# *Low Melt Viscosity Resins for Resin Transfer Molding*

## Final Research Report
on project
NAG3-2572

End Date January 31, 2002

Submitted to

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# "Low Melt Viscosity Resins for Resin Transfer Molding"

## Introduction

In recent years, resin transfer molding (RTM) has become one of the methods of choice for high performance composites. Its cost effectiveness and ease of fabrication are major advantages of RTM.[1] RTM process usually requires resins with very low melt viscosity (< 10 Poise). The optimum RTM resins also need to display high thermal-oxidative stability, high glass transition temperature ($T_g$), and good toughness. The traditional PMR-type polyimides (e.g. PMR-15) do not fit this requirement, because the viscosities are too high and the nadic endcap cures too fast. High $T_g$, low-melt viscosity resins are highly desirable for aerospace applications and NASA's Reusable Launch Vehicle (RLV) program. The objective of this work is to prepare low-melt viscosity polyimide resins for RTM or resin film infusion (RFI) processes. The approach involves the synthesis of phenylethynyl-terminated imide oligomers. These materials have been designed to minimize their melt viscosity so that they can be readily processed. During the cure, the oligomers undergo both chain extension and crosslinking *via* the thermal polymerization of the phenylethynyl groups.[2,3] The Phenylethynyl endcap is preferred over the nadic group due to its high curing temperature, which provides broader processing windows.[4]

This work involved the synthesis and polymerization of oligomers containing zig-zag backbones and twisted biphenyl structures. Some A-B type precursors which possessed both nitro and anhydride functionality, or both nitro and amine functionality, were also synthesized in order to obtain the well defined oligomers. The resulting zig-zag structured oligomers were then end-capped with 4-phenylethynylphthalic anhydride (PEPA) for further cure. The properties of these novel imide oligomers are evaluated.

## Targets of the project

*Uncured forms*

- Tgs or Tms of the oligomers before curing must be below 280°C
- The oligomer must be stable in the melt prior to cure ( wide processing window)
- The melt viscosities of the oligomers must be below 10 poise
- Nontoxic

*Cured forms*

- The Tgs of the cured resins must be above 300°C , preferably above 350°C
- The cured resin must undergo less than 3% weight loss when heated at 550°F ( 288°C ) for 1000 hr in air
- No microcracking (after thermal cycling under stress)
- Acceptable cost

## Strategy of the approach

- ***Star branched oligomers***

In general, $\eta b=0.6\sim0.8\ \eta l$, star branched oligomers may have relative lower melt viscosities compared with the linear oligomers with the same molecular weight.

- ***Linear oligomers***

Some linear oligomers with flexible chain and cardo structures may give the balance properties

- ***Zig-Zag oligomers***

The zig-zag oligomers with twisted biphenyl and flexible linkage together should be helpful to meet the requirements.

- ***Blends of oligomers***

Easy to adjust the properties

## Experimental

***Materials.*** All chemicals were obtained from Aldrich Chemical Company.

***Neat Resin Processing.*** The molding powders (1.25 g) were placed in a 1-inch diameter steel mold preheated to 343°C with contacted pressure for 40 min. and then cured into a disk at 371°C (700 °F) for 2 hrs. under 1200 psi.

***Instrumentation.*** $^1$H-NMR was obtained using a Varian 300 MHz spectrometer. DSC analysis was carried out on resin powder cured at 400°C for 20 min. by a DuPont 2910 DSC with a heating rate of 10°C /min. TMA analysis was performed on cured resin disks on a TA Model 2940 Thermal Mechanical Analyzer with expansion probe at a heating rate of 10°C/min. Absolute viscosities of these reactive oligomers were measured by a Brookfield Viscometer DV-II equipped with a Thermosel heating unit capable of continuous 300°C operation.

### *Synthesis of some key monomers*

Synthesis of 2,2'-bis(o-aminophenoxy)biphenyl

(a) 2,2'–Bis(*o*-nitrophenoxy)biphenyl (I) was synthesized by a modified method according to the literature.[5] mp 145-147°C (lit. mp 154°C); $^1$H NMR (DMSO-$d_6$) $\delta$ 7.880 (2H, d, ArH), 7.467 (2H, m, ArH), 7.328 (4H, dd, ArH ), 7.171 (4H, m, ArH), 6.956 (4H, d, ArH) and 6.848 ppm (4H, d, ArH).

(b) 2,2'-Bis(*o*-aminophenoxy)biphenyl was synthesized from (I) by a catalytic hydrogenation with 5% Pd/C. mp 166-168°C (lit.[5] mp 174-175°C); $^1$H NMR (DMSO-$d_6$) $\delta$ 7.429 (2H, d, ArH), 7.221 (2H, m, ArH), 7.062 (2H, m, ArH ), 6.848 (2H, m, ArH), 6.700 (4H, m, ArH), 6.616 (2H, d, ArH), 6.470 (2H, m, ArH) and 4.733 ppm (4H, d, $NH_2$).

Synthesis of 4-(4-nitrophenoxy)phthalic anhydride

(a) 3,4-Dimethylphenyl 4-nitrophenyl ether (II) was synthesized by a modified method according to the literature.[6] mp 87-89°C; $^1$H NMR (DMSO-$d_6$) $\delta$ 8.10 (2H, dd, ArH), 7.22 (1H, d, ArH), 7.06 (2H, dd, ArH), 6.97 (1H, s, ArH), 6.86 (1H, d, ArH), and 2.22 ppm (6H, s, $CH_3$).

(b) 4-(4-Nitrophenoxy)phthalic acid (III) was synthesized from (II), using the potassium permanganate ($KMnO_4$) as an oxidation agent. mp 167-169°C (lit.[7] mp 167-169°C); $^1$H NMR (DMSO-$d_6$) $\delta$ 13.20 (2H, s, COOH), 8.28 (2H, m, ArH), 7.82 (1H, dd, ArH), 7.35 (2H, m, ArH), and 7.24 ppm (2H, m, ArH).

(c) 4-(4-Nitrophenoxy)phthalic anhydride was prepared by sublimation of 4-(4-nitrophenoxy)phthalic acid (III) at 200 °C to yield the anhydride as an off-white powder: mp 126-128 °C; (lit.[5] mp 129-131°C). $^{1}$H NMR (DMSO-$d_6$) δ 8.36 (2H, dd, ArH), 8.16 (1H, dd, ArH), 7.78 (1H, d, ArH), 7.71 (1H, m, ArH), and 7.35 ppm (2H, dd, ArH).

Synthesis of 4-(phenylethynyl)phthalic anhydride (PEPA)

PEPA can be purchased from Daychem or synthesized according to the literature.[8] mp 147-149°C (lit. mp 146-148°C); $^{1}$H NMR (DMSO-$d_6$) δ 7.46(m, 3H, ArH), 7.63 (m, 2H, ArH), 8.10 (s, 1H, ArH) and 8.22 ppm (d, 1H, ArH).

### *General synthesis of oligomers end-capped with PEPA*

To a 100-mL flask equipped with a $N_2$ inlet, mechanical stirring and a condenser were added 2,2'-bis(o-aminophenoxy)biphenyl (30.00 mmol n=1or 2) and DMAc (25 ml). A solution of 15.00 mmol (n=1) or 20.00 mmol (n=2) of the anhydride in DMAc (25 ml) was added to reaction mixture dropwise. The mixture was stirred at room temperature for 2h, and then 30.00 mmol (n=1) or 20.00 mmol (n=2) of PEPA was added and followed by a DMAc rinse (10 ml). After the mixture was stirred at room temperature for an additional 6 h, isoquinoline was added (4-5 drops). The mixture was allowed to reflux overnight. After cooling down to room temperature, the solution was poured into water to induce precipitation. The solid was collected by filtration and washed twice with water, followed by two rinses with methanol. The resulting oligomer was then dried at 200 °C for 12 h in a vacuum oven.

### *General synthesis of oligomer based on 4-(4-nitrophenoxy)phthalic anhydride (Scheme 1)*

To a 250-mL flask equipped with a $N_2$ inlet, mechanical stirring and a condenser, an aromatic diamine (or triamine) and two equivalents of 4-nitrophthalic anhydride were added to DMAc (120 ml). After the mixture was stirred at room temperature for 6 h, isoquinoline was added (4-5 drops). The mixture was heated to reflux overnight. After cooling down to room temperature, the solution was transferred to a hydrogenation bottle containing 5% Pd/C with a DMAc rinse (30 ml). Then the reaction mixture was subjected to hydrogenation at 45 psi in a Parr hydrogenator agitated at room temperature for 20 h. The reaction mixture was filtered through Celite and washed with DMAc three times. After pouring into water, the resulting solid was collected by filtration and washed twice with water, followed by two rinses with methanol. The solid was then dried at 80 °C in a vacuum oven for 24 h to yield the corresponding muti-amine terminated compounds. These diamines (or triamines) were further reacted with PEPA endcap to obtain the desirable imide oligomers for viscosity screening for RTM process.

## Results and Discussion

**Table 1. Oligomers based on 4-(4-nitrophenoxy)phthalic anhydride**

| | Tg | Viscosity | Tg after cure |
|---|---|---|---|
| PTAM | 200°C | 14 poise at 280°C | 321°C (DSC) |
| MTAM | 172°C | 400 poise at 260°C | 340°C (DSC) |
| APB | 180°C | 14 poise at 260°C | 262°C (DSC) |
| CARDO | 210°C | 280 poise at 280°C | 370°C (DSC) |
| 222DAM | 141°C | 8~23 poise at 280°C | 272°C (DSC) |
| 22DAM | 170°C | 14 poise at 260°C | 340°C (DSC) |

Several well-defined oligomers were synthesized based on a A-B type precursor, 4-(4-nitrophenoxy)phthalic anhydride (Scheme 1). The results showed that the oligomers based on flexible or twisted diamines (APB & 222DAM, respectively) had very low melt viscosities and relative low $T_g$s (Table 1). In contrast, oligomers based on star-branched amines (PTAM & MTAM) showed higher melt viscosities and higher $T_g$s (>320°C). The reason is that the crosslink densities of the oligomers based on star-branched amines were higher than that of the oligomers derived from either flexible or twisted diamines. The Cardo oligomer showed the highest $T_g$ in this series. The best way to balance the viscosity and $T_g$ might be to blend the Cardo structure with oligomers based on flexible and twisted diamines.

**Table 2 Oligomers based on 2,2'-bis(*o*-aminophenoxy)biphenyl (n=1)**

| | $T_g$ | Viscosity | $T_g$ after Cure |
|---|---|---|---|
| No Aromatic Bridge | $T_g$ ~ 135°C | 0.5 poise at 280 °C | 317 °C (DSC)<br>378 °C (TMA) |
| PMDA | $T_g$ ~ 156 °C | 4 poise at 280 °C | 261 °C (DSC)<br>300°C (TMA) |
| BPDA | $T_g$ ~ 169 °C | 15 poise at 280 °C | 253 °C (DSC)<br>274°C (TMA) |
| BTDA | $T_g$ ~ 162 °C | 6 poise at 280 °C | 268 °C (DSC)<br>290°C (TMA) |
| ODPA | $T_g$ ~ 162 °C | 4 poise at 280 °C | 246 °C (DSC)<br>261°C (TMA) |

A new series of oligomers based on 2,2'-bis(o-aminophenoxy)biphenyl were synthesized (Scheme 2) and characterized (Table 2). The viscosities of these oligomers were very low (<10 poise). The $T_g$s of most resins were lower than 300°C, except when the diamine was directly reacted with 2 equivalents of PEPA (no aromatic bridge). The reason might be that the twisted structure introduced more kinks which contributed to lower melt-viscosities and lower $T_g$s. When these resins were subjected to further post-cure at 371°C for 16 h in an attempt to raise the $T_g$, they became very brittle, due to the increased crosslink density.

**Table 3. Oligomers based on 2,2'-bis(*o*-aminophenoxy)biphenyl (n=2)**

| | $T_g$ | Viscosity | $T_g$ after Cure |
|---|---|---|---|
| BPDA | $T_g$ ~ 182°C | 100,000 poise at 280 °C | 249 °C (DSC) |
| BTDA | $T_g$ ~ 156 °C | 300~700 poise at 280 °C | 261 ° (DSC)<br>300°C (TMA) |
| ODPA | $T_g$ ~ 170 °C | 25 poise at 280 °C | 228 °C (DSC) |

To resolve the brittleness of the resins, oligomers formulated with n=2 instead of n=1 were synthesized. However, the higher molecular weight oligomers (n=2, Table 3) displayed much higher viscosities and even lower $T_g$s than those of n=1 (Table 2). Only the viscosity of the oligomer based on ODPA was lower than 30 poise, but the resin also became relatively brittle upon post-cure. It is not clear why these resins remained brittle even when their molecular weights were formulated up to 1400 g/mol. It might be that the oligomer based on this twisted diamine monomer had a relative short chain length. The $T_g$s of the oligomers before cure did not vary considerably with different anhydride structures. Nevertheless, the $T_g$ of the oligomer based on ODPA was much lower than those of BTDA or BPDA after cure, due to the more flexible ODPA structure.

**Table 4. Oligomers obtained from core monomers and PEDA directly**

| | $T_g$ or $T_m$ | Viscosity | Tg after cure |
|---|---|---|---|
| PTAM-E | 353°C | | |
| MTAM-E | 120°C | 1 poise at 260°C | 406°C (TMA) |
| 22DAM-E | 282°C | | |
| 222DAM-E | 135°C | 0.5 poise at 280°C | 317°C (DSC)<br>378°C(TMA) |

On the other side, oligomers with the shortest chain length were obtained from imidization of core monomers and PEDA directly (Scheme 3). PTAM-E and 22DAM-E have $T_m$s higher than 280°C due to their rigid and symmetric structures. MTAM-E and 222DAM-E have extremely low melt viscosities and high $T_g$s after cured. Even though the cured samples are brittle due to high crosslinking densities, the oligomers are good candidates for the blends.

**Table 5. Oligomer blends**

| | Tg | Viscosity | Tg after cure |
|---|---|---|---|
| 60% APB<br>40% MTAM-EI | 200°C and 180°C | 10 poise at 260°C | 330°C (TMA) |
| 75% APB<br>25% CARDO | 200°C | 6~8 poise at 280°C | 319°C (TMA) |
| 60%22DAM<br>40%APBP | 144°C and195°C | 7 poise at 260°C | 300°C (DSC) |
| 60%222PMDA<br>40%222DA-E | 146°C and 157°C | 2 poise at 280°C | |

The oligomer blends were also prepared and studied to find the balance of the melt viscosity, cured $T_g$ and toughness. Thus, several oligomer blends were obtained by solution mixing. All blends displayed very low melt viscosities. The $T_g$s of most of the blends after cure were above 300°C.

## Conclusions

Oligomers based on the A-B precursor with well-defined structures were synthesized and characterized. The results showed that the star-branched oligomers had higher melt viscosities with higher $T_g$s whereas oligomers based on twisted and flexible amines showed much lower melt viscosities and lower $T_g$s. A new series of Zig-Zag oligomers based on 2,2'-Bis(*o*-aminophenoxy) biphenyl were found to display extremely low viscosities. Future work will focus on blends based on these oligomers, since it is easy to tailor the properties of blends by mixing various selected oligomers.

## Acknowledgements

We would like to thank NASA Glenn Research Center for the financial support of this research and Daniel A. Scheiman of QSS Groups, Inc. for Brookfield viscosity measurements and thermal mechanical analyses (TMA).

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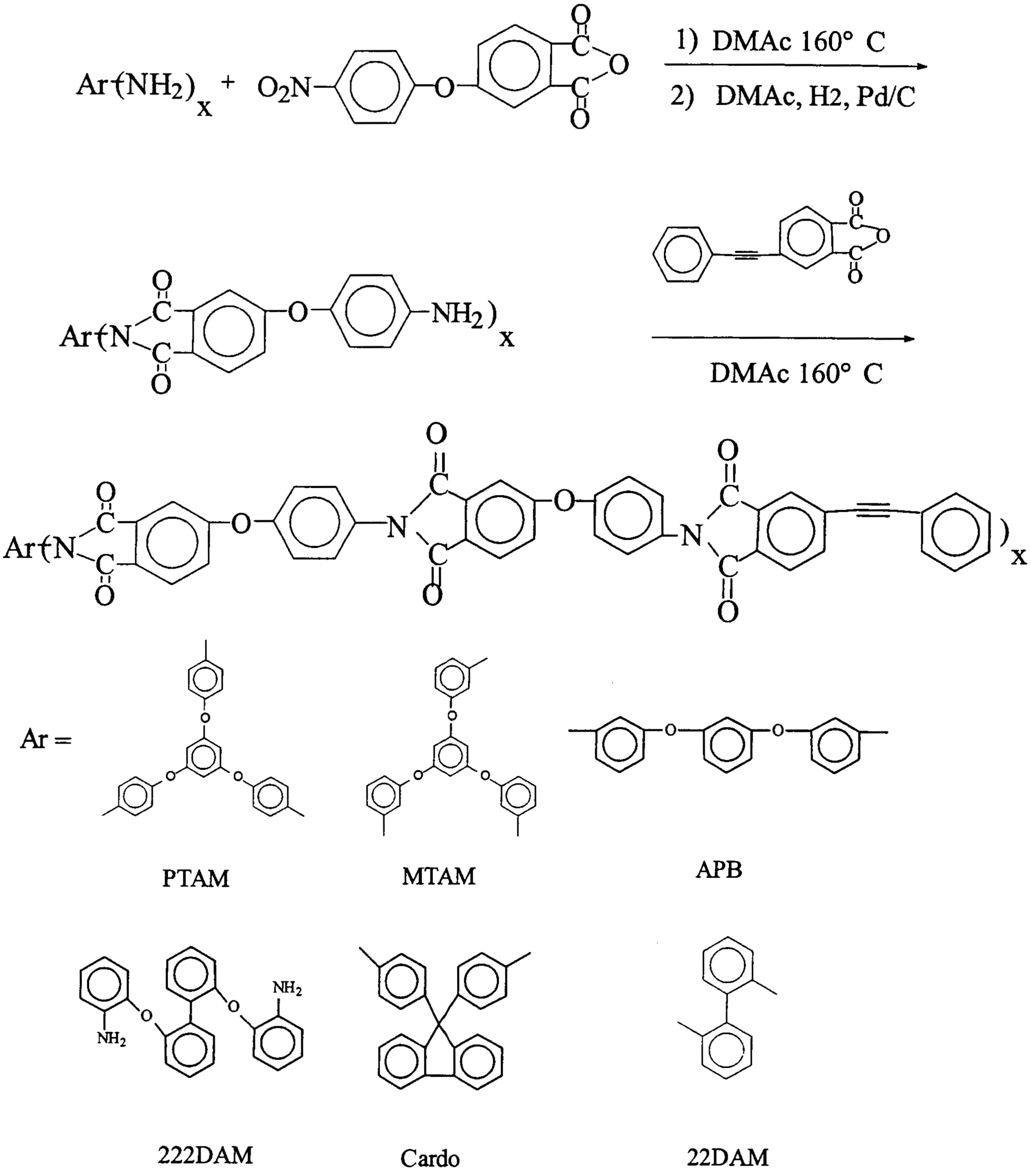
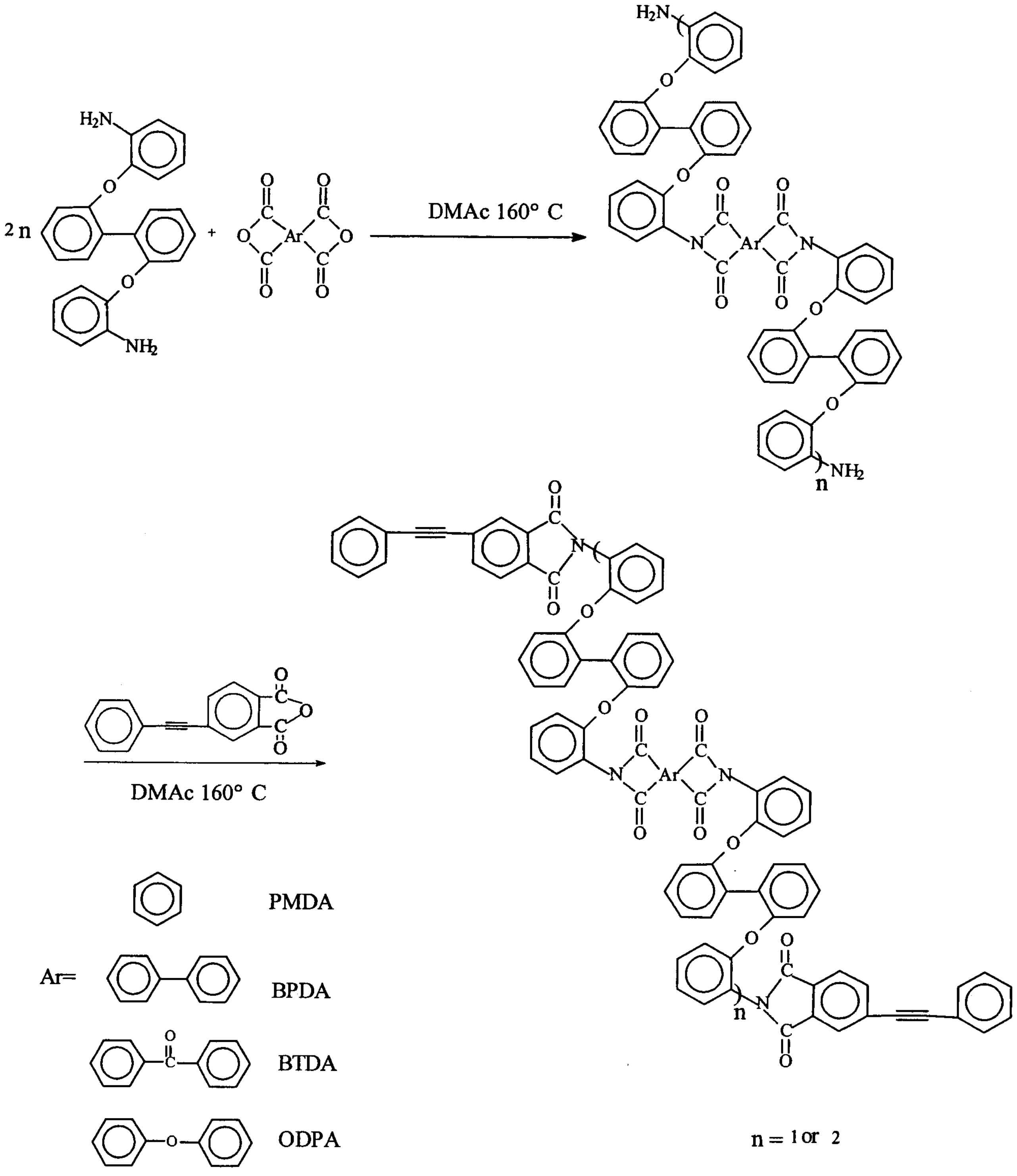
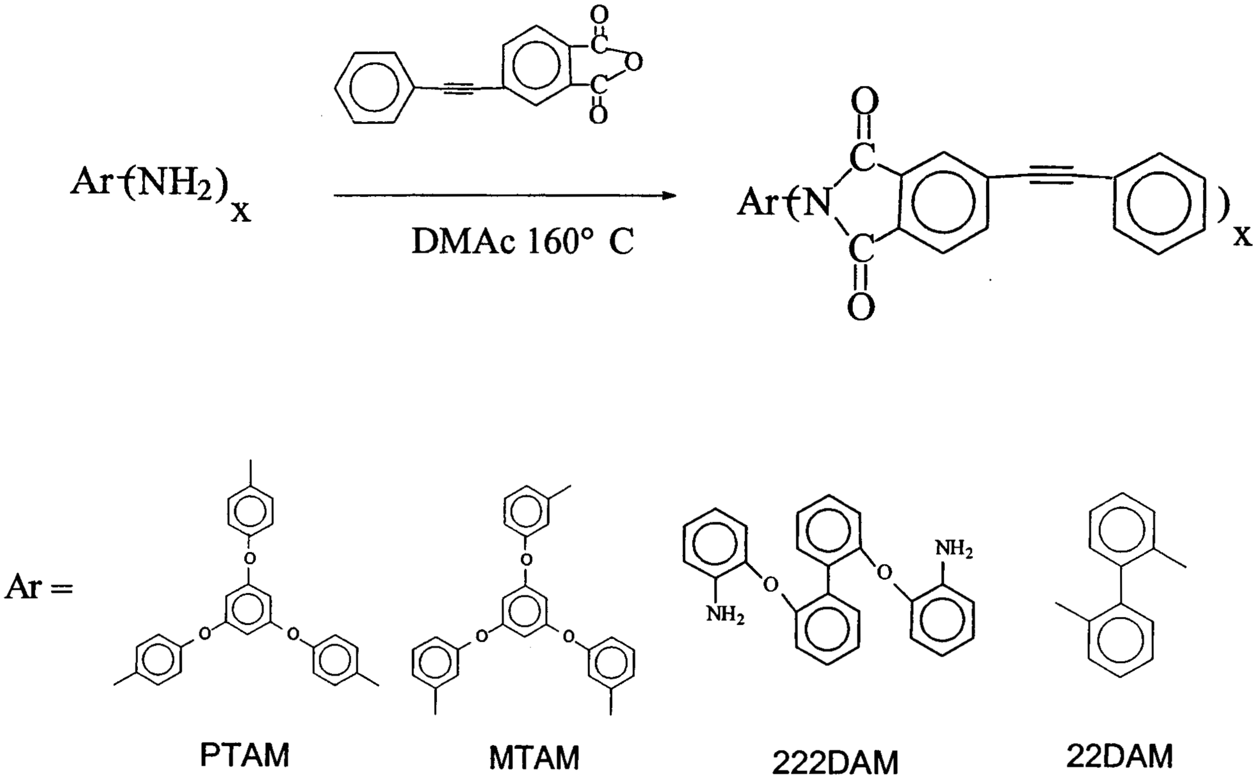


**Scheme 1.**
Synthesis of oligomers based 4-(4-nitrophenoxy)phthalic anhydride



**Scheme 2**
Synthesis of oligomers based on 2,2'-bis(*o*-aminophenoxy)biphenyl



**Scheme 3**
Synthesis of oligomers from core monomers and PEDA directly