Novel Polymers Containing Discrete Conjugated Units, Produced by the Heck Reaction

Sergei FOMINE, Lioudmila FOMINA, Héctor Quiroz FLORENTINO,
Juan Manuel MENDEZ, and Takeshi OGAWA

*Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México,
Apartado Postal 70–360, Coyoacán, México DF, 04510*

(Received April 24, 1995)

ABSTRACT: Novel monomers and polymers containing arylenevinylideneethynylene groups were synthesized *via* the Heck reaction. The polymers were amorphous and soluble in common organic solvents. They showed T_g around 60°C and 5% weight loss in the region of 240–340°C and underwent thermal cross-linking on heating to 170–190°C at the expense of triple bonds. One of the polymers showed strong blue luminescence with emission maxima around 380–390 and 470–480 nm with excitation at 320 nm. All polymers showed nonlinear optical susceptibility of the third order ($\chi^{(3)}$) around 10^{-10} esu.

KEY WORDS Heck Reaction / Acetylenes / Luminescent Polymers /

The main chain conjugated polymers have attracted attention as materials for nonlinear optical applications.¹ Poly(aryleneethynylene)s, in particular, have received considerable attention due to their relatively large third order harmonic generation, ($\chi^{(3)} = 4.7 \times 10^{-11}$ esu) and fluorescent properties.^{2–5} They can be readily prepared by Pd-catalyzed coupling of bis-arylhalides with terminal bis-acetylenes. The processing of poly(aryleneethynylene)s into films and fibers is crucial for the development of these materials. However, poly(aryleneethynylene)s are usually insoluble and infusible due to polarizable π -electrons and rigid polymer chains. Improvement of processability of conjugated polymers has been attempted by incorporation of long aliphatic tails as side chains of poly(aryleneethynylene).^{3–5} A soluble, high molecular weight dendritic poly(aryleneethynylene) has been synthesized by the Heck condensation of 4-ethynyl- β,β -dibromostyrene.⁶ However, the incorporation of bulky side groups often leads to decrease in conjugation because of steric hindrance due to the presence of bulky

side groups in the polymer chain. Thus, even high molecular weight poly(aryleneethynylene)s ($M_w = 10^5$) often showed absorption maxima in the visible region at around 400 nm which reflects only moderate conjugation.⁴ Poly(4-ethyl- β,β -dibromostyrene)⁶ show an absorption maximum at around 400 nm where the corresponding model compound, 4,4'-bis-[(β,β -diethynylphenyl)vinyl]diphenyldiacetylene, showed an absorption maximum in the same region. This means that no conjugation exists between repeating units in the polymers due to steric hindrance in branched macromolecules. Bearing this in mind, it is reasonable to suggest that a polymer consisting of discrete aryleneethynylene moieties linked together by flexible spacers should exhibit $\chi^{(3)}$ values of the order of those showed by conventional poly(aryleneethynylene)s. Thus, polymers containing fluorescein moieties incorporated into a polymer chain showed $\chi^{(3)}$ as high as 2×10^{-10} esu with an excellent transparency.⁷

This work is concerned with the synthesis of some novel polymers by the Heck reaction of dibromides of rigid and conjugated arylene-

Monomer Synthesis

Scheme 1. (a)

Monomer Synthesis

Scheme 1. (b)

Polymer Synthesis

Scheme 1. (c)

vinylideneethynylenes with bisacetylenes with flexible spacer. Arylenevinylideneethynylene groups are more conjugated than aryleneethynylene groups since the conjugations between double and triple bond is better than that between triple bond and benzene ring.

EXPERIMENTAL

Materials

Triethylamine, methylene chloride, and dioxane all from Aldrich, were distilled over CaH₂ and stored under nitrogen. Other reagents (Aldrich) were used as received.

Monomer Synthesis

The synthesis of the monomers and the polymers is shown in Scheme 1 (a, b, c).

β,β -Di(phenylethynyl)-4-ethynyl styrene (**6**), 4-ethynylbenzaldehyde (**3**), and dipropargyl sebacate (**8**) were prepared according to the literature.⁸⁻¹⁰

*4-Formyl-4'-(di(phenylethynyl)vinyl)diphenylacetylene (**9**)*

A solution containing pyridine (200 ml), triethylamine (200 ml), 4-bromobenzaldehyde

(**1**) (7.7 g, 4.2×10^{-2} mol), β,β -Di(phenylethynyl)-4-ethynyl styrene (**6**) (13.6 g (4.2×10^{-2} mol), triphenylphosphine (TPP) (0.7 g), CuI (0.2 g), and PdCl₂ [(TPP)]₂ was refluxed for 6 hours under nitrogen flow. The ammonium salt precipitated was filtered off and washed with hot benzene. The solvents were evaporated under vacuum, and the residue was washed with diluted HCl, water, the dried under vacuum and chromatographed on SiO₂ (hexane/benzene). Yield 63%. $T_m = 139-141^\circ\text{C}$. IR (cm⁻¹) 3080 (C-H, arom), 2210-2180 (C $\equiv$ C), 1697 (C=O, aldehyde), and 1597 (C=C, arom). ¹H NMR (CDCl₃) 7.14 (s, 1H, -HC=C-(C $\equiv$ C-Ph)₂), 7.34-7.39, 7.50-7.58 (m, 12H, arom.), 7.67 (d, 2H, meta to -HC=O), 7.85 (d, 2H, *ortho* to -HC=O), 7.94-7.97 (d, 2H, arom.), 10.02 (s, 1H, HC=O). ¹³C NMR (CDCl₃) 86.93, 89.17, 89.26, 90.29, 93.52, 95.56 (C $\equiv$ C), 104.7 ((Ph-C $\equiv$ C)₂-C=), 122.8, 122.9, 123.0, 128.4, 128.5, 128.6, 129.0, 129.5, 129.6, 131.7, 131.8, 131.81, 132.2, 132.5, 135.6 (all ring atoms), 136.4 (Br₂C=C-Ar), 141.9 (-HC=C-(C $\equiv$ C-Ph)₂), and 191.3 (-HC=O).

4-(β,β -Dibromovinyl)-4'-(di(phenylethynyl)-vinyl)diphenylacetylene (12**)**

To a solution of TPP (15.5 g, 6×10^{-2} mol) in 250 ml dry CH_2Cl_2 , CBr_4 (10 g, 3×10^{-2} mol) was added dropwise during 10 min under nitrogen. The orange solution formed was stirred for 20 min and 4-formyl-4'-(di(phenylethynyl)vinyl)diphenylacetylene (**9**) (12.86 g, 3×10^{-2} mol) in 200 ml of CH_2Cl_2 was added to the solution, and the reaction mixture was stirred for 6 hours at room temperature under nitrogen flow. The solvent was evaporated and the residue extracted with hot hexane. The hexane was evaporated and the crude product was chromatographed on SiO_2 (hexane). Yield 43%. $T_m = 138\text{--}141^\circ\text{C}$. IR (cm^{-1}) 3050 (C–H, arom.) 2200 ($\text{C}\equiv\text{C}$), and 1597 (C=C, arom.). ^1H NMR (CDCl_3) 7.14 (s, 1H, $-\text{HC}=\text{C}-\text{C}\equiv\text{C}-\text{Ph}$), 7.46 (s, 1H, $-\text{HC}=\text{CBr}_2$), 7.32–7.39, 7.47–7.57 (m, 12H, arom.), and 7.92–7.95 (d, 2H, arom.). ^{13}C NMR (CDCl_3) 86.94, 89.06, 89.18, 90.45, 90.91, 95.41 ($\text{C}\equiv\text{C}$), 91.00 ($\text{Br}_2\text{C}=\text{C}$), 104.2 ($(\text{Ph}-\text{C}\equiv\text{C})_2-\text{C}=\text{C}$), 122.7, 122.8, 123.3, 123.6, 126.6, 128.3, 128.4, 128.5, 128.6, 128.92, 128.9, 131.6, 131.7, 131.74, 135.1, 135.8 (all ring aroms), 136.2 ($\text{Br}_2\text{C}=\text{C}-\text{Ar}$), and 142.0 ($-\text{HC}=\text{C}-(\text{C}\equiv\text{C}-\text{Ph})_2$). *Elemental analysis.* ($\text{C}_{34}\text{H}_{20}\text{Br}_2$) Calcd: C, 69.41%; H, 3.43%. Found: C, 69.21%; H, 3.41%.

4-(Formyl)diphenylacetylene (10**)**

A solution containing 4-bromobenzaldehyde (**1**) (24.5 g, 0.13 mol), phenylacetylene (16.4 g, 0.13 mol), TPP (1 g), CuI (0.3 g), PdCl_2 [$(\text{TPP})_2$] (0.4 g) and 300 ml of triethylamine, was refluxed for 4 hours. The ammonium salt precipitated was filtered off and washed with hot benzene. The solvents were evaporated under vacuum and the residue was washed with dilute HCl and water and then dried under vacuum. The product was crystallized from a hexane/benzene mixture. Yield 54%, $T_m = 100\text{--}102^\circ\text{C}$ (lit. 102°C^{11}).

4-(β,β -Dibromovinyl)diphenylacetylene (13**)**

To a solution of TPP (25.4 g, 9.7×10^{-2} mol) in 250 ml of dry CH_2Cl_2 , CBr_4 (16 g, 4.85×10^{-2} mol) was added dropwise during 10 min under nitrogen. The orange solution formed was stirred for 20 min and 4-formyldiphenylacetylene (**10**) (10 g, 4.85×10^{-2} mol) in 200 ml of CH_2Cl_2 was added to the solution and the reaction mixture was stirred for 6 hours at room temperature under nitrogen flow. The solvent was evaporated and the residue was extracted with hot hexane. Hexane was evaporated and the crude product was chromatographed on SiO_2 (hexane). Yield 48%. $T_m = 73^\circ\text{C}$. IR (cm^{-1}) 3040 (C–H, arom.) 2210 ($\text{C}\equiv\text{C}$), and 1601 (C=C, arom.). ^1H NMR (CDCl_3) 7.30–7.40, 7.50–7.60 (m, 9H, arom.), and 7.46 (s, 1H, $-\text{HC}=\text{CBr}_2$). ^{13}C NMR (CDCl_3) 89.10, 90.35 ($\text{C}\equiv\text{C}$), 90.78 ($\text{Br}_2\text{C}=\text{C}$), 123.5, 126.6, 128.3, 128.4, 128.5, 128.6, 131.55, 131.63 (all ring carbons), and 136.2 ($=\text{C}-\text{Ar}$). *Elemental analysis:* ($\text{C}_{16}\text{H}_{10}\text{Br}_2$) Calcd: C, 53.08%; H, 2.78%. Found: C, 53.77%; H, 2.81%.

4-Formyl-4'-nitrodiphenylacetylene (11**)**

A solution containing 4-bromonitrobenzene (7.2 g, 3.57×10^{-2}), 4-ethynylbenzaldehyde (4.66 g, 3.57×10^{-2} mol), TPP (0.3 g), CuI (0.1 g), PdCl_2 [$(\text{TPP})_2$] (0.2 g), 100 ml of triethylamine and 100 ml of pyridine was refluxed for 4 hours. The ammonium salt precipitated was filtered off and washed with a hot benzene. The solvents were evaporated under vacuum and the residue was washed with diluted HCl and water and the dried under vacuum and crystallized from ethanol. $T_m = 206\text{--}207^\circ\text{C}$. Yield 56%. IR (cm^{-1}) 3040 (C–H, arom.), 2843 (H–C=O), 2214 ($\text{C}\equiv\text{C}$), 1703 (C=C, aldehyde), 1601 (C=C, arom.), 1533, and 1340 (NO_2). ^1H NMR (CDCl_3) 7.63 (d, 2H (meta to $-\text{HC}=\text{O}$)), 7.65 (d, 2H (meta to NO_2)), 7.83 (d, 2H (ortho to $-\text{HC}=\text{O}$)), 8.18 (d, 2H (ortho to NO_2)), and 9.98 (s, 1H, $\text{HC}=\text{O}$). ^{13}C NMR (CDCl_3) 90.94, 93.56 (C=C), 123.43, 123.75, 128.24, 129.37, 129.64,

132.41, 132.55, 136.22 (all ring atoms), and 191.15 (–HC=O).

4-(β,β -Dibromovinyl)-4'-nitrodiphenylacetylene (**14**)

To a solution of TPP (4.4 g, 1.7×10^{-2} mol) in 50 ml of dry CH_2Cl_2 , CBr_4 (2.83 g, 8.5×10^{-3} mol) was added dropwise during 10 min under nitrogen. The orange solution formed was stirred for 20 min and 4-formyl-4'-nitrodiphenylacetylene (**11**) (2.14 g, 8.5×10^{-3} mol) in 50 ml of CH_2Cl_2 chloride was added to the solution and the reaction mixture was stirred for 6 hours at room temperature under nitrogen flow. The solvent was evaporated and the residue was extracted with hot hexane. Hexane was evaporated and the crude product was chromatographed on SiO_2 (hexane). Yield 57%. $T_m = 160\text{--}163^\circ\text{C}$. IR (cm^{-1}) 3040 (C–H, arom.) 2210 ($\text{C}\equiv\text{C}$), 1591 (C=C, arom.), and 1336 (– NO_2). ^1H NMR (CDCl_3), 7.49 (s, 1H, –HC=CBr₂), 7.56–7.59 (m, 4H, arom.), 7.66–7.68 (m, 2H, *meta* to NO_2), and 8.20–8.25 (m, 2H, *ortho* to NO_2). ^{13}C NMR (CDCl_3), 88.72, 94.25 ($\text{C}\equiv\text{C}$), 91.01 (Br₂C=), 122.2, 123.7, 128.5, 129.9, 131.8, 132.3 (all ring carbons), 136.0 (=C–Ph), and 147.1 (>C– NO_2). *Elemental analysis*: ($\text{C}_{16}\text{H}_9\text{NO}_2\text{Br}_2$) Calcd: C, 47.21%; H, 2.23%; N, 3.44%. Found: C, 47.89%; H, 2.21%; N, 3.45%.

Polymerization

Polymers **P12**, **P13**, and **P14** were prepared as follows: 1×10^{-2} mol of the monomer **12**, **13**, or **14** and 1×10^{-2} mol of monomer **8** were dissolved in a mixture of 20 ml of dioxane and 20 ml of triethylamine. Nitrogen was bubbled through the solution for 20 min, then catalyzer was added (0.2 g, of TTP, 0.1 g of CuI, and 0.15 g of PdCl_2 [(TTP)₂]) and the reaction mixture was refluxed under nitrogen flow for 24 hours. In all cases, the polymers formed were soluble in the reaction mixture during polymerization. The ammonium salt precipitated during the polymerization was filtered off, and washed with dioxane. The mother

Table I. Elemental analysis data of the polymers **P12**, **P13**, and **P14**

Polymer	Formula	Calcd/%			Found/%		
		C	H	N	C	H	N
P12	($\text{C}_{50}\text{H}_{40}\text{O}_4$) _n	85.2	5.72	—	84.33	5.81	—
P13	($\text{C}_{32}\text{H}_{30}\text{O}_4$) _n	80.31	6.32	—	79.91	6.41	—
P14	($\text{C}_{32}\text{H}_{29}\text{NO}_6$) _n	73.41	5.58	2.68	73.01	5.55	2.43

liquor was concentrated under vacuum and the polymer was precipitated in methanol, which was filtered off, rinsed with water and methanol and dried under vacuum at room temperature. The elemental analysis data are presented in Table I.

Measurements and Sample Preparation

The relative molecular weight was determined using a Varian 9012 instrument at 30°C in THF with polystyrene standard, universal column and a flow of 1 ml min^{-1} . DSC was performed at a heating rate of $20^\circ\text{C min}^{-1}$ under nitrogen with a du Pont 2100. FT-IR-spectra were taken using a Nicolet 510p spectrometer. UV-Visible spectra were taken using a Shimadzu UV-260 spectrometer in chloroform. ^1H NMR and ^{13}C NMR spectra were taken using a Varian spectrometer at 300 MHz and 75.5 MHz, respectively, in CDCl_3 with TMS as an internal standard. Photoluminescence was measured using a Perkin-Elmer LS-2 fluorimeter in CHCl_3 solution or in solid films with excitation wavelength of 320 nm.

RESULTS AND DISCUSSION

The polymerization was carried out in dioxane in the presence of triethylamine as a HBr scavenger. Dioxane is a good solvent to solubilize the Pd complex and polymers. The reaction mixture was homogeneous during polymerization to give soluble film forming polymers with observed molecular weights (M_w) of 41000, 23000, and 18000, for the

polymers **P12**, **P13**, and **P14**, respectively, with a fairly narrow molecular weight distribution for this type of polycondensation ($M_w/M_n = 1.4\text{--}1.6$). The polymers were yellow powders soluble in common organic solvents such as tetrahydrofuran (THF), chloroform and methylene chloride. It is noteworthy that polymer **P12** showed strong blue luminescence in solution and also as a film.

FT-IR spectra of the polymers **P12**, **P13**, and **P14** are shown in Figure 1. All spectra showed absorption bands around 3050 and 2900 cm^{-1} , corresponding to C–H stretching of rigid and soft segments of the polymer chain, respectively. In the region of C $\equiv$ C stretches an absorption band of internal triple bonds of the main and side chain could be seen around 2200 cm^{-1} . An intensive peak of ester carbonyl stretching appeared at 1740 cm^{-1} . Polymer **P14** showed a strong absorption band at

Figure 1. FTIR spectra of polymers **P12**, **P13**, and **P14**.

1342 cm^{-1} due to the nitro group. These data agree well with the polymer structures. None of the polymers showed terminal acetylenic end groups (3300 and 2100 cm^{-1}) which suggests that the polymerization was complete.

^1H NMR spectra of the polymers are shown in Figure 2. Apart from the signals of aromatic protons in the region of 7–8 ppm, all 3 polymers exhibited four multiplets with relative intensity of 1:1:1:2 around 4.8, 2.3, 1.6, and 1.25 ppm, corresponding to the protons of $-\text{CH}_2-$ of propargyl groups, methylene groups next to C=O, methylene groups $-\text{OC}-\text{CH}_2\text{CH}_2-$ and internal methylene groups of methylene spacer, respectively. In ^{13}C NMR spectra, the signals of these methylene carbons appeared at 52.00, 34.00, 29.00, and 24.8 ppm, respectively. Ester carbonyl carbons of polymers **P12**, **P13**, and **P14** appeared at 173 ppm. After the polymerization, signals of the protons of dibromovinyl group ($-\text{HC}=\text{CBr}_2$), in monomers **12**, **13**, and **14** around 7.45 ppm disappeared and a new signal of protons of diethynylvinyl group ($-\text{CH}=\text{C}-(\text{C}\equiv\text{C})_2$) of polymers could be clearly seen around 7.14 ppm. At the same time, the signals of the carbon atoms of dibromovinyl group ($-\text{HC}-\text{CBr}_2$) which appeared around 91 ($-\text{HC}=\text{CBr}_2$)

Figure 2. ^1H NMR spectra of polymers **P12**, **P13**, and **P14**.

CBr_2) and 136 ppm ($-\text{HC}=\text{CBr}_2$), respectively, in the monomers, disappeared after the polymerization and signals of the carbon atoms of diethynylvinyl group could be detected at 104.2 and 144.3 ppm, respectively. Positions of the signals of aromatic protons in ^1H NMR spectra and aromatic carbons in ^{13}C NMR spectra of polymers **P12**, **P13**, and **P14** coincided with those of monomers **12**, **13**, and **14**, respectively.

UV-Visible spectra of the monomers **12**, **13**, **14**, and corresponding polymers **P12**, **P13**, and **P14** are shown in Figure 3. As can be seen the long wave absorption maximum of the monomers shifted to the long wave wavelength from monomer **12** (311 nm) to **14** (380 nm) because of expanding of the conjugation system. An additional long wave shift of long wave absorption maxima took place on polymerization. Thus, polymers **P12**, **P13**, and **P14** showed long wave absorption maximum at 340, 360, and 400 nm, respectively. This additional bathochromic shift of the long wave absorption maxima was due to further extension of the conjugated system in the polymers by the two additional ethynyl groups.

Polymer **P12** exhibited strong blue luminescence in solution and in the solid state (film).

Figure 3. UV-Visible spectra of monomers **12**, **13**, **P14**, and polymers **P12**, **P13**, and **P14**.

The spectra of luminescence are shown in Figure 4. The spectra of both solution and film had two maxima at 380–390 and 470–480 nm.

Preliminary ($\chi^{(3)}$) of polymer films were obtained using a picosecond laser consisting of a mode locked Quantel Nd: YAG laser with frequency doubled to 532 nm. ($\chi^{(3)}$) Values of polymers **P12**, **P13**, and **P14** were found to be of 2.7×10^{-10} , 1.1×10^{-10} , and 1.6×10^{-10} esu, respectively.

DSC and TGA thermograms of polymers **P12**, **P13**, and **P14** are presented in Figures 5 and 6, respectively. The polymers showed a glass transition around 60°C and an exotherm at 175, 190, and 183°C for polymers **P12**, **P13**, and **P14**, respectively. These exotherms are

Figure 4. Luminescence spectra of polymer **P12** (thin film (1), chloroform solution (2)).

Figure 5. DSC curves of polymers **P12**, **P13**, and **P14**.

Figure 6. TGA curves of polymers **P12**, **P13**, and **P14**.

due to thermal cross-linking of the polymers through triple bonds based on a comparison of IR spectra of the polymers before and after heating (absorption band around 2200 cm^{-1} significantly decreased its intensity). According to X ray diffraction data the polymers were amorphous.

5% Weight loss was observed for **P12** at 340, for **P13** at 240, and for **P14** at 250°C. The thermal stability of **P12** was about 100°C higher than that of polymers **P13** and **P14**, which can be explained by higher content of the triple bonds in the former, leading to denser and therefore a more thermostable network with thermal cross-linking.

In conclusion, novel monomers and polymers containing arylenevinylideneethynylene groups were synthesized by the Heck reaction. The polymers were amorphous and soluble in common organic solvents. They showed T_g around 60°C and 5% weight loss in the region of 250–340°C. The polymers underwent thermal cross-linking on heating to 170–190°C at the expense of triple bonds. Polymer **P12** showed strong blue luminescence with

emission maxima around 370–380 and 470–480 nm with excitation at 320 nm.

Acknowledgments. The authors acknowledge the financial support of CONACyT (Consejo Nacional de Ciencias y Tecnología) under contract No. E-9406 (1994–1995). Thanks are also due to C. Vazquez and M. A. Canzeco for the assistance in thermal analysis and UV-spectroscopy, respectively. The authors express their gratitude to Professor D. Rao of Physics Department of University of Massachusetts, Boston for the $\chi^{(3)}$ measurements.

REFERENCES

1. D. Chemla and J. Zuss, Ed., "Nonlinear Optical Properties of Organic Molecules and Crystal, vol. 2, Academic Press, New York, N.Y., 1987.
2. K. Sanechika, T. Yamamoto, and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, **57**, 752 (1984).
3. M. Moroni, J. Le Moigne, and S. Luzzati, *Macromolecules*, **27**, 562 (1994).
4. T. Yamamoto, W. Yamada, M. Takagi, K. Kizu, T. Maruyama, N. Ooba, S. Tomaru, T. Kurhhara, T. Kaino, and K. Kubota, *Macromolecules*, **27**, 6620 (1994).
5. T. Yamamoto, M. Takagi, K. Kizu, T. Maruyama, K. Kubota, H. Kanbara, T. Kurihara, and T. Kaino, *J. Chem. Soc., Chem. Commun.*, 797 (1993).
6. L. Fomina and R. Salcedo, *Polymer*, in press.
7. S. Fomine, A. Pineda, T. Ogawa, R. Perez, and M. Sotelo, *Polym. J.*, **27**, 712 (1995).
8. L. Fomina, H. Allier, S. Fomine, and R. Salcedo, T. Ogawa, *Polym. J.*, **27**, 591 (1995).
9. S. Fomine, S. Sanchez, and T. Ogawa, *Polym. J.*, **27**, 165 (1995).
10. W. Austin, N. Bilow, W. Kelleghan, and K. S. Y. Lau, *J. Org. Chem.*, **46**, 2280 (1981).
11. G. Drefahl and G. Plotner, *Chem. Ber.*, **93**, 990 (1960).