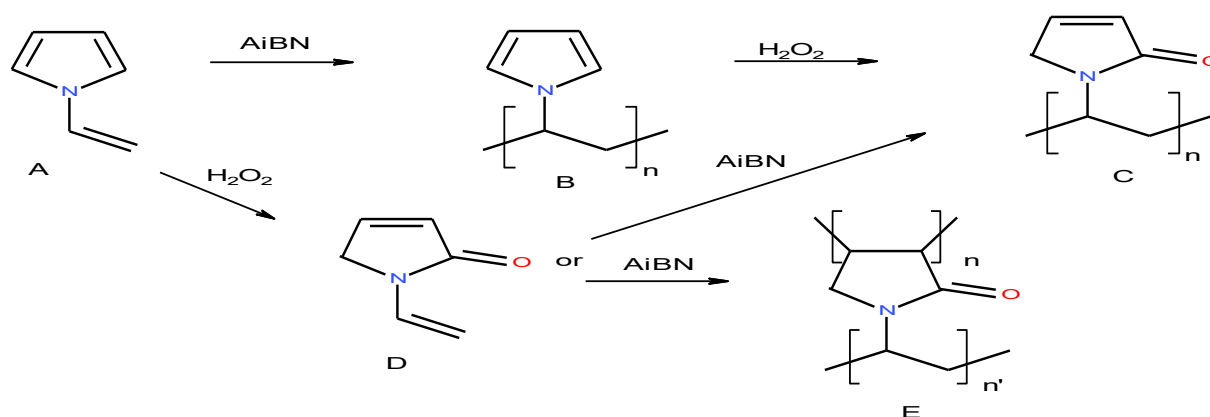


N-VINYLPYRROLES

By: Robert B. Login

I became interested in N-vinylpyrrole chemistry because I had the idea of employing the resulting polymers as sources of poly-3-pyrrolin-2-ones. However, after searching for this vinyl monomer on Google Scholar I was disappointed to find nothing for N-vinyl-3-pyrrolin-2-one or its corresponding polymers!

For example:



Scheme 1: Can poly-3-pyrrolin-2-ones be prepared from polypyrroles by oxidation?

Can D also polymerize employing both double bonds to form E?

Howard, J. K., Rihak, K. J., Bissember, A. C., & Smith, J. A. (2016). The oxidation of pyrrole. *Chemistry—An Asian Journal*, 11(2), 155-167. This very detailed reference doesn't indicate the oxidation of poly-n-vinylpyrrole!

General 3-Pyrrolin-2-one reviews:

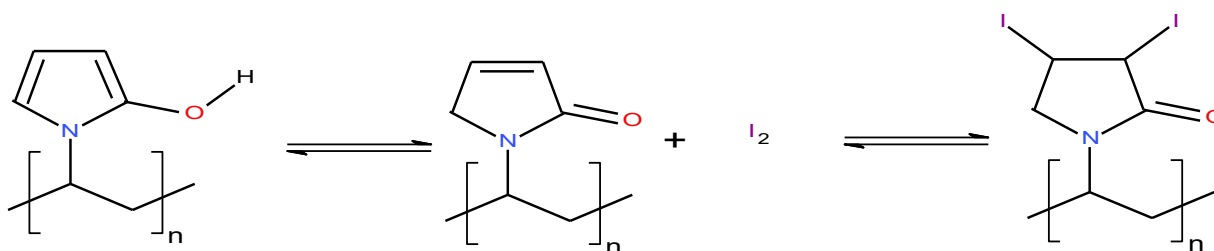
Pelkey, E. T., Pelkey, S. J., & Greger, J. G. (2015). De Novo Synthesis of 3-Pyrrolin-2-Ones. *Advances in Heterocyclic Chemistry*, 151.

Pelkey, E. T., Pelkey, S. J., & Greger, J. G. (2019). Reactions of 3-pyrrolin-2-ones. In *Advances in Heterocyclic Chemistry* (Vol. 128, pp. 433-565). Academic Press.

The above references however, illustrated how pyrroles can be readily oxidized to 3-pyrrolin-2-ones. I thought that n-vinylpyrrole which can be easily polymerized by

radical initiators could then be oxidized to the polymeric 3-pyrrolin-2-ones as a way around this problem.

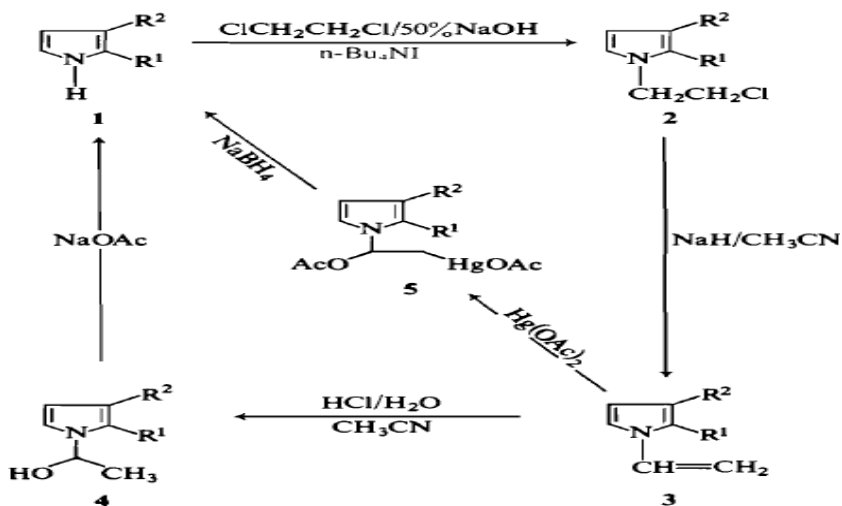
Since the 3-4 double bond of 3-pyrrolin-2-ones can be converted into a variety of derivatives such as epoxides, I propose that it can be reacted with iodine or bromine for example. Copolymers with vinylpyrrolidone, could then be converted to iodophors with both complexed HI3 and 3-4 diiodo derivatives. PVP iodine would then possibly be more long lasting because some of the copolymer would be a 3-4 diiodo derivative that would generate iodine because release of iodine would reestablish the aromatic character of the pyrrolin-2-ones.



Scheme 2: Iodophor(see: <https://patents.google.com/patent/US2739922A/en?q=US2739922#patentCitations>)

Review of N-vinylpyrrole and corresponding polymer synthesis:

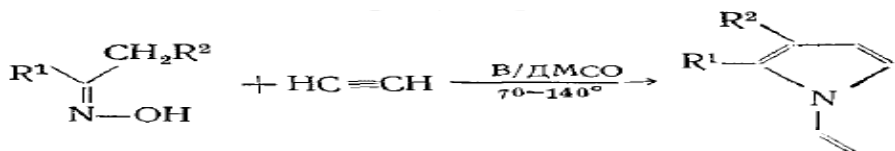
Since I searched the N-vinylpyrrole literature, I thought a brief review might be of value.



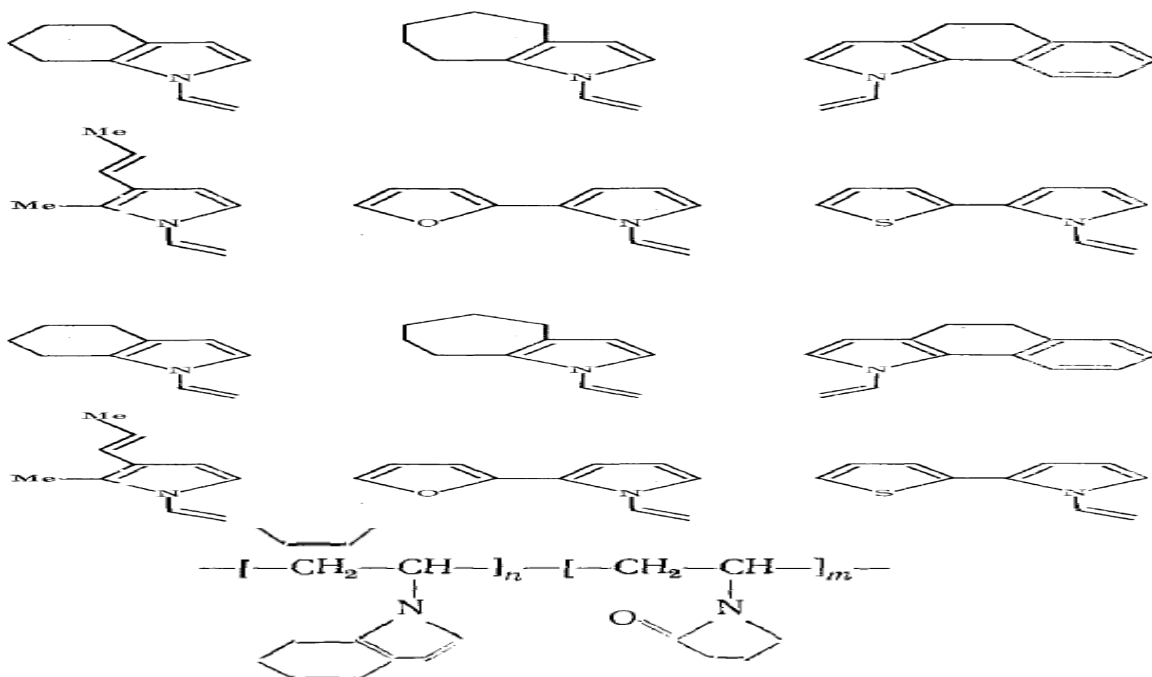
SCHEME 1

Gonzalez, C., Greenhouse, R., Tallabs, R., & Muchowski, J. M. (1983). Protecting groups for the pyrrole nitrogen

atom. The 2-chloroethyl, 2-phenylsulfonylethyl, and related moieties. *Canadian Journal of Chemistry*, 61(8), 1697-1702.

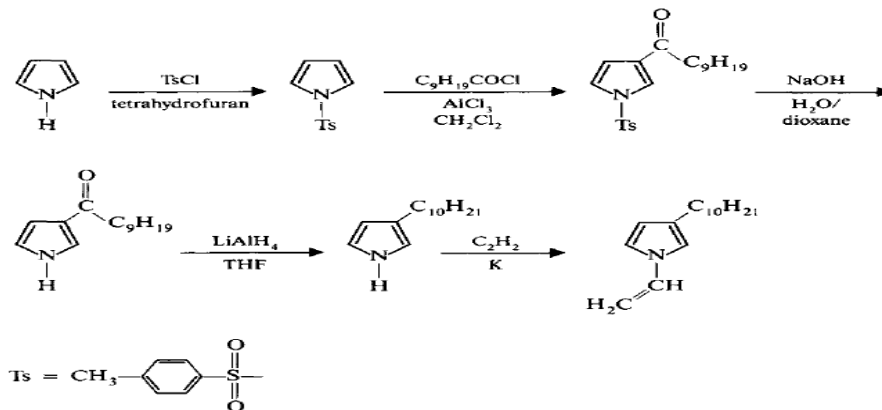


$\text{R}^1, \text{R}^2 =$ алкил, алкенил, арил, аралкил, гетероарил,
 $\text{R}^1-\text{R}^2 = (\text{CH}_2)_n, n = 3-5$; B — сильное основание

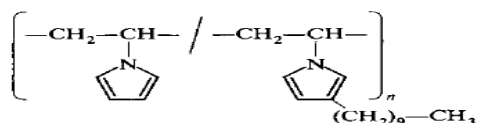


Trofimov, B.A., Mikhaleva, A.I., & Morozova, L.V. (1985). Polymerization of N-vinylpyrroles. *Advances in Chemistry*, 54 (6), 1034-1050.

Scheme 1:



Scheme 2:



Ruggeri, G., Spila, E., Puncioni, G., & Ciardelli, F. (1994). Oxidized poly (N-vinyl-3-decylpyrrole) and poly (N-vinyl-3-decylpyrrole-co-N-vinylpyrrole): soluble electroconducting ladder polymers. *Macromolecular rapid communications*, 15(6), 537-542.

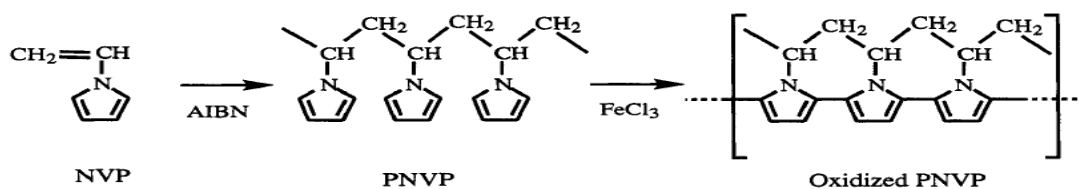


Fig. 1 Preparation procedure of the oxidized poly(N-vinylpyrrole).

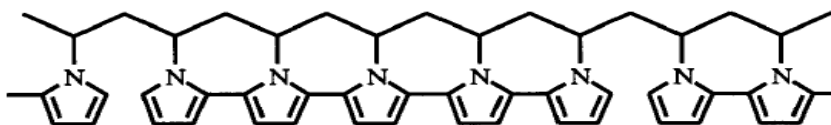
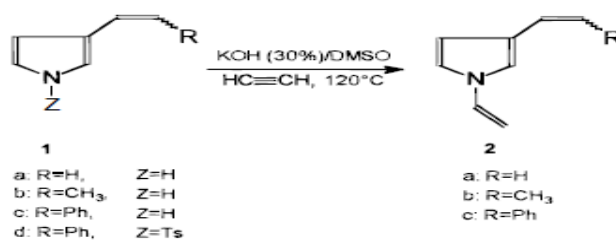


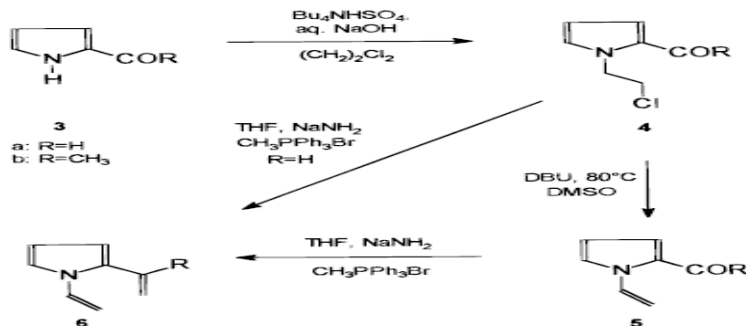
Fig. 3 Schematic structure of partially oxidized poly(N-vinylpyrrole).

Ruggeri, G., Bianchi, M., Puncioni, G., & Ciardelli, F. (1997). Molecular control of electric conductivity and structural properties of polymers of pyrrole derivatives. *Pure and applied chemistry*, 69(1), 143-150.

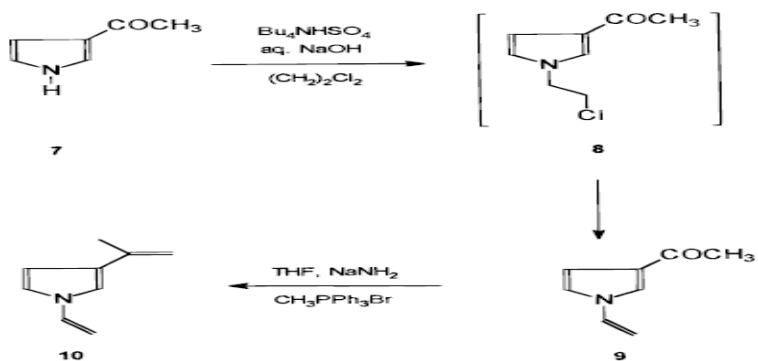
Scheme 1



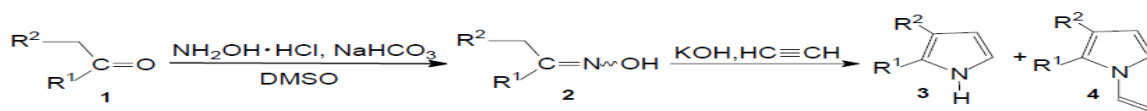
Scheme 2



Scheme 3

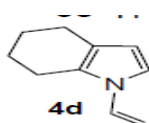
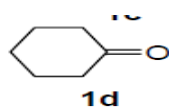


Settambolo, R., Mariani, M., & Caiazzo, A. (1998). Synthesis of 1, 2-and 1, 3-Divinylpyrrole. *The Journal of Organic Chemistry*, 63(26), 10022-10026.



$R^1 = \text{Me}$, $R^2 = \text{H}$ (a); $R^1 = \text{Et}$, $R^2 = \text{H}$ (b); $R^1 = t\text{-Bu}$, $R^2 = \text{H}$ (c); $R^1\text{-}R^2 = \text{-(CH}_2\text{)}_4\text{-}$ (d), $R^1 = \text{Ph}$, $R^2 = \text{H}$ (e); $R^1 = 2\text{-Thienyl}$, $R^2 = \text{H}$ (f); $R^1 = 2\text{-Furyl}$, $R^2 = \text{H}$ (g)

Scheme 1

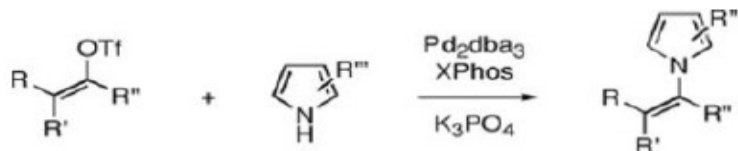


87^e

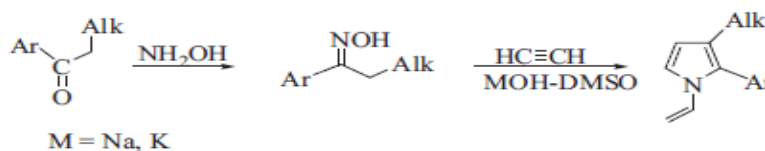
71

87% is crude yield and 71% is isolated yield.

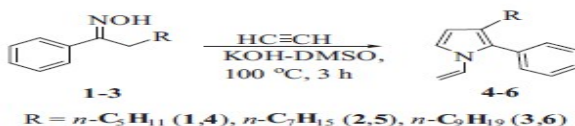
Schmidt, E. Y., Al'bina, I. M., Vasil'tsov, A. M., Zaitsev, A. B., & Zorina, N. V. (2005). A straightforward synthesis of pyrroles from ketones and acetylene: a one-pot version of the Trofimov reaction. *Arkivoc*, 7, 11-17.



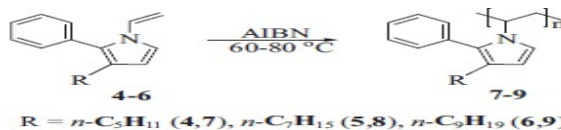
Movassaghi, M., & Ondrus, A. E. (2005). Palladium-catalyzed synthesis of N-vinyl pyrroles and indoles. *The Journal of organic chemistry*, 70(21), 8638-8641.



Scheme 1. Trofimov reaction (synthesis of N-vinylpyrroles).



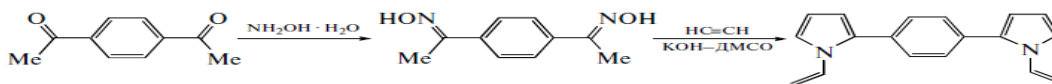
Scheme 2. Synthesis of N-vinyl-3-alkyl-2-phenylpyrroles (4-6).



Scheme 3. Polymerization of N-vinyl-3-alkyl-2-phenylpyrroles (4-6).

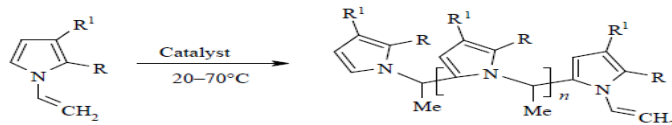
Trofimov, B. A., Markova, M. V., Tatarinova, I. V., Al'bina, I. M., Morozova, L. V., Ol'ga, V. P., ... & Prozorova, G. F. (2010). I₂-doped and pyrrole ring-iodinated semi-conducting oligomers of N-vinyl-3-alkyl-2-phenylpyrroles. *Synthetic metals*, 160(23-24), 2573-2580.

Trofimov, B. A., Markova, M. V., Morozova, L. V., Al'bina, I. M., Lyubov'N, S., Ol'ga, V. P., ... & Petrushenko, K. B. (2010). Cationic and radical polymerization of N-vinyl-2-phenylpyrrole: Synthesis of electroconducting, paramagnetic and fluorescent oligomers. *Synthetic metals*, 160(13-14), 1539-1543.



Trofimov, B. A., Markova, M. V., Morozova, L. V., Mikhaleva, A. I., Schmidt, E. Y., Zorina, N. V., & Hyun, S. H. (2010). Polymerization of 1, 4-bis [2-(N-vinyl) pyrrolyl] benzene. *Polymer Science Series B*, 52(3-4), 193-197.

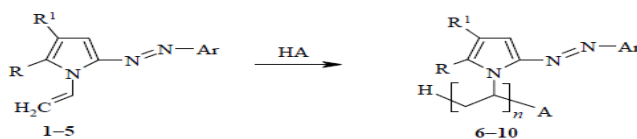
Scheme 1



R = Alk, R¹ = H, Alk

We have shown that, unlike 1-vinylpyrroles not containing azo groups, in the presence of both protic (CF₃COOH, HCl) and aprotic (BF₃) acids (HA) 2-aryloxy-1-vinylpyrroles **1-5** enter into oligomerization at the vinyl group, forming the oligomers **6-10** (Scheme 2, Table 1).

Scheme 2



1, 2, 5-7, 10 Ar = Ph; **3, 8** Ar = C₆H₄OEt-*p*; **4, 9** Ar = C₆H₄Br-*p*;
1, 6 R = R¹ = H; **2, 3, 7, 8** R+R¹ = (CH₂)₄; **4, 9** R = Me, R¹ = H; **5, 10** R = Ph, R¹ = H

Markova, M. V., Shmidt, E. Y., Morozova, L. V., Tatarinova, I. V., Prozorova, G. F., Mikhaleva, A. I., & Trofimov, B. A. (2012). 2-Aryloxy-1-vinylpyrroles: oligomerization in the presence of protic and aprotic acids. *Chemistry of Heterocyclic Compounds*, 48(2), 280-286.

Polymerization of *N*-Vinylpyrroles: Recent Achievements

A. I. Mikhaleva, M. V. Markova, I. V. Tatarinova, L. V. Morozova, and B. A. Trofimov*

Favorsky Institute of Chemistry, Siberian Branch, Russian Academy of Sciences, ul. Favorskogo 1, Irkutsk, 664033 Russia

*e-mail: boris_trofimov@irioch.irk.ru

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Abstract—The data on the polymerization of *N*-vinylpyrroles published for the most part during the past decade are systematized and summarized. Radical, cationic, and anionic polymerization of the mentioned monomers, which became easily accessible owing to the discovery and systematic development of their direct one-step synthesis from ketoximes and acetylene in the superbasic catalytic system KOH/DMSO (the Trofimov reaction), are discussed. Special attention is given to the physicochemical properties of the polymers (conductivity, paramagnetism, photosensitivity, and optical characteristics).

DOI: 10.1134/S1560090414040071

Mikhaleva, A. I., Markova, M. V., Tatarinova, I. V., Morozova, L. V., & Trofimov, B. A. (2014). Polymerization of *N*-vinylpyrroles: Recent achievements. *Polymer Science Series B*, 56(4), 443-463.

(12) **United States Patent**
Park et al.

(10) **Patent No.:** **US 7,989,569 B2**
(45) **Date of Patent:** **Aug. 2, 2011**

(54) **POLYVINYL PYRROLE HOST MATERIAL, LUMINESCENT LAYER COMPRISING THE SAME, AND ORGANIC ELECTROLUMINESCENT DEVICE COMPRISING THE LUMINESCENT LAYER**

(75) Inventors: **Jong-Jin Park**, Yongin-si (KR); **Byoung-Ki Choi**, Hwaseong-si (KR); **Tae-Yong Noh**, Gunpo-si (KR); **O-Hyun Kwon**, Seoul (KR); **Myeong-Suk Kim**, Suwon-si (KR); **Yu-Jin Kim**, Suwon-si (KR); **Sang-Heon Hyun**, Suwon-si (KR); **Boris Aleksandrovich Trofimov**, Irkutsk (RU)

(73) Assignee: **Samsung Mobile Display Co., Ltd.**, Giheung Gu, Yongin, Gyeonggi-Do (KR)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 1239 days.

(21) Appl. No.: **11/588,248**

(22) Filed: **Oct. 27, 2006**

(65) **Prior Publication Data**
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(30) **Foreign Application Priority Data**
Feb. 4, 2006 (KR) 10-2006-0010920

(51) **Int. Cl.**
C08F 126/06 (2006.01)
H01L 51/54 (2006.01)

(52) **U.S. Cl.** **526/258; 526/259; 428/690; 428/917; 313/504; 257/40; 257/E51.033; 257/102; 257/103**

(58) **Field of Classification Search** 428/690, 428/917; 526/258, 259; 313/504; 257/40, 257/E51.033, 102, 103
See application file for complete search history.

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* cited by examiner

Primary Examiner — D. Lawrence Tarazano

Assistant Examiner — J. L. Yang

(74) *Attorney, Agent, or Firm* — Robert E. Bushnell, Esq.

(57) **ABSTRACT**

Provided are a polyvinyl pyrrole host material emitting highly efficient phosphorescence, a luminescent layer using the material, and an organic electroluminescent display device. The polyvinyl pyrrole host material shows highly efficient luminescence having improved energy transfer, and thus is useful for an organic electroluminescent display device and other various light emitting devices.

12 Claims, 5 Drawing Sheets

This patent and US 8,257,839 B2 describes a plethora of examples not discussed in previous references.

Thank you for reading this proposal.

Dr. Robert B. Login rloginconsulting.com