

Synthesis and Characterization of Poly(aryleneethynylene)s and Their Corresponding Platinum-Linked Polymers

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Received 20 March 2011, accepted in final revised form 11 August 2011

This article was published online on 1 September 2011. This notice is included here to indicate that subsequent modifications have been made by authors on 16 October 2011

Abstract

A series of thermally stable organic polymers [poly(2,5-diethynylpyridine) (**5**), [poly(1,4-diethynyl benzene)] (**6**), [poly(2,5-dialkyl-*p*-phenyleneethynylene)] (**7**), and [poly(*p,p*-diethynylbiphenyl)] (**8**), were synthesized by the reaction between diterminal aryleneethynylene, [HCCArCCH] {Ar = C₅H₅N (**1**); Ar = C₆H₆ (**2**); Ar = C₆H₄(CH₃)₂ (**3**); Ar = C₆H₄-C₆H₄ (**4**)} and CuCl in pyridine by Hay's oxidative coupling method. Then the organometallic polymers [Ph (PⁿBu₃)₂Pt-C≡C-(Ar-C≡C-C≡C)_n-Pt((PⁿBu₃)₂Ph) {Ar = C₅H₅N (**9**); Ar = C₆H₆ (**10**); Ar = C₆H₄(CH₃)₂ (**11**); Ar = C₆H₄-C₆H₄ (**12**)} were synthesized by the reaction of organic polymers **5**, **6**, **7** and **8** with metal precursor (PⁿBu₃)₂PtPhCl in diethylisopropyleamine with good yield. These metal-linked polymers were characterized by IR, ¹H-NMR, ¹³C-NMR and ³¹P-NMR spectra. Finally the molecular weight of the organometallic polymers (**9**, **10**, **11** and **12**) was determined by gel permeation chromatography (GPC). It is clearly observed from GPC that the polymers were synthesized with different degree of polymerization.

Keywords: Organometallic polymers; Hay's Oxidative coupling; GPC.

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doi: 10.3329/jsr.v3i3.7293 J. Sci. Res. 3 (3), 587-597 (2011)

1. Introduction

The immense interest in polymer chemistry lies in multifunctional polymeric materials. Organometallic polymers containing transition metal in the centre with conjugated alkynyl ligands are very useful due to their stiff molecular structure and π -electron conjugation along the polymeric chain. These special properties lead the conjugated organic and

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organometallic polymers as semiconductors and have potential applications in light emitting diodes [1, 2], photovoltaic cells [3, 4], field effect transistors [5-7], sensors [8, 9] and lasers [10]. π -Conjugated polymers also arose much attention due to their potential usages for optical switching around 1ps, frequency modulation, wave guiding, practically all optical computing, optical data storage, optical communication and image processing [11]. Due to extensive cloud of π - electrons that are easily polarized in conjugated π -system in the organic polymer with charge asymmetry have been shown to exhibit extremely large second order non linear optical (NLO) properties.

The nonlinearity of such molecules can be enhanced by either increasing the conjugation length, or increasing electron delocalization. It should be equally possible by increasing the length of donor or acceptor groups to improve electron asymmetry within the molecule [12]. In 1998, Swager [13, 14] reported the synthesis of porous PPE derivatives in which pentiptycene modules are incorporated into the PPE main chain useful for molecularly wired sensors for signal application.

Recently, the utility of π - conjugated polymers as materials for an electroluminescence device has been demonstrated [15]. π -Conjugated polymers conduct electricity by transporter mobility (positive and negative), which is the most important parameter for transistor performance. Poly(thiophene-2,5-diyl), (PTh) and its derivatives are the best studied polymers for transistor application [16]. Weder [17, 18] in his two spectacular contributions has shown that PPEs can also be used as photoluminescence polarizer's in LCD displays.

The Pd-catalyzed Heck and Cassar-Sonogashire-Hagilare reaction form the single bond between the arene ring and the alkyne triple bond. It should be equally possible to form the C-C triple bond during the polymerization reaction. In the case of double bond it has been achieved by McMurry [19] coupling, condensation reaction [20] and alkene metathesis [21]. However, the yield of the metathesis product is only moderate; making this catalyst unattractive for the formation of PPEs [22]. However, Pizzoferrato [23] reported the synthesis of PPEs by further improvement of the palladium-catalyzed extended one-pot procedure and demonstrated that the percentage of yield is high within reasonable reaction time. In 1997, Bunz [24], Weiss and Mullen reported the first use of Schrock's tungsten-carbyne [25] for the preparation of some PPEs including 2, 5-dihexyl-PPE. While the Schrock catalyst $(^t\text{BuO})_3\text{W}\equiv\text{C}-^t\text{Bu}$ is superbly active, it has to be synthesized, and is very sensitive toward air and particularly water.

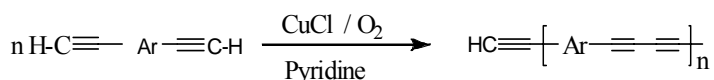
As a consequence the preparation of PPEs utilizing Schrock carbynes is not particularly practical. Kloppenburg, Pschier, and Bunz [26, 27] optimized the reaction conditions of alkyne metathesis utilizing $\text{Mo}(\text{CO})_6$ and 4-chlorophenol by increasing the temperature from 105 °C to 130-150 °C. But this catalyst is not particularly tolerant of hetero atoms with exception of oxygen functionalities; it synthesizes aromatic hydrocarbons in high yield and with unsurpassed ease. In 2001, Huang [28] reported the synthesis of some PPE by alkyne metathesis utilizing $\text{Mo}(\text{CO})_6$ and 1,2-dichlorobenzene and they showed the effect of side chain and geometry on the ground state electronic structure of PPE. Electrochemical methods frequently present new aspects on materials

such as film-formation and an appearance of various oxidation states by electrochemical doping. Thus a novel approach for synthesis of conducting polymers with conjugated carbon-carbon triple bond using electrochemical method is to investigate using CuCl-TMEDA as the mediator according to reference of Hay coupling [29] which is shown in scheme 1.



Scheme-1

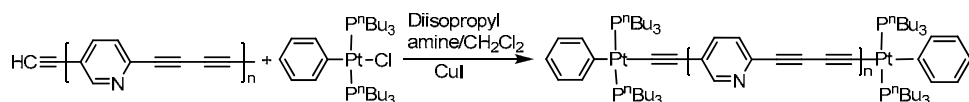
But for simplicity, we synthesized the polymers by chemical method of Hay's oxidative coupling. In this process, the polymers (**5**, **6**, **7** and **8**) were prepared by reacting various amounts of diterminal aryneethynyls in pyridine with a catalytic mixture of CuCl and O₂ (Scheme 2). Polymer **6** was synthesized previously by Kijima *et al* [30].



Scheme-2

It has been demonstrated that the organometallic polymers containing Group 8-10 metals in the backbone are highly soluble in common organic solvents and that the conjugation is maintained through the metal centers linking acetylene units in such polymers. The rigid-rod Pt (II) acetylide polymer was prepared by two synthetic routes: a) by a dehydrohalogenation reaction [31] of diterminal aryneethynyls with Pt (PⁿBu₃)₂Cl₂ in diethylamine using CuI as a catalyst and b) by reacting bis[(trimethylstannyl) ethynyl] pyridine with Pt(PⁿBu₃)₂Cl₂ in toluene containing a catalytic amount of CuI [32]. Silverman in 2005, reported [33] some copolymers and model compounds containing Pt(PⁿBu₃)₂Cl₂ in the backbone of the poly(phenylethynyl)s, where the side chain of the phenyl group varies from alkyl to alkoxy group. They also showed the effect of *m*-linkage of metal precursor in the polymeric and oligomeric backbone unit.

But for availability of reaction materials and maintainable reaction environment, the organometallic polymers (**9**, **10**, **11** and **12**) were synthesized by the reaction of organic polymers (**5**, **6**, **7** and **8**) with Pt(PⁿBu₃)₂PhCl in diisopropylamine and dichloromethane using CuI as a catalyst respectively (Scheme-3).



Scheme-3

2. Experimental

2.1 Materials

All the solvents were freshly distilled, dried, and degassed before use. The solvent e.g.; Et₂NH, diisopropylamine, dichloromethane, *n*-hexane, pyridine and chromatographic silica gel were purchased from E-Mark and BDH. The catalyst e.g.; copper (I) iodide, copper (I) chloride were purchased from Aldrich and were used without further purification. UV-vis spectra were recorded in dichloromethane solution on Shimadzu UV-160A UV-vis Recording Spectrometer. Infrared spectra were recorded in CH₂Cl₂ and solid state (KBr) on Shimadzu FTIR Spectrometer. ¹H-NMR, ¹³C-NMR were recorded on Bruker NMR 400 MHz spectrometer in CDCl₃. ³¹P-NMR were recorded on Bruker 121.53 MHz NMR spectrometer in CDCl₃.

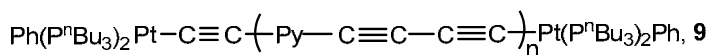
2.2 Synthesis of substituted poly (aryleneethynylenes)

Oxygen was bubbled through a rigorously stirred solution of copper (I) chloride in 15 mL of freshly distilled pyridine for 30 min. Then a solution of substituted aryleneethynyls in 5 mL of pyridine was added and stirred for another 30 min. After the formation of a colored precipitate in the flask, the mixture was diluted with 30 mL of methanol followed by dichloromethane and diethyl ether. The insoluble colored polymer was collected and dried for several hours on vacuum. Using the same procedure four substituted poly(aryleneethynylene)s **5**, **6**, **7** and **8** were synthesized. However, the duration of the reaction time was varied.

IR(KBr): Poly(2,5-diethynylpyridine), **5** : 3288 cm⁻¹ (ν ≡C-H), 2208 cm⁻¹, 2146 cm⁻¹, 2105 cm⁻¹ (ν C≡C), 1635 cm⁻¹, 1458 cm⁻¹, 839 cm⁻¹, poly(1,4- diethynyl benzene), **6** : 3288 cm⁻¹ (ν ≡C-H), 2206 cm⁻¹, 2142 cm⁻¹, 2105 cm⁻¹ (ν C≡C), 1635 cm⁻¹, 1598 cm⁻¹, 1489 cm⁻¹, 829 cm⁻¹, 647 cm⁻¹, poly(2,5-dialkyl-*p*-phenyleneethynylene), **7**: 3299 cm⁻¹ (ν ≡C-H), 2949 cm⁻¹, 2207 cm⁻¹, 2145 cm⁻¹, 2102 cm⁻¹ (ν C≡C), 1636 cm⁻¹, 1485 cm⁻¹, 8341 cm⁻¹ poly(*p,p*-biphenyldiethyne), **8** : 3299 cm⁻¹ (ν ≡C-H), 2212 cm⁻¹, 2146 cm⁻¹, 2106 cm⁻¹ (ν C≡C), 1602 cm⁻¹, 1486 cm⁻¹, 820 cm⁻¹

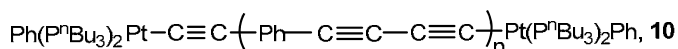
2.3 Synthesis of organometallic polymers

To a freshly dried and degassed diisopropyl amine (50 mL) and dichloromethane (10 mL), copper (I) iodide (0.042 mmol) was added and degassed for 10 minutes. Then previously prepared organic polymer (0.023 mmol) and (P^{*n*}Bu₃)₂PtPhCl (0.069 mmol) were added and stirred the reaction mixture for 20 h at room temperature. The completion of the reaction was confirmed by the change of the color and from IR spectra (no ≡CH bond peak at 3300 cm⁻¹). The solvent was removed under reduced pressure and compounds **9**, **10**, **11**, **12** were obtained in the pure form after column chromatography.



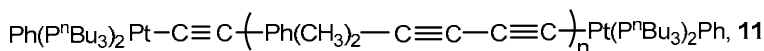
$^1\text{H-NMR}$ (δ ppm, CDCl_3): 0.87 (t, 36 H of $-\text{CH}_3$), 1.31 -1.71 (m, 72 H of $-\text{CH}_2-$), 6.79 (m, 8H of Ph-H), 6.87 (s, 2H of Ph-H), 7.31 (d, $J = 8$ Hz, 1H of Py), 7.52 (d, $J = 7$ Hz, 1 H of Py), 7.97 (d, $J = 8$ Hz, 1 H of Py-H near N). $^{13}\text{C-NMR}$ (δ ppm, CDCl_3): 14.3, 22.4, 24.2, 25.9, 60.5, 69.9, 114.0, 121.5, 127.5, 131.5, 137.2, 143.2, 158.1.

IR (CH_2Cl_2): 2959, 2930.96, 2873, 2091, 1460, 849 cm^{-1} .



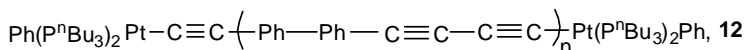
$^1\text{H-NMR}$ (δ ppm, CDCl_3): 0.87 (t, 36 H of $-\text{CH}_3$), 1.31 -1.69 (m, 72 H of $-\text{CH}_2-$), 6.87 (d, $J = 2$ Hz, 8H of Pt-Ph), 7.52 (d, 2 H of Pt-Ph) 7.68 (d, $J = 8$ Hz, 4 H of Ph-H). $^{13}\text{C-NMR}$ (δ ppm, CDCl_3): 14.0, 23.7, 25.9, 30.3, 68.1, 85.1, 121.2, 128.7, 132.4.

IR (CH_2Cl_2): 2961, 2930, 2089.96, 1604.84, 1464, 803 cm^{-1} .



$^1\text{H-NMR}$ (δ ppm, CDCl_3): 0.89 (t, 36 H of $-\text{CH}_3$), 1.24 -1.70 (m, 72 H of $-\text{CH}_2-$), 2.40 (s, 6H of $-\text{CH}_3$), 6.88 (2H of Ph-H middle), 7.82 (m, 10 H of Pt-Ph). $^{13}\text{C-NMR}$ (δ ppm, CDCl_3): 13.7, 22.8, 24.2, 25.9, 29.7, 68.9, 85.4, 121.9, 127.7, 132.0, 136.8.

IR (CH_2Cl_2): 2959, 2930.96, 2083, 1603, 1459, 905.62, 804 cm^{-1} .



$^1\text{H-NMR}$ (δ ppm, CDCl_3): 0.85 (t, 36 H of $-\text{CH}_3$), 1.24 -1.40 (m, 72 H of $-\text{CH}_2-$), 6.79 (s, 2H of Pt-Ph), 6.88 (d, $J = 7.5$ Hz, 4 H of Ph-H) 7.58 (d, $J = 8$ Hz, 4 H of Ph-H). $^{13}\text{C-NMR}$ (δ ppm, CDCl_3): 13.7, 22.8, 24.2, 29.7, 68.9, 88.3, 127.7, 128.0, 132.9, 136.8.

IR (CH_2Cl_2): 2960, 2930, 2873, 2096, 1603, 1459, 804 cm^{-1} .

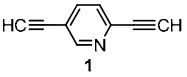
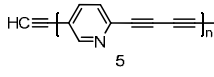
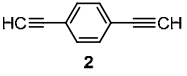
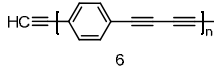
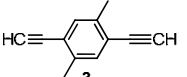
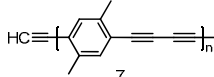
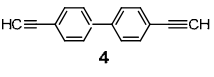
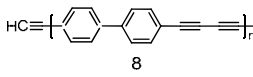
2. Results and Discussion

The important synthetic starting materials diterminal acetylenic compounds (entry: **1-4**) were synthesized by removing trimethyl silylgroup from organosilyl compounds [19] as shown the following Table 1. Most of the compounds were obtained with admirable percentage of yield and had only one product.

The organic polymers were synthesized by Hay's oxidative coupling reaction [30]. Among all of the polymers, compound **5** was synthesized within 30 min but the other polymers took 4-6 h. It seems that heterocyclic compound in the backbone facilitate the formation of polymer. All of the synthesized polymers (**5-8**) were colored and obtained

with high percentage of yield (nearly 100% except compound **7**). But the insoluble nature of these polymers in common organic solvents limit their characterization (shown in Table-1). However, polymer **5** was soluble in formic acid. Polymer **5** showed significant amount of red shift (115 nm) relative to its monomer which confirmed the formation of polymer because in the polymer, it creates conjugated π -system.

Table 1 Synthesis of acetylenic polymers from diterminal alkynes.

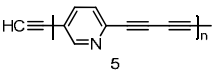
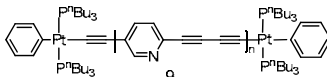
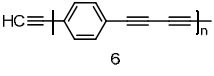
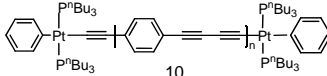
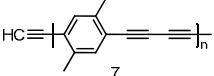
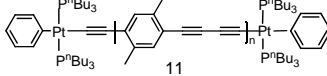
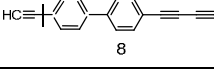
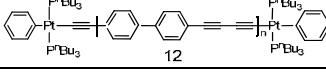
Entry	Starting Material	React. Materials	React. Time (h)	Product	% Yield	Mp ⁱ /Dp ^k
1		CuCl / O_2 Pyridine	0.5		98	130 ^j
2		CuCl / O_2 Pyridine	4		98	163-165 ^k
3		CuCl / O_2 Pyridine	6		85	178 ^k
4		CuCl / O_2 Pyridine	6		97	174 ^k

ⁱMelting point, ^kDecomposition point.

From the IR spectra, it is clearly observed that terminal $\equiv\text{CH}$ peak is absent in the organic polymer at around 3300 cm^{-1} but such peak was present in the starting aryleneethynylene monomer. In the case of polymer **9**, the $\text{C}\equiv\text{C}$ triple bond frequency shifted from 2117 cm^{-1} to 2206 cm^{-1} but in the case of **7** and **8** it was nearly absent indicating the symmetry of the molecule. Since organic polymers were insoluble in common organic solvent, we introduced metal precursor $(\text{P}^n\text{Bu}_3)_2\text{PtPhCl}$ in the polymeric chain to increase its solubility and to diversify practical applications. As expected the resulting organometallic polymer **9**, **10**, **11** and **12** were highly soluble in common organic solvent e.g. CH_2Cl_2 , CHCl_3 (shown in Table 2).

After metal incorporation the $\text{C}\equiv\text{C}$ triple bond stretching frequency shifted from around 2200 cm^{-1} to lower wavelength at around 2100 cm^{-1} , which is the characteristics of $\text{Pt(II)}-\sigma$ -acetylide compounds [31, 32]. Another noticeable observation was strong ($sp^3\text{H}$) $-\text{CH}$ and ($sp^2\text{H}$) $=\text{CH}$ band peak in the organometallic compound which was absent in the corresponding organic polymer.

Table 2 Synthesis of organometallic polymers.

Entry	Starting Material	Reaction Conditions	React. Time (h)	Product
9		$(P^nBu_3)_2PtPhCl$ $(iso\text{-}propyl)_2NH$	18	
10		$(P^nBu_3)_2PtPhCl$ $(iso\text{-}propyl)_2NH$	20	
11		$(P^nBu_3)_2PtPhCl$ $(iso\text{-}propyl)_2NH$	20	
12		$(P^nBu_3)_2PtPhCl$ $(iso\text{-}propyl)_2NH$	20	

Typical 1H -NMR spectrum of $Ph(P^nBu_3)_2Pt-C\equiv C-(py-C\equiv C-C\equiv C)_n-Pt((P^nBu_3)_2Ph)$ (**9**) is given in Fig. 1.

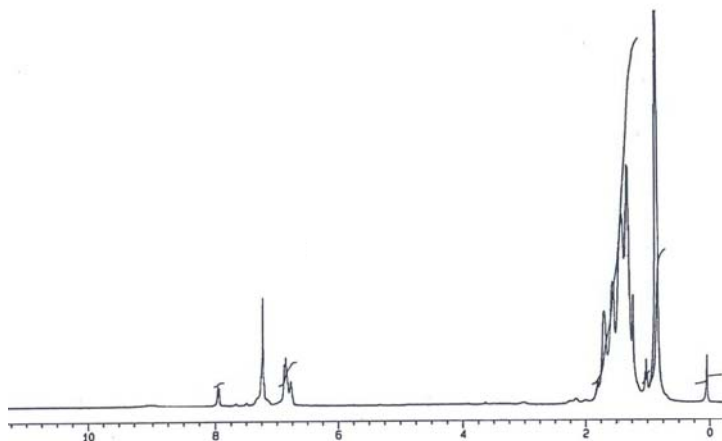


Fig. 1 1H -NMR spectrum of **9** [$Ph(P^nBu_3)_2Pt-C\equiv C-(py-C\equiv C-C\equiv C)_n-Pt((P^nBu_3)_2Ph)$].

The organometallic polymer **9** showed absorption at λ_{max} 381 nm, which is consistent with that of purely organic polymer **5** and indicates that the π -electron delocalization in this polymer is maintained through Pt (II) centers and the metal, participates in this process by contributing $d\pi$ -(metal) to $p\pi$ (alkyne) metal to ligand charge transfer.

The formation of organometallic polymers were also confirmed from expected 1H -NMR and ^{13}C -NMR data. All soluble polymers showed multiplet at δ 6.79-6.87 indicating the protons in the benzene ring. Peaks at δ 7.96-7.98 in compound **9** assigned for the protons in the pyridine ring.

In ^{31}P -NMR, lines at 1.93 with satellite positions at 13.11 and -9.24 measuring $\delta = 11.18$, $J_{\text{Pt-P}} = 2716$ Hz confirmed the formation of polymer **9**. Similarly the same δ value and coupling constant for the others confirmed the formation of the compound. It is also noted that the bimetallic model compound of **12** has also been synthesized by Liu and his group [34]. They got $\delta = 11.67$ ppm, and $J_{\text{Pt-P}} = 2618$ Hz.

Typical ^{31}P -NMR spectrum of $\text{Ph}(\text{P}^n\text{Bu}_3)_2\text{Pt}-\text{C}\equiv\text{C}-(\text{py}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C})_n-\text{Pt}((\text{P}^n\text{Bu}_3)_2\text{Ph})$ (**9**) is given in Fig. 2.

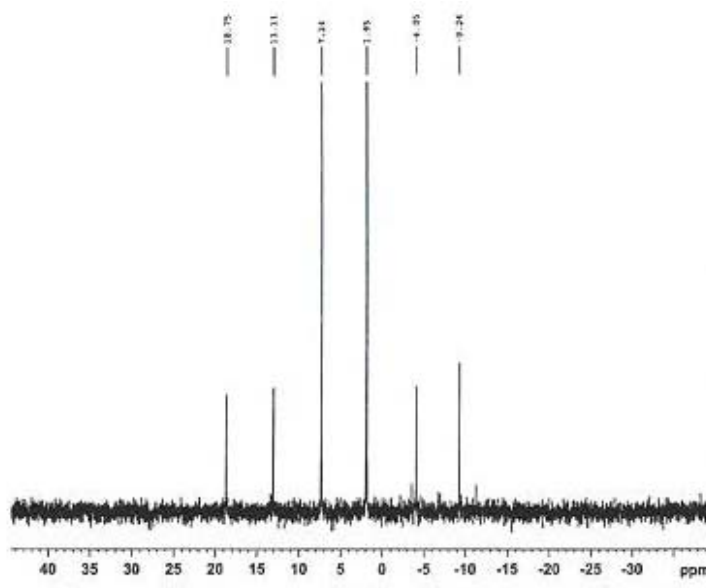


Fig. 2 ^{31}P -NMR spectrum of **9** [$\text{Ph}(\text{P}^n\text{Bu}_3)_2\text{Pt}-\text{C}\equiv\text{C}-(\text{py}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C})_n-\text{Pt}((\text{P}^n\text{Bu}_3)_2\text{Ph})$].

The GPC system was calibrated with polystyrene as calibrant and the results are therefore expressed as the "polystyrene equivalent" molecular weights. There could be a considerable difference between these polystyrene equivalents and the actual molecular weights of the samples. The results are summarised as the calculated molecular weight averages and polydispersity (M_w/M_n) in Table 3.

The refractive index chromatograms of polymers are shown in Fig. 3. These chromatograms are complex and molecular weight data has been computed with exclusion of material with retention volume > 17.15 mL. Sample **9** contained material of the highest molecular weight, ($MW \sim 95,000$) and ($MW \sim 700,000$). The calculated molecular weight averages are also increased by the relative absence of low molecular weight material.

Table 3 Calculated molecular weights and polydispersity.

Sample	Run No	Mw ^a	Mn ^b	Polydispersity
9	6	262,000	3,760	70
(RTL 6955/1)	9	266,000	3,550	75
10	7	11,600	2,200	5.3
(RTL 6955/2)	10	12,500	2,230	5.6
11	8	18,500	2,710	6.8
(RTL 6955/3)	11	21,000	2,790	7.5
12	12	65,400	3,800	17
(RTL 6955/4)	14	65,300	3,800	17

^aWeight average molecular weights ; ^bNumber average molecular weights.

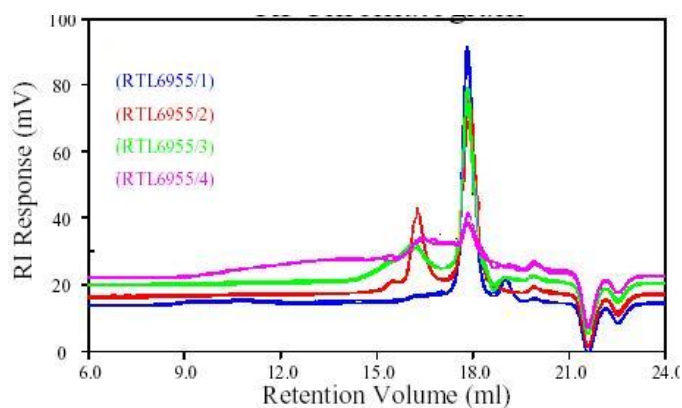


Fig. 3 Refractive index chromatograms for the polymers.

All contained a low molecular weight component eluting at ~17.85 mL. This corresponds to a polystyrene equivalent molecular weight of ~500 and it has been excluded from the molecular weight computations. Inclusion of the component would dramatically decrease the calculated molecular weight averages. This GPC work has been carried out using columns best suited to low/medium molecular weight polymer and while the calculated molecular weight averages are generally low, there is material of lower retention volume (i.e. higher molecular weight) than the highest calibrant – part of the computation therefore depends upon an extrapolation of the calibration (this really only applies to the ‘9’ sample).

4. Conclusion

Hay's oxidative coupling is a very effective process for the synthesis of poly(aryleneethynylene)s. Simplicity and feasible reaction conditions, excellent yield and safety are the key characteristics of this procedure. Though these polymers were insoluble in common organic solvents and limit their characterization by standard solution techniques, however, solid-state IR spectra of these polymers provided the sufficient information for the formation of polymers. This report also demonstrated that 2,5-diethynylpyridine, 1,4-diethynylbenzene, 2,5-dimethyl-*p*-phenylethynylene and *p,p*-diethynylbipenyl are useful precursors for the formation of a series of organometallic poly(yne) materials of group ten transition metals. Our initial synthetic studies showed that the synthesized materials are the mixture of oligomers as evident by GPC. Further studies for the synthesis of high molecular weight polymers and their optoelectronic properties are in progress.

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