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NASA Technical Memorandum **104100**

Effect of Molecular Weight on Polyphenylquinoxaline Properties

(NASA-TM-104100) EFFECT OF MOLECULAR WEIGHT ON POLYPHENYLQUINOXALINE PROPERTIES (NASA) 36 p CSCL 11C N91-26377

Unclas
G3/27 0024801

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May 1991

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INTRODUCTION

In the late 1950s and early 1960s, work was initiated to develop high temperature polymers which were urgently needed for use as structural resins on advanced aircraft, space vehicles, and missiles. Most of the polymers prepared during this effort belong to a class of materials known as aromatic heterocyclic polymers. One family of polymers evolving from this work was the polyphenylquinoxalines (PPQ). These polymers are high temperature thermoplastics which exhibit a favorable combination of processability, physical and mechanical properties. Therefore, PPQ are under development as high performance, high temperature functional (e.g. coatings and films) and structural (e.g. adhesives and composite matrices) resins.

The synthesis of linear PPQ was first reported in 1967.[1] The driving force behind this synthesis was to improve the thermooxidative stability of linear polyquinoxalines. Infrared studies suggested that thermooxidative breakdown at the pyrazine hydrogen on the quinoxaline ring occurred upon aging in air at 371°C. Phenyl substituted polyquinoxalines exhibited slightly higher decomposition temperatures in both air and helium, and better thermooxidative stability when subjected to 316°C (600°F) and 371°C (700°F) isothermal aging than the unsubstituted polyquinoxalines. PPQ were prepared by both melt and solution methods.

Since this initial report, PPQ have been the subject of many investigations. Research published includes PPQ containing aliphatic groups[2], isomeric phenylene linkages[3], flexible tetraamines[4], flexible ether linkages in the bisbenzil[5,6], fused rings in the tetraamine[7], and different pendent groups.[8,9] Characterization of the thermal properties[10-12] and physical and mechanical properties[13-15] of many PPQ has also been reported.

Many papers have discussed the synthesis and characterization of these systems, however, none of these papers fully describes a study on the synthesis of PPQ where the stoichiometry of the monomers was systematically varied, thereby controlling the molecular weight. Since polymer properties are dependent on molecular weight, differences in stoichiometry will be translated to differences in polymer properties. High molecular weight polymers generally have better physical properties but poorer processability than lower molecular weight polymers. The purpose of the work reported herein was to characterize one PPQ when the monomer stoichiometry was systematically varied. This report also investigates some of the reaction parameters which ultimately have an effect on the resulting PPQ properties.

EXPERIMENTAL

Monomers and Solvents

3,3'-Diaminobenzidine (DAB) was obtained from a commercial source and recrystallized twice from water (~20g/L) under a nitrogen atmosphere using sodium dithionite to maintain the solution in a reducing environment. Light brown crystals [m.p. 177-179°C (Lit.[16] m.p. 179-180°C)] were obtained in 70% recovery.

4,4'-Oxydibenzil (ODB) was synthesized by the following procedure. Diphenyl ether (340.4 g, 2.0 mol) and phenylacetyl chloride (616.6 g, 4.0 mol) were dissolved in dry methylene chloride (1 L). The solution was added slowly at ~5°C during 2.5 h to a stirred suspension of anhydrous powdered aluminum chloride (553.2 g, 4.2 mol) in dry methylene chloride (2 L) under a nitrogen atmosphere. After complete addition, the resulting dark reddish brown reaction mixture was stirred at ~5°C for 1 h followed by stirring at ambient temperature overnight. The reddish brown reaction mixture was slowly poured into a stirred, crushed ice and hydrochloric acid mixture followed by stirring an additional 2 h. The acidic water was decanted from the cream-colored emulsion followed by pouring into large drying dishes and periodically decanting water. After drying in air, the solid was pulverized and thoroughly washed twice with water followed by drying in vacuo at ~70°C to afford a cream colored solid in ~90% yield [m.p. 165-170°C (Lit[17] m.p. 169-170°C for p-phenylacetyl phenyl ether)]. The p-phenylacetylphenyl ether (735 g) was recrystallized from N,N-dimethylformamide (3.9 L) producing white crystals in 70% recovery [m.p. 168.5-170°C].

To a stirred mixture of selenium dioxide (239.9 g, 2.16 mol) in glacial acetic acid (2.3 L) at 60°C, powdered p-phenylacetylphenyl ether (437.7 g, 1.08 mol) was added during ~5 min. The reaction mixture was refluxed ~6 h with stirring, followed by a hot filtration to remove the precipitated black selenium. The hot clear yellow filtrate was treated with charcoal, filtered and concentrated under vacuum to ~1.5 L. Upon cooling, a crystalline yellow solid formed in ~80% recovery [m.p. 105-107°C (Lit.[17] m.p. 106.4-107.5°C for 4,4'-oxydibenzil)]. The 4,4'-oxydibenzil (350 g) was recrystallized from glacial acetic acid (1.4 L) to afford yellow crystals in ~85% recovery [m.p. 105.5-107°C]. The total reaction scheme is shown in Eq. 1.

A 50/50 mixture of m-cresol and xylenes was used as solvent for the polymerizations, and enough for the entire project was prepared beforehand. Also, adequate amounts of monomers were prepared beforehand and all polymerizations were run using monomers from the same batch, thereby eliminating the possiblity of introducing variations by using different materials for different polymerizations.

Polymerizations

The polymerization scheme of DAB and ODB to form a polyphenylquinoxaline is shown in Eq. 2. The apparatus used for polymerizations was a 1 L resin kettle equipped with a model HS 6.7 cm (2-5/8 in) diameter Jiffy Mixer connected to a constant torque stirrer and a thermometer. When necessary, an ice bath was used to control the reaction exotherm and maintain temperatures below a preselected point. A polymerization that required heating was carried out in a water bath on a hot plate. All polymerizations were stirred for ~27 h.

At the end of this reaction period, 200 ml of polymer solution were transferred into a 250 ml beaker and brought to 25°C. Using spindle type LTV #3, Brookfield viscosities were measured at five different speeds and averaged to give the reported values. Next, approximately 30 ml of solution were transferred to a centrifuge tube and saved for film casting. The remaining portion was diluted with enough chloroform ($CHCl_3$) to reduce the viscosity to facilitate precipitation and produce relatively small particle size polymer. All polymers were precipitated in methanol in a large Waring blender, washed in fresh methanol, then washed in boiling methanol. After filtering, the yellow polymer was air dried at ~100°C for 4 h.

Ten different polymerizations were conducted using the stoichiometries, reaction temperatures, stirring rates and concentrations given in Table I. The stoichiometry involved +1, +3, +5 mole % excess ODB and -1, -3, -5 mole % insufficient ODB. A constant amount of DAB (20.000g, 0.09334 mol) was used for the polymerizations in Table I. In all cases, ODB was dissolved in 75 volume % of the total polymerization solvent and DAB was added during ~5 min to the stirred solution. Additional solvent was added to wash down residual DAB and obtain the desired concentration. Each of these polymerizations was run at 15% (w/v) solids content and exotherms were controlled such that the reaction temperature was held at or below 32°C. The same apparatus was used for all polymerizations.

Other polymerizations listed in Table I were performed to investigate other reaction parameters using +1 mole % excess ODB. Two of these reactions were run at 10% and 20% (w/v) solids content, with all other reaction parameters held constant, to study the effect of concentration on the resulting polymers. In another polymerization, all reaction parameters were held constant except for the stirring rate (450 rpm). Another reaction in Table 1 was warmed to ~45°C and held within ±3°C during the 27 h of reaction.

In addition, several smaller polymerizations shown in Table II were performed. A polymerization using 3 mole % monofunctional benzil, a yellow, crystalline solid (m.p. 95-96.5°C) with an equimolar amount of ODB and DAB was conducted. DAB (10.000 g, 0.04667 mol) was added during ~5 min. to a solution of ODB (20.276 g, 0.04667 mol), benzil (0.2943 g, 0.00140 mol), and 174 ml of 50/50 m-cresol/xylenes mixture.

Two other polymers were prepared from polymerizations where the stoichiometries were offset by the same magnitude but in opposite directions. Specifically, 30 ml of +5 mole % excess ODB (polymerization #6, Table I) and -5 mole % insufficient ODB (polymerization #1, Table I) reaction solutions were combined and stirred at room temperature (RT) for 2.5 h. In another similar reaction, the same polymers were used except they had previously been precipitated, redissolved, combined and stirred at RT for ~24 h.

Films

Polymer solutions (~30 ml) were centrifuged, cast onto plate glass and dried in a dry air box at 40°C for 16 h. The tack free film on glass was stage-dried in a circulating air oven to 300°C and held at 300°C for 0.5 h. The nominally 0.0076 cm (0.003 in) thick film was removed from the glass using a razor blade to lift a corner and then water to aid removal. On several occasions, when the polymer was removed from the plate, the film tore away a thin layer of glass.

Characterization

Inherent viscosities (η_{inh}) were measured at 25°C on 0.5% $CHCl_3$ on m-cresol solutions. Gel-permeation chromatography (GPC) was performed on a 10^6, 10^5, 10^4, 10^3 Å μ-Stryagel column bank using a Water Associates ALC/GPC-244 high pressure liquid chromatograph, $CHCl_3$ solvent and a flow rate of 2 ml/min. Infrared spectra of polymers were obtained on a Nicolet 3600A FTIR system using a diffuse reflectance technique. Number average molecular weights ($\overline{M}_n$) were determined by Arro Laboratories, Joliet, Illinois, using a membrane osmometer and $CHCl_3$ as the solvent. Weight average molecular weights ($\overline{M}_w$) were determined by low angle laser light scattering on a LDC/Milton Roy CM 100 instrument at 6328 Å using $CHCl_3$ solvent.

Differential scanning calorimetry (DSC) was performed on a DuPont Model 990 Thermal Analyzer in combination with a standard DSC cell at a heating rate of 20°C/min. After heating to 350°C and quenching, glass transition temperature (T_g) was taken at the inflection point in the ΔT versus temperature curve of the second run on the same sample. Thermomechanical analyses (TMA) were performed on a DuPont Model 940 Thermomechanical Analyzer at a heating rate of 5° C/min on films which had been cured to 300°C and 316°C. The T_g was taken at the intersection of the tangent lines of the plot of film elongation versus temperature. Torsional braid analyses (TBA)[18] were performed on glass braids impregnated with 5% polymer solution in $CHCl_3$ (cured to 300°C for 0.5 h) at a heating rate of 3°C/min from -140°C to 400°C. Heat-up and cool-down curves were obtained on the same sample and the T_g was taken at the relative damping peak on the heat-up curve. Thermogravimetric analyses (TGA) were conducted with a Perkin-Elmer

TGS-2 instrument in both air and nitrogen flowing at 15 ml/min on ~2 mg film samples that had been cured to 300°C. Isothermal aging was conducted on film samples in a circulating air oven at 316°C ± 5°C. The samples were weighed periodically on an analytical balance over a period of 460 h.

Mechanical properties of films were measured according to ASTM-D882 on an Instron Tensile Tester at a crosshead speed of 0.508 cm/min (0.2 in/min) and a gauge length of 7.62 cm (3.0 in). Three or more 1.27 cm (0.5 in) wide and nominally 0.0076 cm (0.003 in) thick film specimens were tested for each polymer at RT and 232°C. Polymer moldings were made using 2.54 cm (1 in) or 5.72 cm (2.25 in) diameter stainless steel molds and a Carver hydraulic press equipped with electrically heated platens. In all cases, the polymer-filled molds were introduced into a preheated press and brought to temperature under contact pressure only. When the desired temperature was reached, the pressure was applied and held 0.5 h. The mold was allowed to cool under pressure. Flexural properties were measured according to ASTM D-790 at a 16 to 1 span-to-depth ratio on 0.635 cm (0.25 in) wide molded specimens. A three-point loading system with center loading at a rate of 0.508 cm/min (0.2 in/min) on a simply supported beam specimen was utilized.

RESULTS AND DISCUSSION

Synthesis and Solution Properties

Since the major purpose of this research was to investigate the effect of a systematic variation in monomer stoichiometry on polymer properties, extreme care was exercised to keep all other reaction parameters constant. A secondary objective of this work was to investigate several reaction parameters which may have an effect on final polymer properties. The polymerization parameters studied were stirring rate, concentration and temperature. The various polymerizations are summarized in Tables I and II. Table III contains Brookfield and inherent viscosities, and GPC peak retention times of the ten polymers in Table I. As the stoichiometry approaches a 1:1 mole ratio, the Brookfield viscosity and η_{inh} increased as expected. Also, the GPC data exhibit decreasing retention times as stoichiometry approaches 1:1. The GPC peaks are relatively broad indicating a relatively broad molecular weight distribution. Typical polydispersity factors ($\overline{M}_w/\overline{M}_n$) for polycondensations are about 2, but for the PPQ reaction the polydispersity is normally greater than 3[19].

The five polymerizations utilizing +1 mole percent excess ODB (#4, 7, 8, 9 and 10, Table 1) deserve comment. In Table III, #4, 7 and 8, which correspond to reaction concentrations of 15, 10 and 20% solids respectively, show the effect of monomer concentration on resulting viscosity. Viscosities increase with increasing concentration even at the same stoichiometry. The 20% solids content polymerization (#8, Table 1) at +1 mole percent excess ODB became very viscous after only 3.5 h. To avoid gelation, it was diluted to 15% solids content. A solution quickly formed from what appeared to be a near gel-state. The diluted reaction was continued for a total of 27 h, then subjected to Brookfield viscosity measurement. The 10% solids content reaction at ±1 mole % excess ODB (#7, Table I) was not subjected to a Brookfield viscosity measurement since the values at different concentrations would not be comparable.

The other two +1 mole % excess ODB polymerizations (#9 and 10, Table I) investigated the effect of temperature and stirring rate. Although the GPC peak retention times are similar, the polymer from the reaction stirred at 450 rpm had a lower Brookfield viscosity but essentially the same inherent viscosity as a polymer made at a lower stirring rate (#4, Table I).

The polymer made at 45°C (#9, Table I) exhibited a slightly lower Brookfield viscosity and lower inherent viscosity than the polymer made at <32°C (#4, Table I). A possible explanation follows. It has been reported[19] that the branching frequency of 0.20 M preparations of PPQ is relatively constant with one branch unit per 180 ± 10 chain units. These authors view the polymerization mechanism as an initial rate-determining reaction between an amine and a ketone group, followed by a much faster ring closure reaction. They state that if the rate of the initial reaction is increased, branch formation becomes more probable. Since one reaction was heated, an increase in the rate of the initial reaction was expected, leading to a more highly branched system. Furthermore, a branched polymer of equal molecular weight compared to its linear counterpart has a lower mean square radius of gyration, $<S^2>$[20]. This lower $<S^2>$ leads to lower inherent viscosity, consistent with the experimental data. Although this polymer has a lower inherent viscosity, which is a dilute solution viscosity measured at 0.5% solids concentration, it has a higher Brookfield viscosity, measured at 15% solids concentration. It has been reported[21] that in some cases, the ratio of viscosity of the branched polymer (η_B) to the viscosity of the linear polymer (η_L) begins to increase rapidly at high concentrations. Furthermore, it is possible that η_B may overtake and exceed the η_L by orders of magnitude. The concentration where enhancement of viscosity begins depends on the structure of the branched polymer and the length of the branches. This viscosity enhancement has been observed in star, comb and tree branched polymers. One could reason from the evidence that the PPQ which was made at 45°C contained more branches than the PPQ made at <32°C. In addition, the PPQ made with more rapid stirring appears to have less branching (lower Brookfield viscosity) than the polymer made at a slower stirring rate.

Experimental values of $\overline{M}_n$ determined by membrane osmometry are shown in Table IV. Other data included in the table are $\overline{M}_w$ determined by low angle laser light scattering and polydispersity ($\overline{M}_w/\overline{M}_n$). There is a systematic increase in molecular weight with decreasing monomer offset (approaching 1:1 stoichiometry). Furthermore, diamine-terminated polymers (#1 and 2) are of higher molecular weight than benzil-terminated polymers made at the same offset in stoichiometry (#6 and 5, respectively). These data correlate with viscosity data shown in Table III. The plot of log η_{inh} versus log $\overline{M}_w$ and log $\overline{M}_n$ shows this correlation (Fig. 1). The trend of diamine-terminated polymers having higher η_{inh} than benzil-terminated polymers made at the same offset in stoichiometry has been reported previously.[22]

The polymers made on a smaller scale (see Table II) were also characterized. The data for viscosity and GPC peak retention times are presented in Table V. The reaction (#11, Table II) with monofunctional monomer (benzil) at a 3 mole % addition was performed to control molecular weight. Comparing the viscosities of this polymer to the viscosities of the two polymers made with 3 mole % excess and insufficient ODB (#2 and 5, Table I), it was apparent that both methods are equally effective in controlling molecular weight. Although the GPC retention time (17.40 min) for polymer #11 is slightly higher than for polymers #2 and 5 in Table III (17.10 and 17.30 min respectively), the η_{inh} of #11 is between those of polymers #2 and 5 (Table III). The slight variation in GPC time may be due to differences in molecular weight distribution. The GPC conditions were not discriminating enough to measure a difference in peak width of the three curves.

The two other small scale reactions in Table II were done to investigate the possiblity of increasing molecular weight of the polymers after the initial reaction was complete. In the first reaction, equal portions of the +5 mole % excess ODB polymer solution and the -5 mole % insufficient ODB solution were combined and stirred. The reaction increased to very high molecular weight, as evidenced by the large increase in solution viscosity. The original η_{inh}'s for the +5 and -5 mole % ODB polymers were 0.36 dl/g and 0.46 dl/g, respectively. This reaction produced a polymer with η_{inh}=1.33 dl/g in only 2.5 h, as shown in Table V. Since this reaction was successful, the polymers were also reacted after they had been precipitated, washed, and boiled in methanol. The solid polymers were redissolved in the reaction solvent, then added together and stirred. The final polymer had an η_{inh}=1.11 dl/g, as shown in Table V, again indicating that higher molecular weight polymer had been produced. It was somewhat surprising that this reaction was so successful using precipitated polymers. One may expect the precipitation and work-up to affect the end-group or the stoichiometry (by dissolving low molecular weight material) such that polymer with viscosity this high would not be formed.

Polymer Characterization

Infrared spectra (ir) were obtained on potassium bromide blends of various polymers using diffuse reflectance techniques. A 1674 cm^{-1} band is present in the +5 mole % ODB polymer spectrum and absent in the -5 mole % ODB polymer spectrum. This band has been identified as the carbonyl stretching absorption and supports the fact that the +5 mole % excess ODB polymer is benzil terminated. The other region relevant to this discussion is from 3330 cm-1 to 3480 cm^{-1}. Two absorptions are present in the -5 mole % ODB polymer spectrum but absent in the +5 mole % spectrum. These bands have been identified as the symmetric and asymmetric N-H stretching vibrations. This evidence indicates that the -5 mole % polymer is amine terminated. The carbonyl absorption is present in both the +3 and +1 mole % polymer, but less intense in the latter. The amine absorption is just slightly more intense than the background noise in the -3 mole % offset spectrum, primarily because it is a weak absorption and the amine concentration is very low in the polymer.

Apparent T_gs were measured using thermal and thermo-mechanical methods. Polymer T_gs by DSC, TBA and TMA are listed in Table VI. TBA is good not only for detecting polymer T_gs, but also lower energy transitions, such as β-transitions. TMA's were run on film samples cured to 316°C and two grams of load were added to slightly stress the film. The T_gs varied with the method of determination and heating rate. However, the same trend in polymer T_gs is prevalent regardless of the method of determination.

As the benzil-terminated polymers (+5, +3, +1 mole % offset) approach a 1:1 stoichiometry and therefore higher molecular weight, the polymer T_g increased. For example, the T_g by DSC was 277°C and 298°C for the +5 and +1 mole % ODB polymers (#6 and 4, Table I), respectively. The diamine terminated polymers (#1 and 2, Table I) exhibited the opposite trend in T_gs. Lower molecular weight polymers had higher T_gs as measured by DSC; 306°C and 295°C for the -5 and -3 mole % ODB polymers, respectively. The explanation for this phenonomenon is crosslinking of the diamine-terminated polymers. Crosslinking restricts cooperative segmental motion and therefore increases T_g. To determine if the 300°C cured films had crosslinked, solubility tests were performed. A crosslinked film does not dissolve but may swell. After 24 hours in chloroform, all benzil terminated polymer films had dissolved, and therefore were not crosslinked. The amine terminated polymer films were insoluble even after weeks in $CHCl_3$. The -5 and -3 mole % ODB polymer films swelled, with more swelling in the latter film (larger linear segments between crosslinks exhibit more swelling than smaller segments). The final temperature of cure also had an effect on crosslink density since the 316°C cured polymer films appeared to swell less than those cured at 300°C.

As mentioned previously, TBA is effective at detecting secondary transitions, usually called β-transitions. While polymer T_g, which is an α-transition, is related to cooperative segmental motion of the polymer chains, the β-transitions arise from motions of specific molecular groups or side chains. The movements that cause these low temperature transitions act to dissipate energy absorbed during impact. It has been shown in many cases that the specific polymer property of impact strength is related to these low temperature transitions.[23] As shown in the TBA data in Table VII, PPQ's have significant β-transitions.

Furthermore, PPQ's are relatively tough[24] and impact resistant[25], which agrees nicely with the previous discussion.

Mechanical Properties

The results of the room temperature tensile testing of films are shown in Table VIII. It is difficult to recognize any real differences in mechanical properties other than the increased values for the tensile strength and tangent modulus for polymers #11 and #12 (Table II). There is an increase in elongation with increasing molecular weight, as expected. Films were also tested at 232°C (450°F) with results listed in Table IX. Initial discussion will involve the five polymers which were made by a simple adjustment in stoichiometry. Except for the -5 mole % ODB polymer, both tensile strength and tangent modulus increase as the offset in stoichiometry decreased, therefore as molecular weight increased. One would expect higher molecular weight polymers to display better mechanical properties. The -5 mole % ODB (#1, Table I) which does not follow this trend, had the highest mechanical properties. The crosslinking in the 300°C curing of this polymer was responsible for the increase in high temperature mechanical properties shown in Table IX (higher Tg, see Table VI). The -3 mole % ODB polymer (#2, Table I) was also crosslinked, but the degree of crosslinking was so slight that the 232°C mechanical properties were not improved. Elongation, like tensile strength and tangent modulus, increased as stoichiometry approaches 1:1. The other two samples listed in the table (#11 and 12) displayed poor properties at 232°C.

Another type of mechanical test performed on the polymers was the flexure test. Polymer moldings were made from 5.72 cm (2.25 in) diameter molds using 5.5 g of polymer under 2.07 MPa (300 psi) and held at 371°C (700°F) for 0.5 h. The moldings produced were nominally 0.18 cm (0.070 in.) thick and specimens 0.64 cm (0.25 in.) wide were cut from these discs. These mini-flex specimens, were tested in a three-point bending mode at RT. No data will be presented because the specimens exhibited plasticity and did not fail. This type of behavior indicates that PPQ are relatively tough polymers.

Thermal Properties:

Seven of the polymers were subjected to thermogravimeteric analysis. These seven included both diamine and benzil-terminated polymers. The data from those seven samples are very similar and weight loss curves are virtually superimposable. However, several interesting features were found. A sample of -3 mole % ODB polymer (#2, Table I) film cured to only 250°C in flowing air for 0.5 h exhibited weight loss beginning at 200°C and lost 2% of its weight by 400°C. This weight loss is probably due to residual solvent since a film cured to 300°C in flowing air for 0.5 h exhibited no weight loss below 400°C. It is interesting to note that the boiling point of m-cresol is 202°C, almost exactly where the 250°C cured film began weight loss. This solvent apparently has a high affinity for the polymer and remains in the films even when cured above its boiling point. The data suggest that it is necessary to cure the films slightly above their Tgs to remove the last traces of m-cresol. Curing at these temperatures allows movement of the polymer chains, letting trapped solvent molecules escape. Furthermore, the -5 mole % insufficient ODB diamine-terminated polymer (#1, Table I) began gaining weight at ~150°C in an air atmosphere. The weight gain was slight (~2%) presumably due to oxidation of the residual amino groups.

A more discriminating test for the thermooxidative stability of the polymers was isothermal aging at 316°C (600°F). Five polymer films (#1, 2, 4, 5 and 6, Table I) with the same thermal history, were introduced into a flowing air oven at 316°C. After an initial 15 h conditioning period, the samples were periodically removed, cooled in a dessicator, and weighed on an analytical balance with results presented in Table X. The films became progressively darker and more brittle with aging and after 460 h were shiny black and too brittle to handle. As shown in the table, the diamine terminated films are much more sensitive to thermooxidative degradation than the benzil-terminated films.

Processability:

One important property of a thermoplastic which demands discussion is processability. The limiting factor concerning applications for many high performance, high temperature thermoplastics is not their thermal or mechanical properties, but their ability to be processed into a useful part. It has been recognized that thermoplastics would have a distinct cost advantage over thermosets provided they can be reliably processed. If a part made from a thermosetting resin is not acceptable, due to voids, shape, etc., it cannot be reprocessed. If a part made from a thermoplastic is unacceptable, the same material can be reprocessed to correct defects. One of the major differences between thermoplastics and thermosets, concerning processing, is their bulk viscosities. Thermosets usually have low viscosities when first prepared due to low molecular weight. However, as the resin is cured at elevated temperatures, the molecular weight and viscosity increase. Thermoplastics have much higher viscosities and therefore, relatively poor flow. Good flow is necessary when making adhesive bonds, moldings or composites.

In order to study the differences in processabiltiy for the PPQ, 2.54 cm (1 in) and 5.72 cm (2.25 in) diameter moldings were made. Five of these polymers (#1, 2, 4, 5, 6, Table I) were processed under the same conditions and a significant difference in flow was apparent. One gram of polymer in the mold was introduced to the preheated press, heated to 343°C (650°F), 0.7 MPa (100 psi) was applied and held for 0.5 h. The mold was allowed to cool under pressure and the moldings were examined visually to find differences in uniformity. There was a large difference in the processability of these polymers. The +5 mole % excess ODB polymer (#6, Table I) formed a uniform, transparent amber disk. The +3 mole % excess ODB polymer (#5, Table I) disk was also uniform but not as transparent. The +1 mole % excess ODB polymer (#4, Table I) was not uniform and only a small part was transparent. The remainder of the disk was opaque and yellow, due to fibrous polymer which did not flow. The processability of the -3 and -5 mole % insufficient ODB (#2 and 1, Table I) polymers was also governed by polymer viscosity with the molding from polymer #1 being slightly better than the molding from polymer #2. However, areas of yellow, fibrous polymer which did not soften and flow are apparent, although not as obvious as in the case of the +1 mole % excess ODB polymer. These conditions were selected because differences in processability could be detected. Under the right conditions (~750°F and 300 psi) even the high molecular weight polymer formed a uniform molding. As expected, an increase in pressure or temperature was effective in increasing flow.

SUMMARY

A series of polyphenylquinoxalines with different molecular weights and end-groups were readily prepared by varying monomer stoichiometry. The effects of reaction concentration, temperature, and stir rate were also studied. The addition of a monofunctional monomer, benzil, proved to be equally effective in controlling polymer properties. PPQ was found to have "living polymer" character since the reaction continues with the addition of the proper reactive groups. Number and weight average molecular weights were determined and correlated well with viscosity data. Glass transition temperatures were determined by a variety of methods and were found to be dependent upon molecular weight. Furthermore, diamine-terminated polymers were found to crosslink when cured at temperatures near 300°C, leading to a crosslinked system with higher T_g and decreased solubility. Mechanical properties of films from polymers of different molecular weights were essentially indentical at RT but showed significant differences at 232°C. Diamine-terminated polymers were found to be much less thermooxidatively stable than benzil-terminated polymers when aged at 316°C (600°F) even though dynamic thermogravimetric analysis revealed only slight difference. Lower molecular weight polymers exhibited better processability by compression molding than higher molecular weight polymers.

REFERENCES

1. P. M. Hergenrother and H. H. Levine, J. Polym. Sci., A-1, 5, 1453 (1967).
2. P. M. Hergenrother, J. Polym. Sci., A-1, 6, 3170 (1968).
3. W. Wrasidlo and J. M. Augl, J. Polym. Sci., A-1, 1, 3393 (1969); J. Polym. Sci., B, 7, 281 (1969).
4. W. Wrasidlo and J. M. Augl, Macromolecules, 3, 544 (1970).
5. H. M. Relles, C. M. Orlando, D. R. Heath, R. W. Schluenz, J. S. Manello and S. Hoff, J. Polym. Sci., 15, 2441 (1977).
6. A. K. St. Clair and N. J. Johnston, J. Polym. Sci., 15, 3009 (1977).
7. F. L. Hedberg, F. E. Arnold and R. F. Kovar, J. Polym. Sci., 12, 1925 (1974).
8. P. M. Hergenrother, J. Appl. Polym. Sci., 18, 1779 (1974).
9. P. M. Hergenrother, Macromolecules, 7, 575 (1974).
10. W. Wrasidlo, J. Polym. Sci., A-1, 8, 1107 (1970).
11. W. Wrasidlo, J. Polym. Sci., A-2, 9, 1603 (1971).
12. J. M. Augl, J. Polym. Sci., A-1, 10 2403 (1972).
13. J. V. Duffy, J. M. Augl, and H. J. Booth, U. S. Nat. Tech. Inform. Serv., 1973, #766454/3 (Citation: Govt. Rep. Announce. U. S. 1973, 73(21), 137). Avail: NTIS.
14. P. M. Hergenrother and D. J. Progar, Adhes. Age, 20, 12, 38 (1977).
15. C. L. Hendricks and S. G. Hill, Sampe Quart., 12, 4, 32 (1981).
16. H. Vogel and C. S. Marvel, J. Polym. Sci., 50, 511 (1961).
17. M. A. Ogliaruso, L. A. Shadoff and E. I. Becker, J. Org. Chem., 28, 2725 (1963).

18. S. K. Dalal, G. L. Carl, A. T. Inge, and N. J. Johnston, Polym. Preprints, 15 (1), 576 (1974).

19. G. L. Hagnauer and G. D. Mulligan, Macromolecules, 6, 477 (1973).

20. G. C. Berry, and T. G. Fox, Adv. Polym. Sci., 5, 261 (1968).

21. W. W. Graessley, Accounts of Chem. Res., 10, 332 (1977).

22. P. M. Hergenrother, J. Macromol. Sci. - Revs. Macromol. Chem., C6 (1), 1 (1971).

23. L. E. Nielsen, Mechanical Properties of Polymers, Reinhold Pub. Co., 1962.

24. P. M. Hergenrother, SAMPE Quart., 3 (1), 1 (1971).

25. P. M. Hergenrother, Polym. Eng. Sci., 16 (5), 303 (1976).

TABLE I.
POLYMERIZATION PARAMETERS

Polymerization Number	Moles ODB	MASS ODB, g	Mole % Offset ODB to DAB	Solvent, ml	Conc., %Solids	RX Temp, ℃	RX Time, h	Stirring Rate, rpm
1	0.08867	38.524	-5	332	15	32	27	225
2	0.09054	39.335	-3	336	15	32	27	225
3	0.09241	40.146	-1	341	15	32	4	225
4	0.09427	40.957	+1	345	15	32	27	225
5	0.09614	41.768	+3	350	15	32	27	225
6	0.09801	42.579	+5	355	15	32	27	225
7	0.09427	40.957	+1	549	10	32	27	225
8	0.09427	40.957	+1	244	20	32	27	225
9	0.09427	40.957	+1	345	15	45	27	225
10	0.09427	40.957	+1	345	15	32	27	450

TABLE II
SMALL SCALE POLYMERIZATION PARAMETERS*

Polymerization Number	Reactants	Solvent, ml	Time, h
11	DAB (10.000 gms, 0.04667 moles) ODB (20.276 gms, 0.04667 moles) Benzil (0.2943 gms, 0.00140 moles)	174	27
12	30 ml +5 mole % reaction soln. (Rxn. 6) 30 ml -5 mole % reaction soln. (Rxn. 1)	----	2.5
13	4.000 gms +5 mole % polymer (Rxn. 6) 4.000 gms -5 mole % polymer (Rxn. 1)	43	24

TABLE III
SOLUTION CHARACTERIZATION

Polymerization # Table I	Brookfield viscosity,[1] cps	ηinh,[2] dL/g	GPC Retention Time, min
1	700	.46	17.46
2	2490	.62	17.10
3	>200,000	insoluble gel	14.03, 16.20[4]
4	4080	.72 (.98)[3]	16.88
5	538	.45 (.60)[3]	17.30
6	237	.36	17.84
7	----	.67	16.95
8	5720	.75	16.90
9	3730	.60	16.96
10	3260	.70	16.96

1) 25°C and 15% concentration
2) 0.5% concentration in $CHCl_3$ at 25°C
3) 0.5% concentration in m-cresol at 25°C
4) bimodal molecular weight distribution

TABLE IV
MOLECULAR WEIGHT DETERMINATIONS

Polymerization #	$\overline{M}_n$, g/mole	$\overline{M}_w$, g/mole	$\frac{\overline{M}w}{\overline{M}n}$
1	18,700	42,200	2.26
2	26,200	85,700	3.27
4	31,400	109,200	3.48
5	15,400	54,100	3.51
6	12,000	46,800	3.90
9	27,400	--------	-----
10	28,300	--------	-----

TABLE V
SOLUTION CHARACTERIZATION
(Small Scale Reactions)

Polymerization # Table II	Brookfield viscosity,[1] cps	ηinh,[2] dL/g	GPC Retention Time, min
11	709	0.50	17.40
12	100,000[3]	1.33	13.70, 16.48[4]
13	---------	1.11	13.88, 16.56[4]

1) 25°C and 15% solids
2) 0.5% conc. in $CHCl_3$ at 25°C
3) unstable reading
4) bimodal molecular weight distribution

TABLE VI
GLASS TRANSITION TEMPERATURES (°C)

Polymerization #	DSC	TBA	TMA[1]
1	306	312	321
2	295	308	317
3	297	----	----
4	298	298	306
5	286	288	299
6	277	284	288
7	297	297	306
8	300	298	305
9	293	293	306
10	292	294	305
11	292	317	299
12	306	301	312
13	307	298	-----

1) Film elongation

TABLE VII
β TRANSITION TEMPERATURES (°C)

Polymerization #	TBA
1	-85
2	-100
3	-----
4	-97
5	-105
6	-85
7	-110
8	-110
9	-109
10	-105
11	-91
12	-110
13	-102

TABLE VIII
RT MECHANICAL PROPERTIES OF THIN FILMS[1]

Polymerization #	Tensile Strength MPa	Tensile Strength (ksi)	Tangent Modulus, GPa	Tangent Modulus, (ksi)	Elongation, %
1	88.9	(12.9)	2.21	(320)	8.6
2	77.9	(11.3)	1.93	(280)	9.3
3	-----		-----		----
4	87.6	(12.7)	2.07	(300)	9.9
5	82.0	(11.9)	1.99	(290)	7.7
6	84.1	(12.2)	2.07	(300)	7.2
7	84.1	(12.2)	2.21	(320)	11.1
8	87.6	(12.7)	1.99	(290)	15.5
9	86.9	(12.6)	1.99	(290)	11.4
10	89.6	(13.0)	2.21	(320)	10.6
11	114.4	(16.6)	2.62	(380)	7.7
12	104.1	(15.1)	2.34	(340)	8.3

1) Average of four specimens

TABLE IX
232°C MECHANICAL PROPERTIES OF THIN FILMS[1]

Polymerization #	Tensile Strength GPa	Tensile Strength (ksi)	Tangent Modulus, GPa	Tangent Modulus, (ksi)	Elongation, %
1	51.0	(7.4)	1.79	(260)	26.2
2	42.1	(6.1)	1.52	(220)	70.0
4	48.3	(7.0)	1.72	(250)	73.3
5	43.4	(6.3)	1.65	(240)	13.6
6	34.5	(5.0)	1.59	(230)	2.7
11	27.6	(4.0)	1.31	(190)	22.6
12	32.4	(4.7)	1.65	(240)	38.0

1) Average of three specimens

TABLE X
ISOTHERMAL AGING AT 316°C[1]

Polymerization #	Weight Retention after time (h) at 316°C					
	24	50	125	200	315	460
1	99.6	99.4	97.2	93.3	73.0	36.7
2	99.6	99.3	97.5	93.4	73.5	37.1
4	99.6	99.7	98.4	97.4	92.1	69.1
5	99.4	99.5	98.5	97.3	91.2	61.5
6	99.4	99.6	98.7	97.6	94.3	75.5

1) % weight retention on ~0.15 g film sample

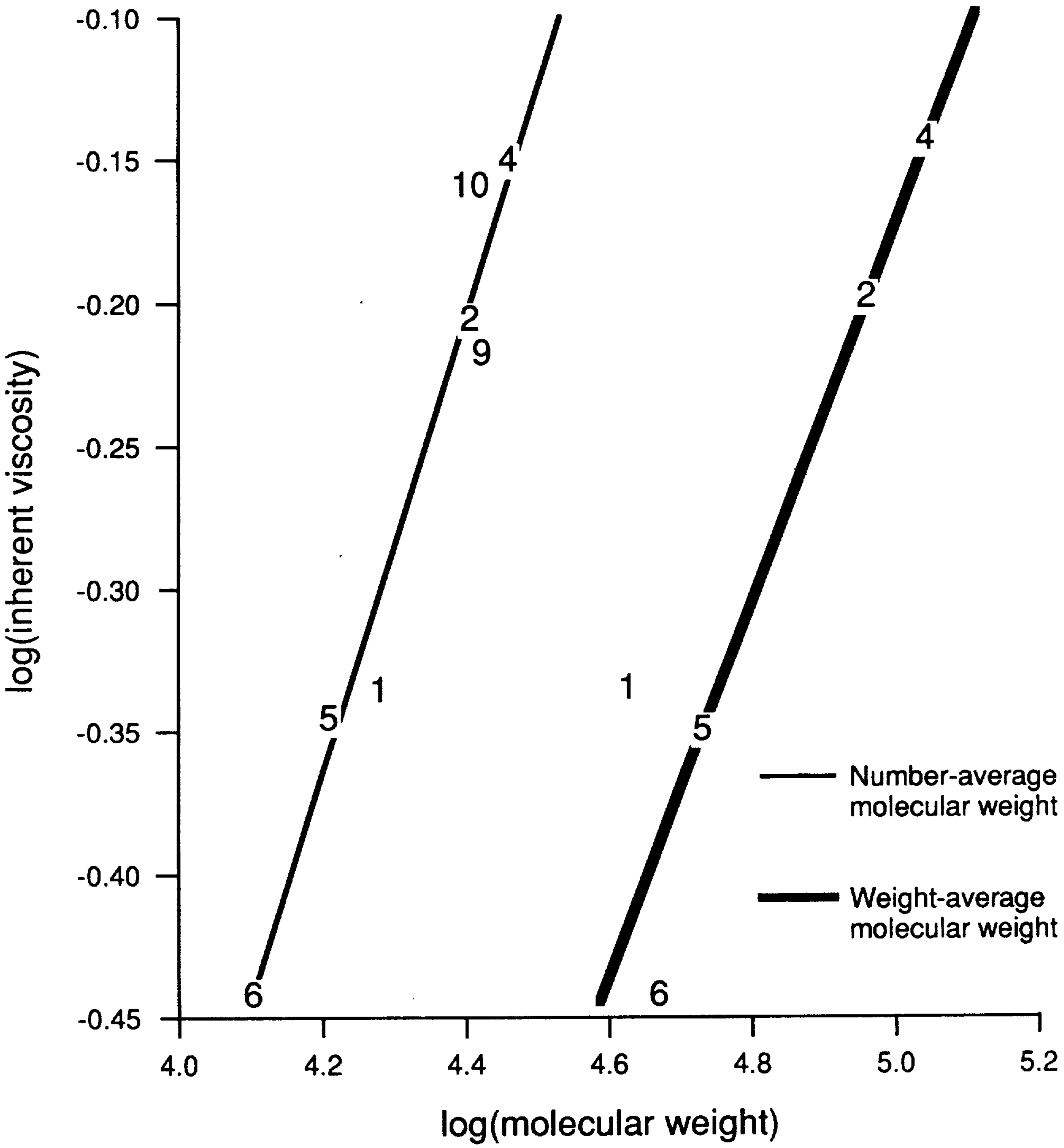
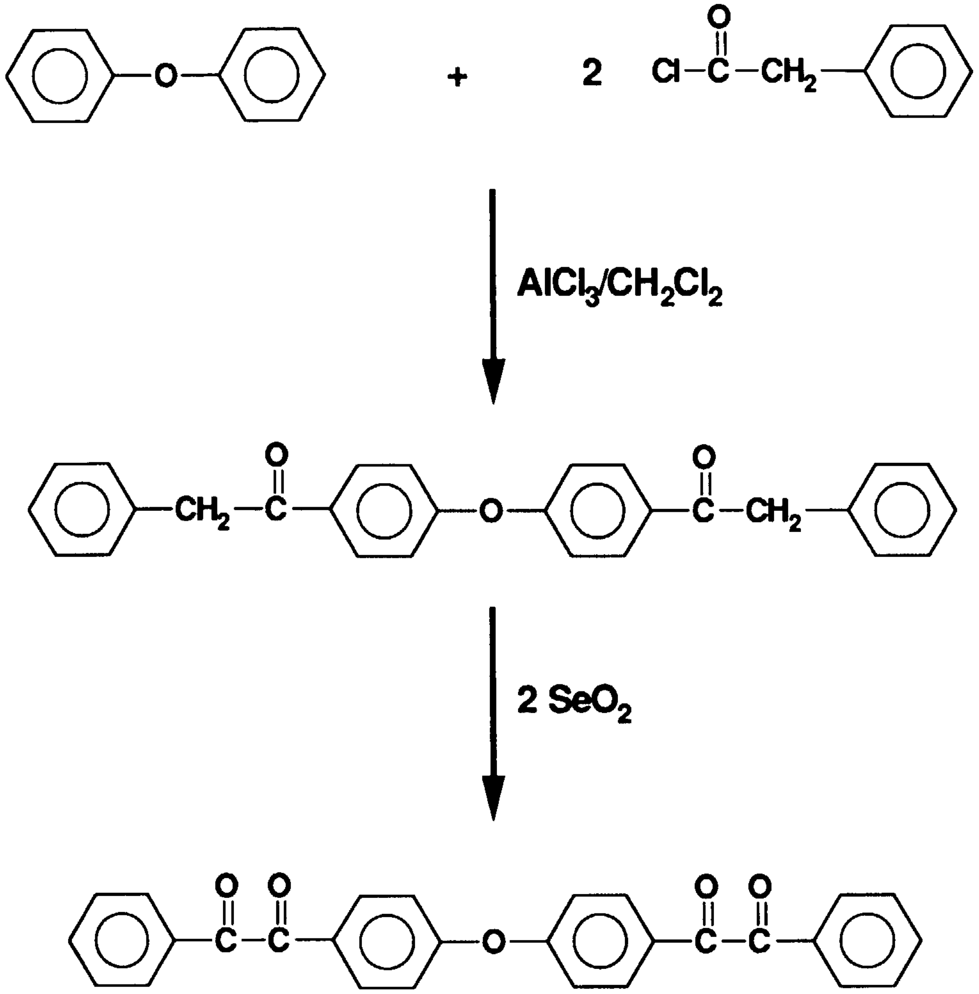


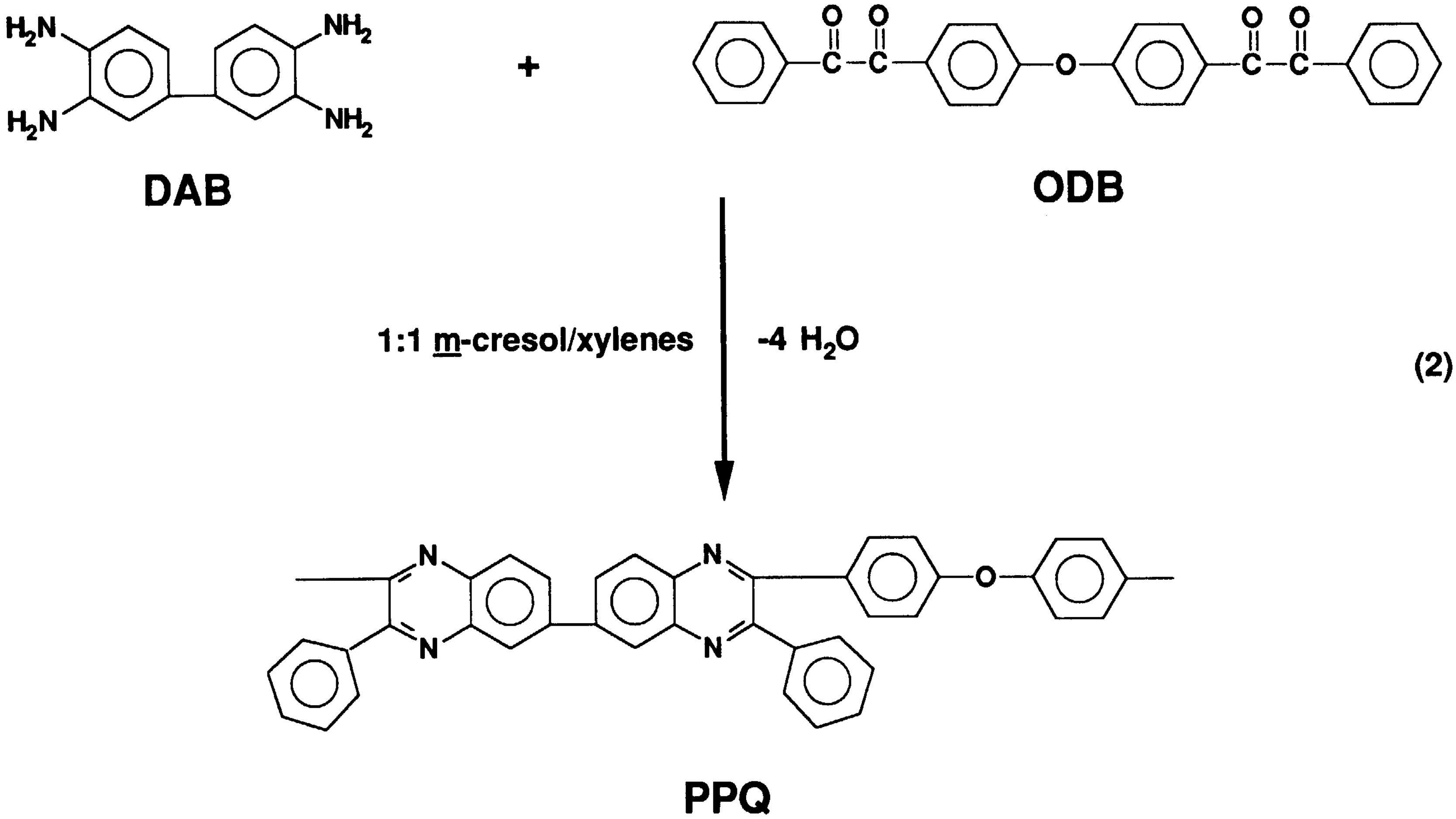
Figure 1. log(inherent viscosity) versus log(molecular weight)



4,4'-oxydibenzil

(ODB)

(1)



(2)

National Aeronautics and
Space Administration

Report Documentation Page

1. Report No. NASA TM-104100	2. Government Accession No.	3. Recipient's Catalog No.

4. Title and Subtitle

Effect of Molecular Weight on Polyphenylquinoxaline Properties

5. Report Date

May 1991

6. Performing Organization Code

7. Author(s)

Brian J. Jensen

8. Performing Organization Report No.

10. Work Unit No.

505-63-50-01

9. Performing Organization Name and Address

NASA Langley Research Center
Hampton, VA 23665-5225

11. Contract or Grant No.

12. Sponsoring Agency Name and Address

National Aeronautics and Space Administration
Washington, DC 20546-0001

13. Type of Report and Period Covered

Technical Memorandum

14. Sponsoring Agency Code

15. Supplementary Notes

Use of trade names or names of manufacturers does not constitute an official endorsement of such products or manufacturers, either expressed or implied, by the National Aeronautics and Space Administration.
Brian J. Jensen: NASA Langley Research Center, Hampton, Virginia

16. Abstract

A series of polyphenylquinoxalines with different molecular weight and end-groups were prepared by varying monomer stoichiometry. Thus, 4,4'-oxydibenzil and 3,3'-diaminobenzidine were reacted in a 50/50 mixture of m-cresol and xylenes. Reaction concentration, temperature and stir rate were studied and found to have an effect on polymer properties. Number and weight average molecular weights were determined and correlated well with viscosity data. Glass transition temperatures were determined and found to vary with molecular weight and end-groups. Mechanical properties of films from polymers with different molecular weights were essentially identical at room temperature but showed significant differences at 232°C. Diamine-terminated polymers were found to be much less thermooxidatively stable than benzil-terminated polymers when aged at 316°C even though dynamic thermogravimetric analysis revealed only slight differences. Lower molecular weight polymers exhibited better processability than higher molecular weight polymers.

17. Key Words (Suggested by Author(s)) Polyphenylquinoxaline Molecular Weight Mechanical Properties	18. Distribution Statement Unclassified - Unlimited Subject Catagory - 27

19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of pages 35	22. Price A03

NASA FORM 1626 OCT 86