Preparation and Nonlinear Optical Property of Azobenzene Substituted Polyacetylene

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Abstract: Two new functional polyacetylenes bearing different azobenzene group, -{HC=C[azo-N(CH$_3$)CH$_2$CH$_2$OH]}$_n$-, [poly(EHAB); azo = 4,4´-azobenzene] and -{HC=C[azo-N(CH$_3$)CH$_2$CH$_2$OCOC$_3$H$_7$]}$_n$-, [poly(EEAB)]} were prepared by [Rh(nbd)Cl]$_2$-Et$_3$N catalysts. Poly(EHAB) has poor solubility while poly(EEAB) can be dissolved in common solvent. The polymers were characterized by FTIR, ^{1}H NMR, UV and GPC. The nonlinear optical property of the soluble poly(EEAB) was investigated with 8 ns width pulse at 532 nm by Z-scan technique. The results show that poly(EEAB) is endowed with the larger third-order nonlinear optical property.

Keywords: Substituted polyacetylene, nonlinear optics, azobenzene.

Polyacetylene is an extensively conjugated polymer that shows the large third-order electric susceptibilities. However, its insolubility, instability and improcessability limit its practical applications as a functional material[1]. Introduction of some substituents into polyacetylenes can remarkably improve its solubility and stability. However, many substituted polyacetylenes show the smaller third-order nonlinear optical properties due to the decrease of π-conjugated degree[2-4]. Schuling found that the third-order nonlinear optical susceptibility (γ) depends on $γ_e^0$, a term related to the movement of electron, and β, the second-order nonlinear optical susceptibility[5]. Thus, the incorporation of a functional group with large second nonlinear optical susceptibility into polyacetylene can improve the nonlinear optical properties of polyacetylene. In this paper, we report the preparation and nonlinear optical property of polyacetylenes directly conjugatively linked with different substituted π-conjugated azobenzene group (**Scheme 1**).

Experimental

[Rh(nbd)Cl]$_2$, WCl$_6$, MoCl$_5$ and Ph$_4$Sn were all purchased from Aldrich and kept in inert atmosphere glovebox. Dioxane was distilled from sodium benzophenone ketyl *prior to* use. The synthesis of the monomers was performed according to ref.[6].

All polymerization reactions were carried out under nitrogen using a vacuum-line system. Into a baked 20 mL Schlenk tube with a side arm was added 1 mmol of the

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monomer.   3 mL dioxane was injected into the tube to dissolve the monomer.   The catalyst solution was prepared in another tube by dissolving 4.6 mg (0.01 mmol) [Rh(nbd)Cl]$_2$ and 2.02 mg (0.02 mmol) Et$_3$N in dioxane (2 mL), which was transferred to the monomer solution using a hypodermic syringe.   The reaction mixture was stirred at room temperature for 3 h.   The mixture was then diluted with 5 mL dioxane.

The purification of poly(EHAB): the diluted solution gave no any isolable polymeric product when it was added dropwise to 200 mL methanol under stirring.   The precipitate produced during the polymerization was collected and dried under vacuum at 40 °C to a constant weight.   Yield: 48%.   FT-IR (KBr, cm^{-1}): 3424 (OH), 2924, 2861 (CH$_3$, CH$_2$), 1657, 1508, 828 (Ar).

The purification of poly(EEAB): the diluted solution was added dropwise to 200 mL methanol under stirring.   The precipitate was centrifuged and redissolved in THF.   Then the THF solution was added dropwise into 200 mL methanol to precipitate the polymer.   The dissolution-precipitation process was repeated three times, and the finally isolated precipitant was dried in vacuum at 40 °C to get red black powder.   Yield: 61%. GPC: M_w 39.1× 10^3, M_w/M_n: 2.5 (polystyrene calibration). FT-IR (KBr, cm^{-1}): 2923, 2856 (CH$_3$, CH$_2$), 1735 (C=O), 1602, 1516, 832 (Ar). ^{1}H NMR (CDCl$_3$, δ ppm): 6.40-8.41 (br., Ar-H and *trans* =C-H), 6.05 (br., *cis* =C-H), 4.25 (br., 2H, NCH$_2$CH$_2$), 3.62 (br., 2H, NCH$_2$CH$_2$), 2.91 (br., 3H, NCH$_3$), 2.21 (br., 2H, CH$_2$CH$_2$CH$_3$), 1.59 (br., 2H, CH$_2$CH$_2$CH$_3$), 0.86 (br., 3H, CH$_2$CH$_2$CH$_3$).

The nonlinear optical property of the sample measured by *Z*-scan technique was performed with a Q-swithed ns/ps Nd:YAG laser system continuum with pulse width of 8 ns at 1 Hz repetition rate and 532 nm wavelength.   The experiment was set up as ref.[7]. The relation between the normalized transmittance T(z) and z position was obtained by moving the samples along the axis of the incident beam (*z* direction) with respect to the focal point.   The incident and transmitted energies were detected simultaneously by an energy meter (Laser Precision Corporation Rjp-735).   The input energy was 100 μJ.

Results and Discussion

We first attempted to polymerize the monomers using the classical metathesis catalysts, such as WCl$_6$, WCl$_6$-Ph$_4$Sn, MoCl$_5$, MoCl$_5$-Ph$_4$Sn.   However, we did not get any isolable polymeric product, which may be due to the deactivation of the catalyst by the azo group.   Fortunately, [Rh(nbd)Cl]$_2$ can catalyze effectively to polymerize the monomers in moderate yield.   Although the monomer EHAB can be successfully polymerized by Rh catalyst, the resulting polymer can not be dissolved in any solvents, which may be the rigid planar *p*-azobenzene groups to adopt stacked structures[6].   When EHAB was esterified by butyric acid to obtain the monomer EEAB, a soluble, high molecular weight (M_w up to 39100) poly(EEAB) was obtained, indicating that the incorporation of flexible group effectively improve its solubility of the functional polyacetylene.

The characteristic ν_s (≡C-H) and ν_s (C≡C) absorption bands of the monomers disappeared in the IR spectra of their polymers, which proved the transformation of C≡C bond to C=C unit.   All the peaks in the ^{1}H NMR spectrum of poly(EEAB) change broad

Scheme 1 Synthetic route of the polymers

poly(EHAB): R = H, poly(EEAB): R = COC$_3$H$_7$

a) Rh(nbd)Cl$_2$-Et$_3$N, dioxane, 30 ^{o}C
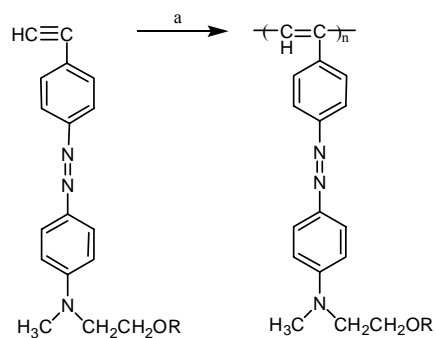
Figure 1 UV-Vis spectra of EEAB and poly(EEAB) in THF
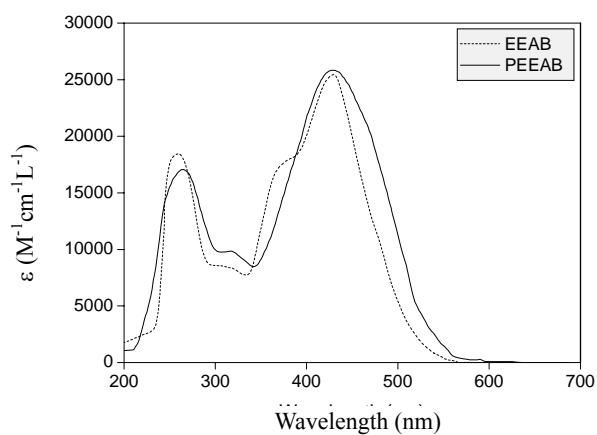
Figure 2 *Z*-scan data of poly(EEAB)
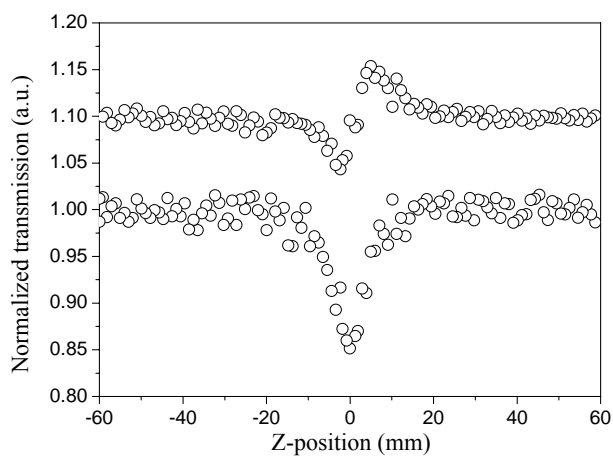
and a new broad peak appeared in the olefin absorption region (δ 5.9-6.2) corresponding to the *cis* olefin absorption of poly(EEAB) compared with the spectrum of the monomer EEAB, which further proved that the C≡C transfered to C=C.

    Figure 1 shows the UV spectra of poly(EEAB) and its monomer EEAB in THF. EEAB has four absorption peaks at 258, 315, 371, 429 nm, which corresponds to the absorption bands of the phenyl group, the amino auxochromic group, the conjugated ethynyl group and the π-π* transition absorption of azobenzene chromophores, respectively.   However, there are only three absorption peaks locating at 268, 325, 430 nm in the UV-Vis spectra of poly(EEAB).   The characteristic ethynyl group absorption peak disappeared and the cutoff wavelength increased in the spectrum of poly(EEAB) compared with that of EEAB, indicating that the monomer EEAB has been polymerized and poly(EEAB) has larger π–electronic conjugation than its monomer EEAB, which may be attributed to the contribution of conjugated polyacetylene backbone.

    The nonlinear optical property of poly(EEAB) was measured by *Z*-scan technique. **Figure 2** shows the results of the *Z*-scan obtained with an aperture and without an aperture.   The third-order susceptibility of poly(EEAB) was calculated to be 2.43×10^{-11} esu base on the experimental data.   The third-order susceptibility of poly(EEAB) is almost two orders of magnitude larger than that of poly(phenylacetylene)[2-4] or poly(2-pyridylacetylene)[5].   The large susceptibility of poly(EEAB) may be attributed to the contribution of the large second-order susceptibility of azobenzene and the larger conjugation between polyacetylene main chain and the side chain of azobenzene chromophoric group.   Thus, the incorporation of flexible group into polyactylene effectively improved its solubility and the direct linking of azobenzene to polyacetylene enhanced the third-order susceptibility of polyacetylene.   This work paves the way for designing new soluble functional polyacetylene with large nonlinear optical property.

References

1.   W. S. Fann, S. Benson, J. M. Madey, *et. al.*, *Phys. Rev. Lett.*, **1989**, *62*, 1492.
2.   M. Falconieri, R. D'Amato, A. Furlani, M. V. Russo, *Syn. Met.*, **2001**, *124*, 217.
3.   D. Nehert, A. Kaltbeitzelz, A. Wolf, C. Bubeck, G. Wegner, *J. Phys. D: Appl. Phys.*, **1991**, *24*, 1193.
4.   H. Okawa, K. Kurosawa, T. Wada, H. Sasabe, *Syn. Met.*, **1995**, *71*, 1657.
5.   A. Schuling, *Chem. Phys. Lett.*, **1967**, *1*, 195.
6.   M. Terguchi, T. Masuda, *Macromolecules*, **2000**, *33*, 240.
7.   M. S. BaHae, A. A. Said, T. H. Wei, *et. al.*, *IEEE J Quantum Electron*, **1990**, *26*, 760.