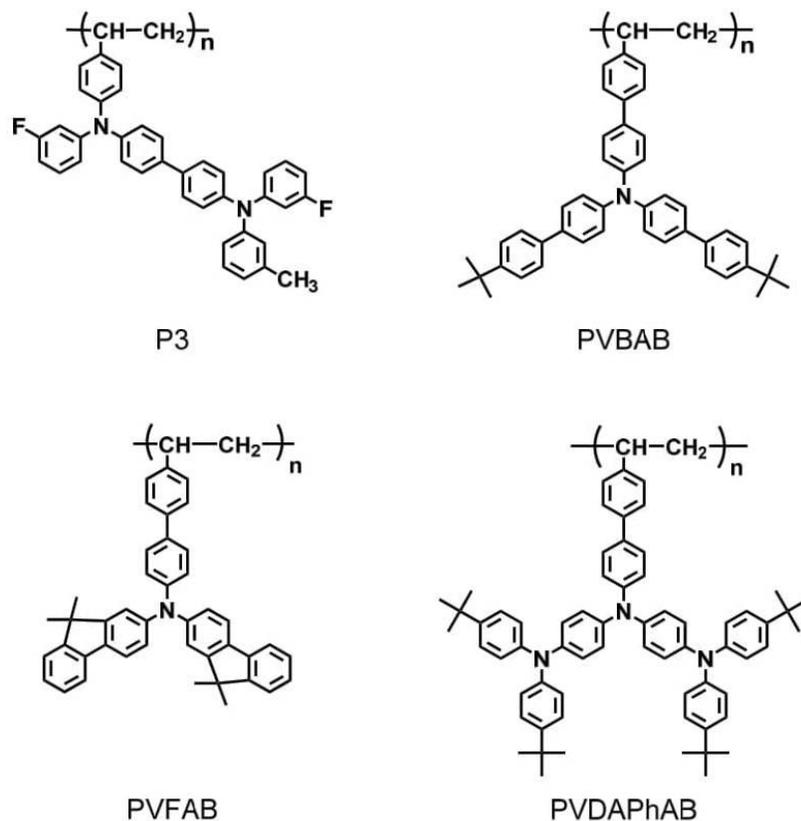
Figure 1. Chemical structures of hole-transporting vinyl polymers, P3, PVBAB, PVFAB, and PVDAPhAB.

Electron-transporting polymers include vinyl polymers with such side groups as trifluoromethyl-substituted quaterphenyl, 2,5-diphenyl-1,3,4-oxadiazole, and diphenyl-quinoxaline,[20] and methacrylate polymers containing a diphenyl 1,3,4-oxadiazole moiety[21] or a naphthalene imido moiety (PNI) as shown in Figure 2.[22,23] PNI has a LUMO energy level of −3.0 eV. A device using poly(p-phenylenevinylene) (PPV) as the hole-transporting layer and PNI as the electron-transporting, emitting layer where the emissive 4-(dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4H-pyran (DCM) is doped, ITO / PPV / DCM-doped PNI / Ca, exhibited ca. 1,000 cdm^{-2} with an external quantum efficiency of 2.25%.[23]
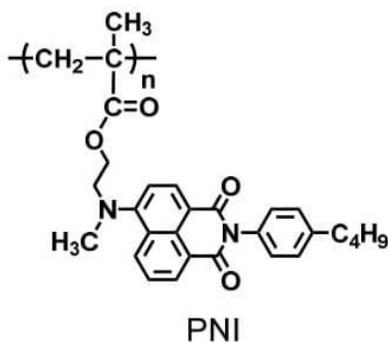

Figure 2. Chemical structure of PNI.

4. Emitting Polymers

Emitting materials should possess proper HOMO and LUMO energy levels so as to accept both holes and electrons injected through the hole- and electron-transport layers, respectively. In addition, injected charge-carriers, namely, the cation-radical and anion-radical species of emitting materials, should be stable; in other words, their oxidation and reduction processes should be reversible. These requirements mean that emitting materials should have bipolar character. Furthermore, emitting materials should have high quantum efficiencies for luminescence.

Figure 3 shows emitting polymers, e.g., poly(N-vinylcarbazole) (PVCz),[24] PNI,[23] a vinyl copolymer of N-vinylcarbazole with 9-(4-vinylphenyl)anthracene (*1*)[25] and polysiloxane containing pyrene as a pendant group (*2*);[26] however, OLEDs using these polymers as emitting materials have been reported to exhibit relatively low performance.

Figure 3. Chemical structures of PVCz, a vinyl copolymer of N-vinylcarbazole with 9-(4-vinylphenyl)anthracene (*1*), and polysiloxane containing pyrene as a pendant group (*2*).

Novel emitting polymers with bipolar character, poly(2-{4-[4-vinylphenyl(4-methylphenyl)amino]phenyl}-5-dimesitylborylthiophene) (PVPhAMB-1T) with a glass-transition temperature of 194 °C[16] and poly[4-(7-[4-[N,N-bis(9,9-dimethylfluoren-2-yl)amino]phenyl]-2,1,3-benzothiadiazol-4-yl)phenylethene] (PVFABT) with a glass-transition temperature of 199 °C,[27] have been developed (Figure 4). PVPhAMB-1T emits green fluorescence with a peak wavelength of 521 nm and a quantum efficiency of 0.58 in solution. The HOMO and LUMO energy levels of PVPhAMB-1T are ca. −5.6 and −2.8 eV, respectively, as estimated from the cyclicvoltammetry.[16] PVFABT emits orange fluorescence with a peak wavelength of 653 nm and a quantum efficiency of 0.65 in solution. The HOMO and LUMO energy levels of PVFABT are ca. −5.6 and −3.3 eV, respectively.[27] A multilayer OLED using PEDOT:PSS as the hole-injection layer, PVPhAMB-1T as the emitting layer, 5,5'-bis(dimesitylboryl)-2,2'-bithiophene (BMB-2T) as the hole-blocking layer, and Alq_3 as the electron-transporting layer, ITO / PEDOT:PSS (50nm) / PVPhAMB-1T (50nm) / BMB-2T (30nm) / Alq_3 (20nm) / LiF (0.5nm) / Al, showed a maximum luminance of 15,600 cdm^{-2} at an applied voltage of 11.0 V, a luminous efficiency of 1.4 lmW^{-1}, and an external quantum efficiency of 0.9%.[16] Likewise, an OLED, ITO / PEDOT:PSS (50 nm) / PVFABT (50 nm) / BMB-2T (30 nm) / Alq_3 (20 nm) / LiF (0.5 nm) / Al, exhibited a maximum luminance of 21,000 cdm^{-2} at 14 V with an external quantum efficiency of 1.2 %.[27]
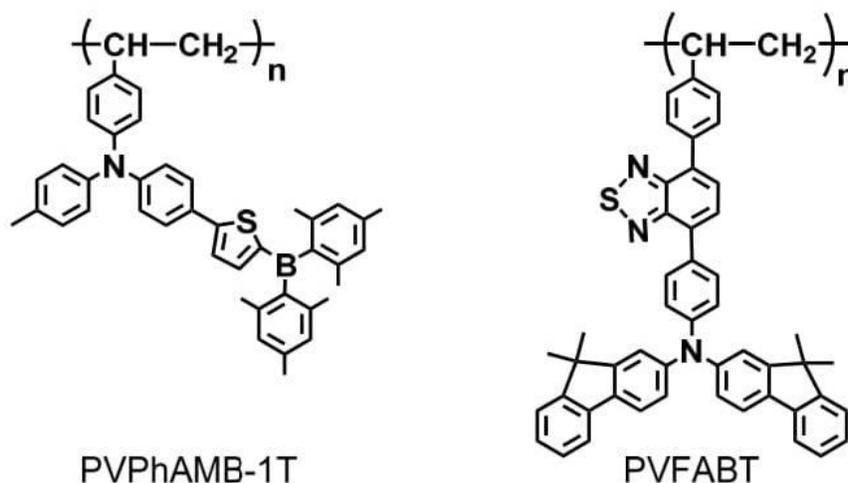
Figure 4. Chemical structures of bipolar emitting polymers, PVPhAMB-1T and PVFABT.

Fluorescence-based OLEDs utilizing TADF generated by the thermal up-conversion from the triplet exciton to the singlet exciton have recently been developed.[28] TADF-based OLEDs are expected to show much higher performance than the conventional fluorescence-based OLEDs. TADF-based emitting materials are called the third generation OLED emitters, which have advantages over phosphorescent materials in that they do not require transition metals. Materials that emit TADF have been designed so as to possess a small singlet-triplet energy splitting (ΔE_{ST}) so that the reverse intersystem crossing should be promoted.

Developed materials that emit TADF include both small molecular materials and polymers. Non-conjugated polymers that emit TADF are exemplified by a block copolymer with triazine-amine-triazine emitter units (**3**)[29] and a copolymer of styrene with a vinyl monomer having a pendant TADF unit (**4**) as shown in Figure 5.[30] Other TADF-emitting polymers include a carbazole-based dendrimer,[31] copolymers with a backbone of polycarbazole,[32] and polymers with a backbone consisting of alternating electron-donating units and accepting benzophenone units.[33] A multilayer OLED consisting of the hole-injection layer, hole-transport layer, and the TADF emitting layer of compound **3** with $\Delta E_{ST} = 0.22$ eV, ITO / PEDOT:PSS (65nm) / poly(2,5-dihexylbenzene-N-(4-(2-butyl)phenyl)-diphenylamine)) (40nm) / **3** (80nm) / NaF (2nm) / Al (100nm) / Ag (100nm), emitted green light with Commission Internationale de L'Eclairage (CIE) coordinates of (0.32, 0.58), showing performance with a maximum external quantum efficiency of 10%.[29] A multilayer OLED consisting of the hole-injection layer, the emitting layer of compound **4** with $\Delta E_{ST} = 0.35$ eV, and the electron-transport layer, ITO / PEDOT:PSS (40nm) / **4** (10%) + 1,3-di(N-carbazolyl) benzene (mCB) (90%) (45nm) / 2,2',2"-(1,3,5-benzenetriyl)-tris-[1-phenyl-1H-benzi midazole] (TPBi) (30nm) / LiF (1nm) / Al (100nm), emitted green light with an emission peak wavelength of 533 nm and CIE coordinates of (0.36, 0.55), exhibiting maximum power, current, and external quantum efficiencies of 40.1 lmW^{-1}, 61.3 cdA^{-1}, and 20.1 %, respectively.[30]
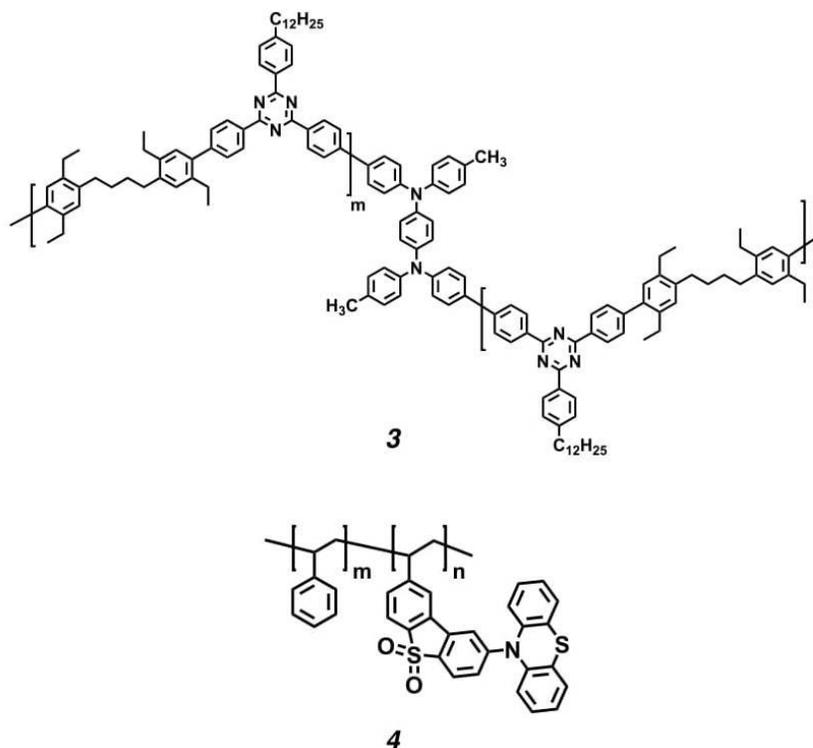
Figure 5. Chemical structures of a block copolymer with triazine-amine-triazine emitter units (**3**) and a copolymer of styrene with a vinyl monomer having a pendant TADF unit (**4**).

5. Polymer Host Materials

Materials that function as hosts for emissive dopants play a role as the charge recombination center to generate excitons and then transfer the excitation energy to emissive dopants via singlet – singlet and triplet – triplet excitation energy transfer. Consequently, host materials should have bipolar character to accept both holes and electrons. In addition, both the excited singlet and triplet energy levels of the host material should be higher than those of the emissive dopant for the exothermic energy transfer to take place, back energy transfer from the dopant to the host being prevented.

PVCz with hole-transporting properties and a relatively high triplet-energy level of 2.5 eV[34] has been reported to function as a host material for a phosphorescent dopant. An OLED, ITO / PEDOT:PSS (40 nm) / Ir(ppy)$_3$-doped PVCz (~ 30 nm) / TAZ (30 nm) / Alq$_3$ (20 nm) / MgAg, has been reported to give a luminous efficiency of 1.8 %.[35] In devices without the electron-transporting layer, both an electron-transporting material and a phosphorescent metal complex are co-doped in PVCz.[36-43] There is also an example of doping of fluorescent molecule in PVCz.[44]

A triphenylamine-based polysiloxane (PTPAMSi) (Figure 6) with good amorphous film-forming ability and a sufficiently high triplet-energy level of 2.9 eV has been reported to serve well as a host material for a phosphorescent iridium complex. A iridium-bis(4,6-difluorophenyl-pyridinato-N, C^2)-picolinate (Flrpic)-based device using PTPAMSi as a host material has been reported to show a maximum external quantum efficiency of 3.8 %.[45] A bipolar alternating copolymer containing phenylcarbazole and triphenylphosphine oxide moieties linked to the backbone of polysiloxane, poly(phenylcarbazole-alt-triphenylphosphine oxide)siloxane (PCzPOMSi) (Figure 6), has a relatively high glass-transition temperature of

118 °C and a sufficiently high triplet-energy level of 3.0 eV. A bis(3,5-difluoro-4-cyanophenyl)pyridine)iridium picolinate (FCNIrpic)-based device using PCzPOMSi as a host has been reported to display a maximum external quantum efficiency of 4 %.[46]
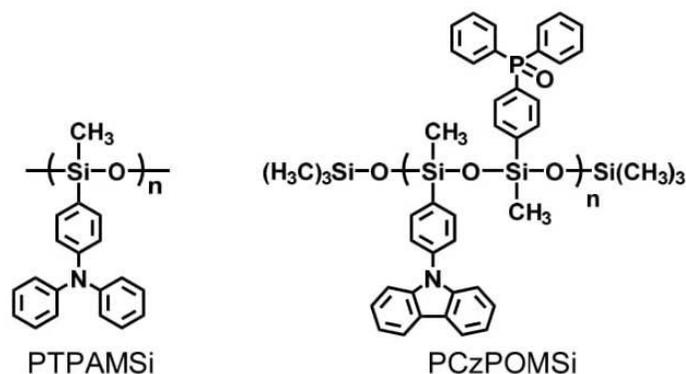

Figure 6. Chemical structures of polysiloxanes with pendant groups as host materials, PTPAMSi and PCzPOMSi.

6. Polymers with Multi-functions for OLEDs

Phosphorescent complexes doped in a host matrix tend to cluster in the host matrix, resulting in the quenching of luminescence.[47-49] An effective approach to avoid this problem is to incorporate emissive phosphorescent complexes into polymers, either in the main chain or in the side chain. Copolymers with an emissive iridium complex and a hole-transporting carbazolyl moiety as side chains have been synthesized.[50-58] A copolymer having an orange-emitting iridium complex and a 2,7-di(carbazol-9-yl)fluorene group as different side chains (**5**) (Figure 7) has also been reported.[49] A multilayer OLED using this polymer, ITO / a cross-linkable hole-transporting polymer (35nm) / **5** (20~25nm) / bathocuproine (BCP) (40nm) / LiF (1nm) / Al, exhibited current and external quantum efficiencies of 8.8 cdA^{-1} and 4.9 %, respectively.
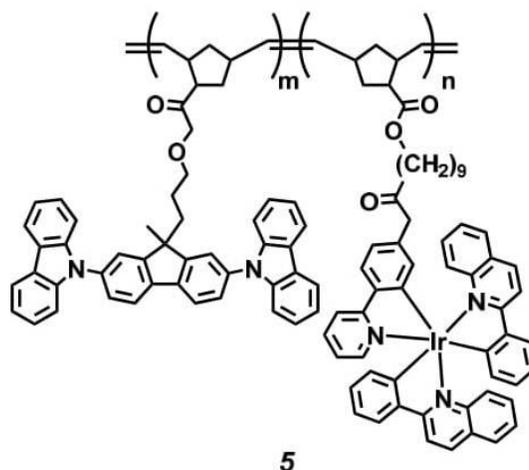
Figure 7. Chemical structure of a copolymer having iridium complex and 2,7-di(carbazol-9-yl)fluorene as side groups (**5**).

One approach to overcome the difficulty of fabricating layered structures for polymers is the use of polymers containing hole-transporting, electron-transporting, and emissive units. Such polymers may enable the fabrication of single-layer devices. A new class of emitting polymers composed of a liquid-crystal-forming moiety, an emitting 1,3,4-oxadiazole moiety with electron-transporting character, and a hole-transporting arylamine moiety in the same side chain (polymers **6** and **7** in Figure 8) have been synthesized.[59-61] A single-layer OLED using the liquid-crystalline polymer sandwiched between ITO and MgAg electrodes has been reported to exhibit polarized blue EL emission with an emission peak wavelength of 458 nm. The origin of the polarized emission has been attributed to the anisotropic arrangement of the mesogenic chromophore.[62]
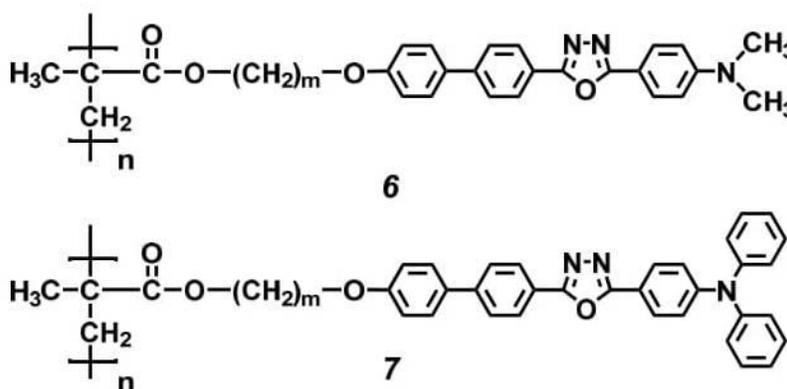
Figure 8. Chemical structures of liquid-crystalline polymers with electron- and hole-transporting units.

A single-layer OLED of a vinyl copolymer having a hole-transporting TPD moiety, an electron-transporting 2-(4-biphenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (PBD) moiety, and an emitting iridium complex in different side chains (polymer **8** in Figure 9) has been reported to give high external quantum efficiencies up to 11.8 %.[63]
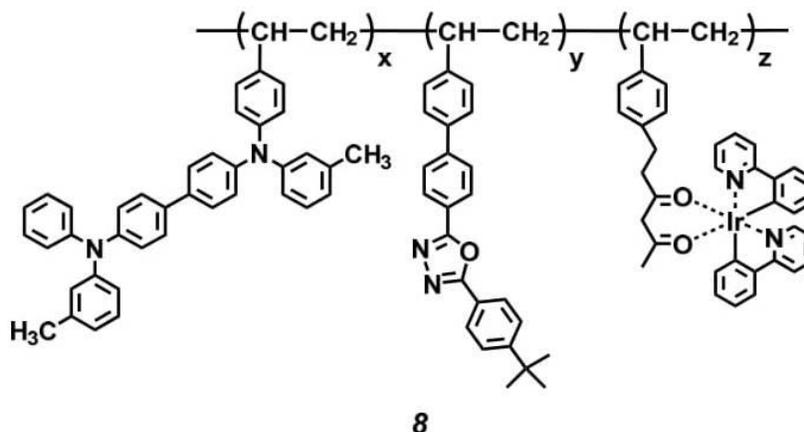

Figure 9. Chemical structure of a vinyl copolymer having TPD, PBD, and iridium complex as side groups (**8**).

7. Concluding Remarks

Materials research for OLEDs have been directed to both small molecular materials and polymers. Small molecular materials that have been developed for use in OLEDs are amorphous molecular materials that readily form amorphous glasses with definite glass-transition temperatures and uniform amorphous films by thermal deposition in vacuum. They have actually been put to practical use. Polymers studied for use in OLEDs include π-conjugated polymers, non-conjugated polymers containing side-chain groups, and dendrimers. This article is concerned with an overview of research works on non-conjugated polymers with side-chain groups for OLEDs.

Like amorphous molecular materials, non-conjugated polymers having side-chain groups form uniform amorphous films by solution processing. Non-conjugated pendant polymers have an advantage over amorphous molecular materials in that polymer films have mechanical strength; however, the vacuum-deposition method for film formation is not applicable to polymers. A problem encountered with polymers is the difficulty of the construction of layered device structures because of the film formation by solution processing. Although the fabrication of single-layer devices with high performance is ideal, development of polymers with different solubility remains to be solved. Fabrication of devices using composite materials among π-conjugated polymers, non-conjugated polymers with pendant groups, dendrimers, and small molecular materials including emissive dopants still remains to be studied from the standpoints of the performance and durability of devices.

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