# Final Report

Funding Period: September 2004-July 2006

In September 2004, Albemarle Corporation and the Georgia Institute of Technology started a research program at GeorgiaTech in the group of Marcus Weck to investigate the effect of polymer backbone flexibility and nature on the fluorescent properties on supported aluminum tris-8-hydroxyquinolines (Alq_3). The research program was initiated as a result of Albemarle's interest in new applications of high-value aluminum materials and Marcus Weck's expertise on Alq_3 functionalized polymers. The work original proposed included the synthesis of styrene, acrylate, cyclooctene, and vinyl-ether based monomers containing Alq_3 in the side-chain, their polymerization behavior and finally their basic photophysical characterization characterization.

Poly(cyclooctene)s

Before the Albemarle contract, the Weck group reported in several publications and one patent the use of poly(norbornene)s as promising materials for OLEDs. We proposed in the original research proposal to Albemarle to investigate more flexible polymer backbones such as poly(cyclooctene)s that can be compared to poly(ethylene)s. Poly(cyclooctene)s have, on average, an 80 degree Celsius lower glass transition temperature (T_g) in comparison to poly(norbornene)s. This lower T_g is a clear indication of their increased flexibility. During the funding period, we have synthesized a series of poly(cyclooctene)s with pendant aluminum tris-8-hydroxyquinoline (Alq_3). In all cases, carbazole-based comonomers were used to increase the solubility of the polymers and to obtain energy transfer from carbazole units into the metal complexes. The basic polymerization strategy is outlined in Scheme 1.
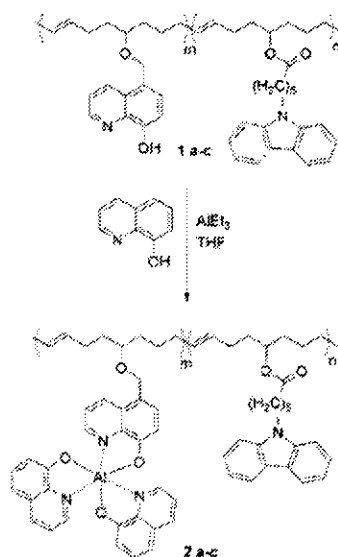
Scheme 1. Syntheses of Alq₃ copolymers.

The molecular weights of polymers **1a-c** are listed in Table 1. The polydispersity indices (PDIs) of copolymers **1a-c** are dependent on the monomers and the catalyst ratios. When the results of this and our published studies are compared, PDIs are found to be decreasing with decreasing monomer to catalyst ratios. GPC analyses of copolymers **2a-c** were not possible probably due to either the reversible coordination of aluminum to the polymer backbone or the formation of aggregates. Copolymers **1a-c** have glass transition temperatures of approximately – 15 °C. No glass transition temperatures were observed upon the formation of the metal complex functionalized copolymers **2a-c**. Copolymers **2a-c** decomposed around 290 °C.

Absorption and Photoluminescence Characterization.

The photophysical characterizations of all copolymers are also outlined in Table 1. The absorption spectra of copolymers **1a-c** are a combination of the two monomers. Complexation of compounds **1a-c** with aluminum to produce **2a-c** resulted in absorption bands around 390 nm, indicating the coordination of the metal to the polymers through the quinoline ligands in the side-chains. Using excitation spectra, we have observed significant energy transfer from the carbazole units into Alq₃ moieties. These results prove that carbazole groups in copolymers **2a-c** act not only as spacer and solubilizing groups but also as efficient photoactive units that lead to enhanced optical properties. These results in combination with the known hole-transporting

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ability of carbazole make these copolymers promising candidates as materials for OLED applications.

Table 1. Photophysical properties of the copolymers

| Compound	$\lambda_{abs}{}^a$ (nm)	$\lambda_{em}{}^{a,h}$ (nm)	$\lambda_{em}{}^{b,h}$ (nm)	Φ^c	τ^f (ns)	τ^g (ns)
2a	331, 345, 388	516	522	0.53^d	13	15
2b	331, 345, 395	517	520	0.56^d	12	16
2c	331, 345, 392	514	516	0.45^d	10	11

[a] in chloroform solutions. [b] solid state. [c] in deaerated THF solutions. [d] relative to Alq₃. [f] luminescence lifetime in THF solution. [g] luminescence lifetime in deaerated THF solution. [h] all polymers were excited at 380 nm.

Summarizing the poly(cyclooctene) work, we have synthesized via ring-opening metathesis polymerization poly(cyclooctene)s containing carbazole and Alq₃ moieties in the side-chains. By characterizing the optical properties of these materials, we were able to prove significant energy transfer from the carbazole units into the metal complexes for each copolymer. Furthermore, we were able to show that the copolymers retained the optical properties of their corresponding metal complex analogues. These results in combination with the random coil configuration of the poly(cyclooctene) backbone, which can provide a morphology that can be highly beneficial during device fabrication, make our copolymers promising candidates as materials for OLEDs. These results have been submitted to Albemarle three months ago and will be submitted for publication within the next two-three weeks.

Poly(styrene)s

The vast majority of the work during the funding period was carried out on poly(styrene)-based materials. As outlined in the original proposal, poly(styrene)s are commodity materials that are low cost and their fabrication has been established over the past century. Also, poly(styrene)s can be synthesized using controlled radical methods. Furthermore, from a photochemistry viewpoint, poly(styrene) is relatively inert toward electron or energy transfer because of its very high oxidation and low reduction potentials with no low-lying excited states. Therefore, poly(styrene) is the polymer scaffold of choice for metallated 8-hydroxyquinoline complexes. We have synthesized a poly(styrene) backbone that can be functionalized with a variety of metal precursors in a modular fashion.

The synthetic route towards 8-hydroxyquinoline functionalized poly(styrene)s is outlined in Scheme 2. The synthesis commences with the co-polymerization of styrene and p-(chloromethyl)styrene via free radical polymerization. Ratios of 2:1 and 9:1 of styrene and p-(chloromethyl)styrene were co-polymerized as outlined in the literature using AIBN as the initiator, yielding the copolymers **P33Cl** (M_n = 6,100, PDI = 1.89) and **P10Cl** (M_n = 6,400, PDI = 1.50) respectively. The chemical compositions of both copolymers were characterized by ^{1}H NMR and elemental analyses. Elemental analysis data of **P33Cl** [calculated based on the repeating unit $(C_{25}H_{25}Cl)_n$: C, 83.20 %; H, 6.98 %; Cl, 9.82 %. Found: C, 82.47 %; H, 7.01 %; Cl, 10.09 %] and **P10Cl** [calculated based on the repeating unit $(C_{81}H_{81}Cl)_n$: C, 89.26 %; H, 7.49 %; Cl, 3.25 %. Found: C, 88.66 %; H, 7.45 %; Cl, 3.47 %.] clearly demonstrates that the copolymers have the same monomer composition as the monomer feed. The conversion of the chloro methylated poly(styrene)s to their corresponding amine derivatives were carried out according to literature procedures, by first treating the copolymers with potassium phthalimide in DMF to yield the phthalimide-derivatized polymers quantitatively, followed by the reaction with hydrazine monohydrate in ethanol to provide the fully amino-functionalized polymers **P33NH₂** and **P10NH₂**. Coupling of 5-aldehyde-8-hydroxyquinoline with **P33NH₂** or **P10NH₂** afforded the corresponding Schiff bases **P33N=CH-q** and **P10=CH-q** that were reduced to the corresponding amines with NaBH₄ to yield the desired 8-hydroxyquinoline-functionaliezd polymers **P33-q** and **P10-q**.
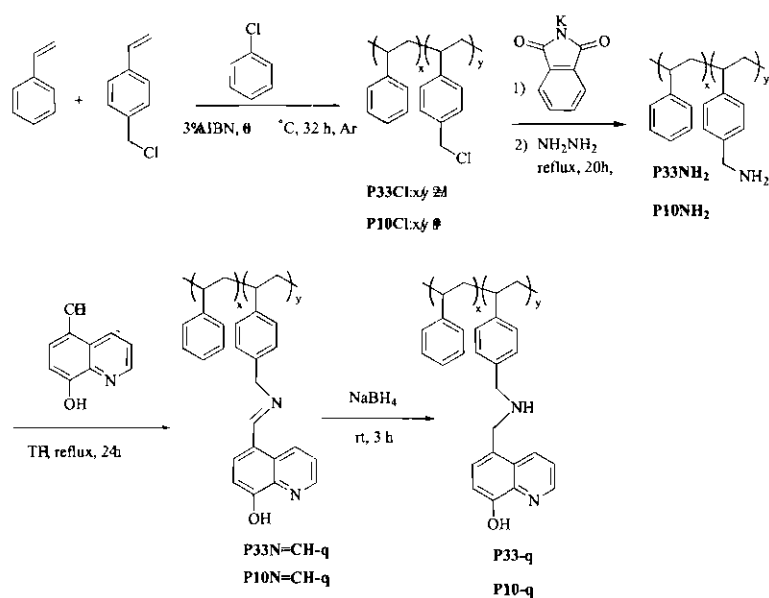
Scheme   Synthesis of 8-hydroxyquinoline functionalized poly(styrene)s.

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Using NMR techniques, we have proven the successful and quantitative attachment of the 5-aldehyde-8-hydroxyquinoline to the poly(styrene) backbone. Synthesis of Alq₃-containing polymers followed the widely employed procedures in the literature and is outlined in Scheme 3. In order to reduce the extent of polymer cross-linking that is possible via the Alq₃ formation between two or three different polymer chains, a large excess of 8-hydroxyquinoline and triethylaluminum were used. Nevertheless, polymer **P33-q** containing 33 % of 8-hydroxyquinoline-functionalized side-chains failed to achieve full solubility after Alq₃-functionalization. This limited solubility is most likely due to the readily occurrence of inter-chain crosslinking. However, **P10-Alq₃** and **P10-Alq(qCHO)₂** are yellow luminescent solids that are readily soluble in common organic solvents, such as $CHCl_3$, CH_2Cl_2 and THF. The polymers **P10-Alq₃** and **P10-Alq(qCHO)₂** were purified from low molecular weight Alq₃ by several cycles of reprecipitations into methanol (Alq₃ is readily soluble in MeOH while all polymers are not) until the methanol solution after precipitation is not colored anymore.
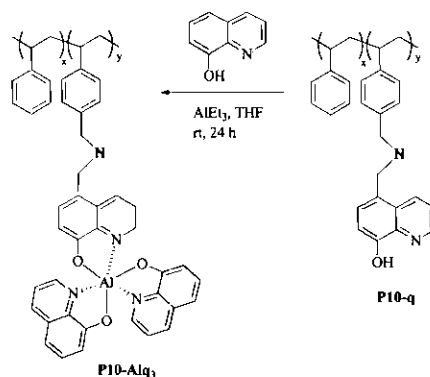
Scheme 3. Synthesis of Alq₃-pendant polymers.

Absorption and Photoluminescence Characterization.

Investigations of the absorption and photoluminescence properties of the polymers were carried out in dilute chloroform solutions as well as in the solid films. Thin films of the polymers and the reference compound Alq₃ were cast on quartz slides from chloroform solutions. The absorption and emission results are summarized in Table 2.

Table 2. Absorption and Emission Data of Polymers.

Compound	Solution Absorption[a] λ_{max}, nm	Solution Emission[a] λ_{max}, nm	Thin Film Emission[b] λ_{max}, nm	Φ	τ, ns
Alq₃	384	517	516	0.09	21
P10qAlq₂	389	516	514	0.04	13
P10qAl(qCHO)₂	395	524	511	0.03	--

All polymers were excitated at 380 nm; (a) CHCl₃ solution at rt; (b) quartz slide at rt; (c) standard: Quinine sulfate (Φ=0.54, 0.1M H₂SO₄).

The absorption and photo-luminescent spectra (solution and thin film) of **P10-Alq₃** are almost identical to that of the reference compound Alq₃ with the lowest energy absorption maximum and emission maximum at around 390 nm and 516 nm respectively. These results clearly indicate that the poly(styrene) backbone does not interfere with the photophysical properties of the pendant Alq₃ moiety. The solution absorption and emission of **P10-Alq(qCHO)₂** is approximately 8 nm red-shifted compared to that of Alq₃. These findings are consistent with previous reports from our group that introduction of electron-withdrawing and/or -donating groups at the 5-position of 8-hydroxyquinoline can tune the emission wavelength. Luminescent quantum yields for **P10-Alq₃** and **P10-Alq(qCHO)₂** are 0.04 and 0.03, respectively. These quantum yields are slightly smaller than the one for the molecular compound Alq₃ (Φ=0.09), but still acceptable for polymer-supported analogues.

In conclusion, in this first poly(styrene) study, we have developed an efficient synthetic approach for the attachment of 8-hydroxyquinoline ligands onto the side-chains of poly(styrene) polymers. The resulting polymers can serve as versatile precursors to form a variety of pendant 8-hydroxyquinoline metal complex-based polymers. Alq₃-functionalization was successfully carried out by using these poly(styrene) scaffolds. Solution and thin film characterization of these Alq₃-containing polymers show luminescent properties similar to those of the respective model compound, Alq₃, suggesting that these materials might be excellent precursors for organic light-emitting diodes.

These results were published in Macromolecules after the permission from Albemarle was obtained ("Poly(styrene)-Supported Alq₃ and BPh₂q"; Xian-Yong Wang and Marcus Weck* *Macromolecules* **2005**, *38*, 7219-7224.). Furthermore, the materials have been submitted to our collaborator in electrical engineering here at GeorgiaTech (Bernard Kippelen) for device

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fabrication and to 3M Corporation for investigations into the laser spotting of these materials to fabricate devices. 3M reported successful laser transfer with all polymers and a good line edge of the transferred material. These preliminary studies did not allow for optimization of any devices and the one preliminary device that was fabricated showed low efficiencies.

The syntheses of the above-described materials were based on the metallation of polymers. However, a higher degree of control should be possible through the polymerization of fully functionalized monomers. Therefore, we investigated an efficient method to synthesize poly(N-vinylcarbazole)-co-poly(styrene)s and poly[9-(4-vinylbenzyl)-9H-carbazole]-co-(styrene)s supported Alq₃ by using free radical polymerization method. Again, these polymer backbones were chosen for the attachment of Alq₃, because (i) poly(N-vinylcarbazole) (PVK) and other carbazole containing polymers have been employed extensively as host for a variety of small molecule dye dopants in OLEDs as a result of the outstanding hole-transporting properties and high energy singlet excited state of carbazole, (ii) both PVK and poly(styrene) have excellent film-forming properties with high thermal stability and (iii) poly(styrene) is a commodity polymer, which is an ideal polymeric precursor for polymerization derivatization.

Over a period of 9-12 months, we investigated a variety of synthetic strategies to obtain polymerizable monomers. In Scheme 4, we outline the most successful route (other routes have been reported before in quarterly reports to Albemarle).
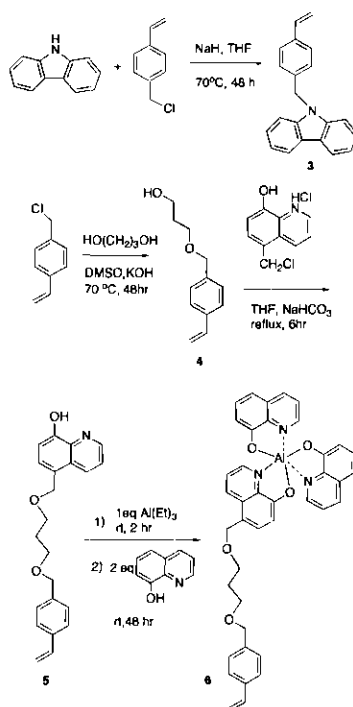
Scheme 4. Synthetic route to the monomers.

Copolymerization of monomer **6** with various ratios of N-vinylcarbazole or compound **3** via free radical polymerization using AIBN as the initiator yielded the Alq₃-functionalized copolymers (Scheme 5). The M_w of the copolymers, determined by GPC, range from 4,030 to 17,670 with polydispersities (PDI) between 1.66 to 3.31. The increase of the polymerization temperatures resulted in the higher polymerization yields. The results are summarized in Table 3. All copolymers were fully characterized by NMR and GPC. All obtained copolymers are readily soluble in common organic solvents, such as $CHCl_3$, CH_2Cl_2 and THF.
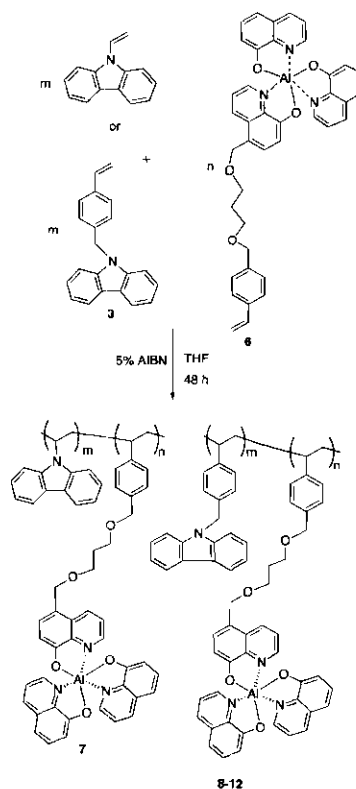

Scheme 5. Synthetic route to the Alq₃-containing copolymers.

Table 3. Properties of Alq$_3$-Copolymers

sample	m/n[a]	°C[b]	%[c]	M$_n$	M$_w$	PDI	Φ[d]	τ ns[d]	λ$^{abs}_{max}$(nm) solution[d]	λ$^{emiss}_{max}$(nm) solution[d]	solid[e]
Alq$_3$							0.09	21	388	515	508
7	10/1	80	36	2420	4030	1.66	0.035	12	296, 329, 343, 388	523	517
8	10/1	80	37	3690	8300	2.25	0.022	11	296, 329, 345, 388	524	524
9	10/1	70	24	6110	12250	2.00	0.042	11	294, 330, 343, 386	521	519
10	10/1	60	8	5130	11670	2.27	0.030	11	294, 330, 343, 386	519	514
11	5/1	80	44	5990	10770	1.80	0.034	11	294, 330, 343, 386	525	519
12	3/1	80	41	5150	17670	3.31	0.031	11	294, 329, 343, 388	525	518

a) ratio of monomers; b) polymerization temperature; c) polymerization yield; and d) in CH_2Cl_2 solutions at λ_{ex} = 380 nm and quinine sulfate (Φ = 0.54 in 0.1 M H_2SO_4) as reference for Φ; e: on quartz slide.

Absorption and Photoluminescence Characterization.

The copolymers, **7-12** exhibit very similar photophysical behaviors to the polymers outlined above of the 'polymer functionalization strategy' (Table 3). The UV-vis absorption spectrum of copolymer **8** is shown in Figure 1. The strong absorption bands in the UV region from 250 nm to 350 nm with maxima at 295, 330 and 343 nm are assigned as π-π* transitions stemming from the carbazole and benzene, while the weak and broad absorption band extending from 360 to around 450 nm with maximum at 388 nm is typical of the singlet transition of Alq₃. The backbones of the copolymer **7-12** do not have any absorption activity in the visible region.
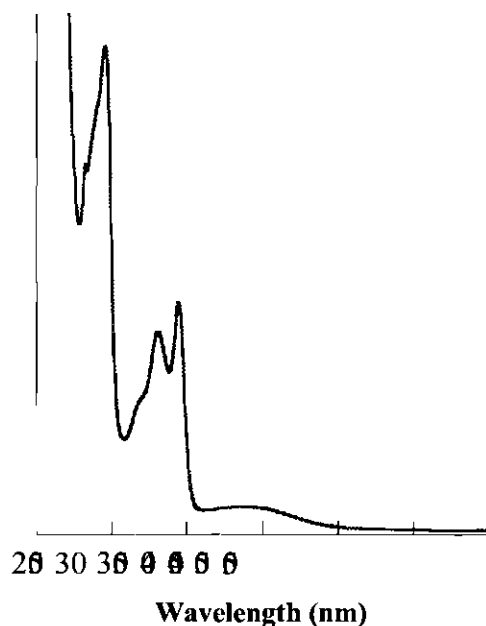
26 30 36 0 0 0 0

Wavelength (nm)

Figure 1. Solution absorption spectrum of **8** in CH_2Cl_2.

Copolymers **7-12** exhibit almost identical emission profiles in solution and the solid state to that of the reference compound Alq_3 (Table 3). These results indicate that the polymer backbones do not interfere with the emission properties of the pendant Alq_3 moiety. The solution luminescence of the copolymers exhibits a spectral red-shift relative in comparison to the solid-state spectra. Luminescent quantum yields of the copolymers range from 0.02-0.04. These quantum yields are slightly smaller than the one of the Alq_3 (Φ=0.09), but still acceptable for polymer-supported analogues. Luminescence lifetimes of Alq_3-containing polymers ($\tau = 11$) are shorter than that of their respective analogous Alq_3 ($\tau = 21$). These results are consistent with their lower luminescent quantum yields. For all copolymers, their fluorescent decays fit well a single exponential, indicating that luminescent excited states are mainly from the attached Alq_3. The lower quantum yields and luminescent lifetimes of **7-12** are possible due to enhanced exciton diffusion to randomly distributed traps within the polymer chains.

In this study, we have developed an efficient synthetic approach for the synthesis of Alq_3 complex functionalized poly(9-vinylcarbazole)-co-poly(styrene)s and poly[9-(4-vinylbenzyl)-9H-carbazole]-co-(styrene)s. The resulting polymers have photophysical properties similar to those of the corresponding small molecule Alq_3. Again, these results clearly demonstrate that Alq_3 complex functionalized copolymers are potentially outstanding emissive and hole transporting materials for polymeric OLED devices. This data has been partially disclosed to

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Albemarle during the past 12 months. We wish to submit a manuscript on these results within the next two months pending Albemarle's approval.

Over the past six months, we have investigated the employment of controlled radical polymerization methods to gain a larger degree of control over the polymerization. Unfortunately, none of the three common methods that were studied (atom-transfer radical polymerization (ATRP), reversible addition-fragmentation transfer (RAFT) polymerization, and nitroxide mediated polymerization (NMP)) were successful in polymerizing the above outlined monomers in high yields and in a controlled fashion.

Poly(acrylate)s

While we synthesized acrylate-based Alq$_3$ containing monomers within the first 6 months of the funding period, two publications appeared in the literature reporting such monomers, their polymerization behavior and finally their photo and electrophysical characterization. Since these literature reports prevented Albemarle and us from ever filing any IP on such monomers, we did not investigate any poly(acrylate)s further.

Summary

In the original proposal, we suggested that 'at the end of a two-year funding period, optimized synthetic strategies towards the formation of Alq$_3$ functionalized polymers for specific applications such as OLEDs will be available (detailed synthetic strategies and experimental description are available if requested by Albemarle). Furthermore, we will suggest a modular approach to different polymer backbones thereby creating a library of materials that can be tailored towards specific application, requirements, and ultimately customers for Albemarle Corporation.'. Over the past two years, we have synthesized and characterized a library of Alq$_3$ containing materials and provided Albemarle with synthetic strategies towards the synthesis of such materials. Furthermore, we studied and provided two modular polymer functionalization strategies (poly(styrene) and poly(cyclooctene) based) that allow for an easy metallation with a variety of aluminum precursor (during our initial norbornene studies we have demonstrated that the emission color of Alq$_3$ containing polymers can be tuned through small changes on the ligand spheres). Finally, we have provided a collaborator (Kippelen) and a company that has collaborations with both, Albemarle and GeorgiaTech, samples for device testing.

During the 22 months funding period, one postdoctoral fellow, Dr. Xian-Yong Wang was supported by Albemarle. The research carried out by the postdoc has (or will) results in three publications in premier international polymer journals. The research contract was terminated slightly ahead of schedule due to a decision by Albemarle to not pursue any aluminum-based OLED work anymore. GeorgiaTech and myself would like to thank Albemarle for a fruitful two-year collaboration.