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Notes

Ruthenium-Catalyzed Knoevenagel Condensation: A New Route toward Cyano-Substituted Poly(*p*-phenylenevinylene)s

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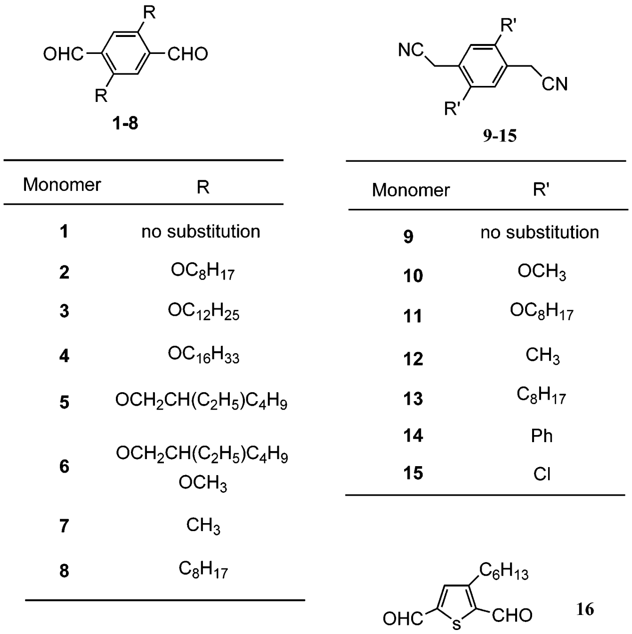
CN-PPV, a poly(*p*-phenylenevinylene) (PPV) derivative with cyano groups on the vinyl units, is one of the most important conducting polymers for use as electron-transporting materials in highly efficient organic light-emitting diodes (LEDs).[1−5] The introduction of an electron-withdrawing CN group to π-conjugated polymer backbone reduces the lowest unoccupied molecular orbital (LUMO) energy levels and increases the electron affinity of the polymer. As a result, the electroluminescence efficiency (photons emitted/charge injected) is greatly improved due to the enhanced electron injection and transport. Up to now, the only method available for the preparation of CN-PPV is base-catalyzed Knoevenagel condensation between equimolar amounts of terephthaldehyde and benzene-1,4-diacetonitrile derivatives.[6,7] The condensation polymerization takes place upon addition of an excess strong base such as tetrabutylammonium hydroxide, potassium *tert*-butoxide, and sodium methoxide in a 1:1 v/v mixture of *tert*-butyl alcohol and tetrahydrofuran. Under these conditions, crossing-linking caused by Michael addition side reaction occurs during the reaction and/or purification. This reaction condition is also not compatible with the synthesis of the polymers containing functional groups that are sensitive to basic conditions. Furthermore, the resulting polymers precipitate out quickly from the reaction medium due to poor solubility of the polymers in alcohols, which makes it difficult to control the polymer structures and molecular weights. These findings prompted us to explore milder conditions to prepare CN-PPV. As part of our ongoing projects aimed at the development of new strategies for the synthesis and assembly of conducting polymers, we have been studying transition-metal complex-mediated polycondensation for the preparation of multifunctional conjugated polymers.[8]

The C−H activation with low-valent ruthenium hydride complexes for the formation of α,β-unsaturated nitriles has been recently studied by Murahashi et al.[9,10] The reaction mechanism involves an oxidative addition of hydridoruthenium species to the α-C−H bond adjacent to nitriles to afford α-cyanoalkylmetal hydride complex, which can be trapped with electrophiles such as carbonyl compounds to give a carbon−carbon bond at the α-position of nitriles. The general reaction conditions in the synthesis of small molecules via the ruthenium-catalyzed aldol reaction have been well documented. This catalytic transformation proceeds highly efficiently under neutral and mild conditions.[11] Herein, we demonstrate the feasibility of the ruthenium complex-mediated Knoevenagel coupling in polycondensation. This approach provides us an alternative method to the synthesis of cyano-substituted conjugated polymers.



1-8

9-15

Monomer	R
1	no substitution
2	OC_8H_{17}
3	$OC_{12}H_{25}$
4	$OC_{16}H_{33}$
5	$OCH_2CH(C_2H_5)C_4H_9$
6	$OCH_2CH(C_2H_5)C_4H_9$ OCH_3
7	CH_3
8	C_8H_{17}

Monomer	R'
9	no substitution
10	OCH_3
11	OC_8H_{17}
12	CH_3
13	C_8H_{17}
14	Ph
15	Cl

16

Figure 1. Structures of the monomers for the ruthenium-catalyzed Knoevenagel reactions.

Figure 1 lists the monomers involved in this study. The monomers were synthesized in good yields, and the synthetic details are given in the Supporting Information.[12−14] The syntheses of polymers are outlined in Scheme 1. The polymerization was carried out in dry tetrahydrofuran (THF) in the presence of ruthenium dihydride complex $RuH_2(PPh_3)_4$ (3 mol %) and 1,2-bis(diphenylphosphino)ethane (dppe) (6 mol %) at 60 °C under an argon atmosphere. The typical reaction time was around 30 min when the polymer started to precipitate out. The polymerization was quenched by pouring the reaction mixture into methanol. After purification, the polymers were obtained in over 90% yields. The structures of polymers were confirmed by spectroscopic studies and elemental analysis. In the ^1H NMR spectra of polymers, the chemical shifts of two vinyl protons appear at around 8.10 ppm and those of aromatic protons appearing at around 7.95, 7.70, and 7.30 ppm. The features of the UV/vis and fluorescence

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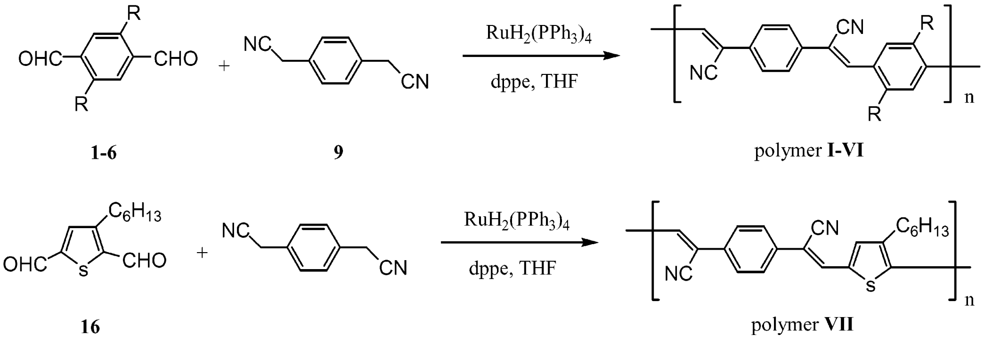
Scheme 1. Synthesis of Cyano-Substituted Conjugated Polymers



spectra are consistent with the results reported in the literature.[1,7] The thienylene–phenylene copolymer **VII** possesses a lower band gap than polymers **I**–**VI**. As shown in Figure 2, the maximum absorption peaks corresponding to $\pi-\pi^*$ transition appear at 510 nm for polymer **VII** and at around 470 nm for CN-PPVs. The fluorescence spectrum of polymer **VII** in 1,1,2,2-tetrachloroethane gives an emission maximum at 700 nm. The synthesized polymers are only partially soluble in THF, the solvent used in our gel permeation chromatography (GPC) measurements. The typical weight-average molecular weight (M_w) measured by GPC is around 7 kDa, and the polydispersity (PD) is about 1.3 using polystyrene as standards, which reflects only the THF-soluble part of the polymers. Robust free-standing films can easily be cast from polymer solutions. These results are comparable to the polymers synthesized by KOBu^t-catalyzed Knoevenagel condensation in our parallel experiments.

We next investigated the scope and optimized reaction conditions of this ruthenium-catalyzed Knoevenagel polycondensation. Because of low reactivity of aromatic cyanide, addition of a catalytic amount of an electron-donating bidentate phosphine such as dppe was found to be necessary for the polymerization. Without dppe no reaction was observed, and only monomers were recovered. Among bidentate phosphine ligands such as 1,3-bis(diphenylphosphino)propane (dppp), 1,1-bis(diphenylphosphino)methane (dppm), 1,4-bis(diphenylphosphino)butane (dppb), and 1,4-bis(diphenylphosphino)-butane, dppe gives the best results. $RuH_2(PPh_3)_4$ is the best catalyst among the catalysts examined which include $RuH(C_2H_4)(PPh_3)_2$, $RuH_2(CO)(PPh_3)_3$, $ReH(N_2)(PMe_2Ph)_4$, and $Pd_2(dba)_3CHCl_3$. The amount of catalysts was also found crucial to the polymerization process. In dilute solution, when the concentrations of $RuH_2(PPh_3)_4$ and dppe were lower than 6 and 12 mM, respectively, no polymerization occurred, and only dimers or trimers were obtained. The optimized concentrations of $RuH_2(PPh_3)_4$ and dppe are 12 and 24 mM, respectively. It is worth mentioning that the polymerization also proceeds efficiently at room temperature, although longer reaction time (about 12 h) is needed for the completion of reaction. The solvent is known to play an important role in polymerization, which affects both the stability of catalyst and the molecular weights of the resulting polymers.[15] It was found that this ruthenium-catalyzed polycondensation can be operated in a variety of organic solvents, such as benzene, toluene, chloroform, DMF, NMP, and CH_3CN. This provides us flexibility in selecting solvents to match the solubility of the resulting polymers.

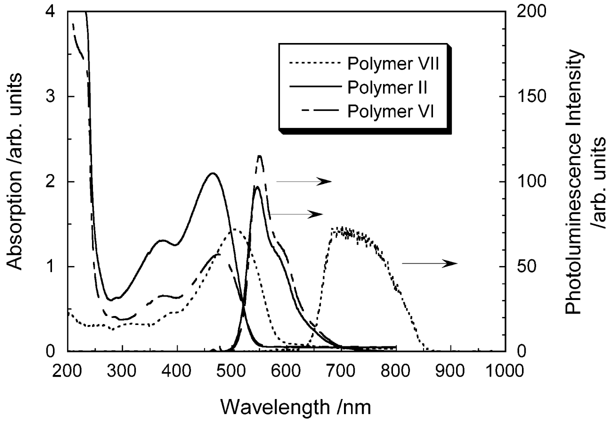


Figure 2. UV/vis and fluorescence spectra of polymers **II**, **VI**, and **VII** in tetrachloroethane.

As expected, the monomer structure drastically affects the polymerization process as well. Benzene-1,4-diacetonitrile with 2,5-substituted groups including diphenyl, dichloro, dialkyl, and dialkoxyl with different chain lengths have been tested. None of the substituted ones (monomers **10**–**15**) produced polymers. In most cases, no reaction occurred and the starting monomers were recovered. These results indicate that the oxidative addition and/or the transmetalation steps in the ruthenium-catalyzed Knoevenagel reaction are extremely sensitive to the steric bulkiness of the substituent on the reactants. Similar results have been observed in palladium-catalyzed Stille coupling polycondensation.[16] On the other hand, terephthaldehyde bearing dialkoxy-substituted side chains (monomers **2**–**6**) exhibits much higher reactivity than the similar dialkyl-substituted terephthaldehyde. For dialkyl-substituted terephthaldehyde (monomers **7** and **8**), the polymerization could not proceed further after forming dimers or trimers. We reason that electron-donating alkoxy side chains stabilize hydrido(aldolato)–ruthenium(II) intermediate formed by the interaction of hydrido(enolate)–ruthenium with an aldehyde. The enolate ruthenium is an oxidative addition product of ruthenium dihydride complex with nitrile.[11] This result is consistent with the observed remarkable effect of electron-donating phosphine ligands in the polymerization. Similarly, monomer **16**, 3-hexyl-2,5-thiophenedicarboxaldehyde, can be polymerized smoothly to yield the copolymer **VII**. The electron-donating property of sulfur atom is believed to facilitate the reaction.

In conclusion, the ruthenium-catalyzed Knoevenagel reaction has been developed for the preparation of cyano-substituted conjugated polymers. Compared with the conventional inorganic base-catalyzed reaction, the Knoevenagel polycondensation mediated by transition-metal complexes enjoys the advantages of neutral and mild reaction conditions and a wide range of operating solvents, making it an alternative route for the synthesis of cyano-substituted conjugated polymers.

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Supporting Information Available: Synthetic procedures and characterization data for the synthesized monomers and polymers. This material is available free of charge via the Internet at http://pub.acs.org.

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