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Communications to the Editor

Regiospecific, Functionalized Poly(phenylenevinylene) Using the Heck Coupling Reaction

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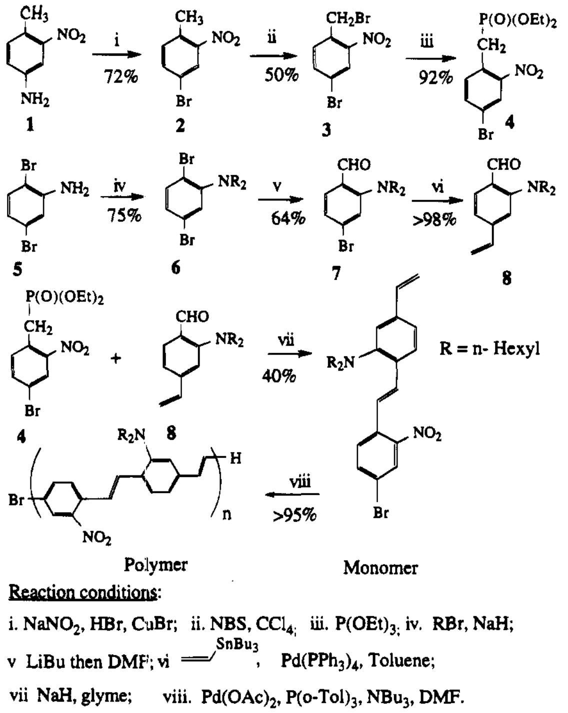
Our research has involved the synthesis of functional and multifunctional polymers, such as the synthesis of photorefractive polymers, second-order nonlinear optical polymers with exceptionally high thermal stability, and conjugated liquid crystalline polymers.[1−7] One question we keep asking ourselves is, can we synthesize functional polymers with better controls in either stereochemistry or architectural structures or both? The past several decades witnessed three trends in the development of polymer chemistry, that is, (1) design and synthesis of different functional polymers, (2) architectural (i.e., size and shape) controls of polymers, and (3) stereochemical controls (i.e., asymmetric polymerization).[8−10] These trends reflected the tremendous advance in modern chemistry and demonstrated that chemistry has evolved to a stage that sophisticated controls in polymers' structures and properties are possible. However, despite this exciting progress, the target sought by many polymer scientists is still to combine all three of these trends to prepare polymers with defined function or functions, defined architecture, and defined stereochemistry as Mother Nature does in living systems. It is, of course, extremely challenging to achieve that goal. It will be a significant progress even if the goal is partially achieved. We then initiated a research project aimed at this goal. In this paper, we present our encouraging preliminary results which indicate that careful structural design can lead us to success.

The structure of the first such polymer is shown in Scheme 1 where the synthetic approach is also outlined. It is a poly(phenylenevinylene) (PPV) functionalized regiospecifically with donor and acceptor groups. It is known that PPVs exhibit very interesting electroactivity and have been extensively studied.[11] In this work, however, we were not particularly interested in merely preparing a new conducting polymer. We intended to explore the following two aspects: (1) the versatility of the Heck reaction in the synthesis of functional polymers and the advantages in utilizing the Heck reaction for the synthesis of polymers with regiospecificity; (2) new physical properties due to the defined chemical structures of polymers.

Scheme 1. Synthesis of Functional Monomer and Regiospecific Polymer



Reaction conditions:

i. $NaNO_2$, HBr, CuBr; ii. NBS, CCl_4; iii. $P(OEt)_3$; iv. RBr, NaH;
v LiBu then DMF; vi $SnBu_3$, $Pd(PPh_3)_4$, Toluene;
vii NaH, glyme; viii. $Pd(OAc)_2$, $P(o\text{-}Tol)_3$, NBu_3, DMF.

Many approaches are known for the synthesis of PPV; however, all of these approaches exhibit difficulties in incorporating the nitro and amino groups into the PPV backbone even merely in a random fashion. This difficulty can be overcome by the monomer design shown in Scheme 1 and by utilizing the Heck coupling reaction for polymerization.[12] Seven steps were needed to prepare the monomer. Various reaction conditions and yields are indicated in the scheme. The synthesis of compound **4** was straightforward. The synthesis of compound **6** utilized the preferential bromide−lithium exchange directed by the amino group at low temperature and a further Stille coupling reaction yielded compound **8**.[13] The Wittig coupling reaction between compounds **4** and **8** was carried out in ethylene glycol dimethyl ether (EGDE), yielding the monomer. The design idea of the monomer is worthwhile to mention: the bromo group is specifically introduced into the phenyl ring bearing the nitro group so that it can be activated by the electron-withdrawing group.[12] To reduce the steric hindrance of the substituents, the dihexylamino and nitro groups were attached to the positions as shown. By that arrangement, the steric hindrance for the Heck reaction in polymerization can be minimized although the yield of the monomer was not very high (40%). The dihexyl groups were introduced to enhance the solubility of the resulting polymer.

The monomer was an orange liquid, and the spectroscopic studies and microanalysis results support the molecular structure.[14] The polymerization was easily effected in DMF using a typical Heck reaction condition as indicated.[9,10] The polymer, a red solid, was obtained in an almost quantitative yield and was soluble in THF, chloroform, and 1,2-dichloroethane. GPC studies revealed a weight-average molecular weight (M_w, relative to polystyrene standards, THF as the eluent) of 35K with a polydispersity of 3.0. The microanalysis results indicated a close match with the structure expected.[14]

Compared to the NMR spectrum of the monomer, changes were noticeable in the NMR spectrum of the

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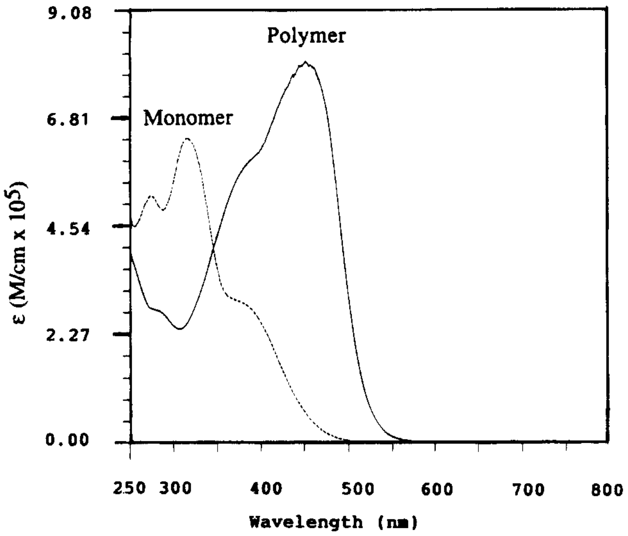


Figure 1. UV/vis spectra of the monomer and the polymer in THF.

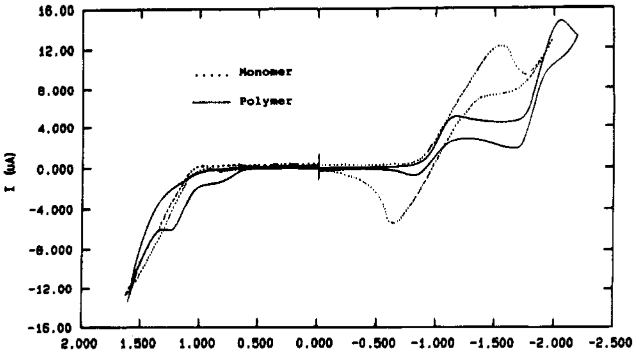
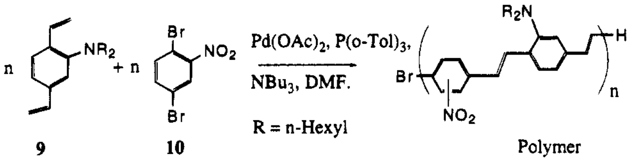


Figure 2. Diagrams of cyclic voltammetry (vs SCE) of the monomer and the polymer in THF. n-Bu$_4$NBF$_4$ was used as the supporting electrolyte, and the scan rate was 100 mV/s.

Scheme 2. Synthesis of Randomly Substituted PPV from the Heck Reaction



polymer. The integration area of the chemical shifts due to styryl protons was reduced dramatically although the residual peaks were still visible due to the end groups. Other aromatic chemical shifts became overlapped and were hard to assign. However, the integration ratio between aliphatic and aromatic (vinyl) protons is correct, ca. 24/10. The chemical shifts in the aliphatic region were not changed significantly. The chemical shifts of the methyl protons appeared at 0.8 ppm and that of methylene linked to the amine appeared at 3.05 ppm.

The FTIR spectrum of the polymer exhibited features for all of the functional groups. The strong absorption due to C−H stretchings of methyl and methylene moieties appeared in the region between 2800 and 3000 cm^{-1}. The absorption bands due to nitro groups appeared at 1360 and 1523 cm^{-1}. The absorption band at 950 cm^{-1} can be attributed to the *trans*-vinyl linkage.

The electronic absorption spectrum of the polymer exhibited a large change in comparison with that of the monomer. An absorption maximum at 391 nm was observed for the monomer which might be attributed to the absorption due to the charge transfer between donor and acceptor. The polymer exhibited an additional absorption maximum at a longer wavelength (452 nm, with a band edge at ca. 522 nm), indicating that the electron delocalization was lengthened (see Figure 1).

The TGA trace of the polymer indicated two weight loss processes at ca. 260 and 400 °C. The first one might be related to the end-group decomposition and the second one corresponds to the backbone decomposition. DSC studies indicated no thermal transition before the polymer started to decompose (at about 260 °C).

Cyclic voltammetry studies of the monomer and the polymer were carried out in THF using Bu$_4$NBF$_4$ as the electrolyte. Significant differences were observed between the monomer and the polymer (Figure 2). Only a reversible reduction process for the monomer was observed at −1.11 V vs SCE reference electrode. For the polymer, however, three redox processes appeared: two reversible reduction processes at −1.00 and −1.87 V and an irreversible oxidation process at ca. 1.22 V. The reduction wave around −1.11 V for the monomer can be attributed to the reduction of the nitro groups, which still existed and exhibited only a slight change in the polymer.[15] The reduction wave in the polymer at about −1.87 V could be attributed to the reduction of the delocalized π-system. The oxidation wave in the polymer may be attributed to the oxidation of the π-system because the oxidation wave of the amino group was not observed in the monomer. Considering the fact that, in UV/vis spectra, the donor−acceptor charge-transfer band (λ_{max} = 391 nm in the monomer and polymer) was not changed significantly after the polymer was formed, the above assignments seem to be reasonable.

As a comparison, we attempted to synthesize a similar polymer with random substitutions (Scheme 2). It was found that no polymerization occurred and only a small amount of oligomer (yield <10%) was obtained. The steric hindrance from the substituents is one of the major reasons for the failure of polymerization. This result demonstrated the power of the rational structural design in polymer synthesis.

Because of the donor−acceptor arrangement, the polymer was expected to exhibit a cascading effect to enhance the third-order optical nonlinearity.[16] Detailed physical studies will be reported separately.

In summary, we have synthesized a new PPV with donor and acceptor groups regiospecifically attached to the backbone. This work revealed the following important points: (1) Careful designs of the monomer structure can lead to success in the synthesis of well-controlled polymers. (2) The Heck reaction has the potential to be explored for the synthesis of novel materials because the functional groups for the Heck reaction (vinyl and halide groups) are easy to handle. (3) The synthetic approach reported here is versatile, as this polymer system is just an example of a series of well-defined functional polymers. New properties due to regiospecific arrangements of the functional groups are imaginable.

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