Preparation of Polyimides Utilizing the Diels−Alder Reaction. 1,4-[*N*,*N*′-Bis(butadienyl-2-methyl)diamido]-2,3,5,6-tetramethylbenzenes with Bismaleimides

Joseph G. Smith, Jr., Fred Sun, and Raphael M. Ottenbrite*

Department of Chemistry, Virginia Commonwealth University,
Richmond, Virginia 23284-2006

Received November 15, 1994; Revised Manuscript Received October 27, 1995[⊗]

ABSTRACT: Bis(amide-1,3-diene) monomers were prepared from 1,4-[*N*,*N*′- bis(butadienyl-2-methyl)-diamino]-2,3,5,6-tetramethylbenzene and several alkyl and aryl acid chlorides. The corresponding poly-(amide imide)s were prepared by the Diels−Alder reaction involving these bis(amide-1,3-diene)s with bismaleimides. The polymers exhibited inherent viscosities of 0.21−0.81 dL/g and glass transition temperatures ranging from 202 to 269 °C. Moderate thermal stability was observed by dynamic thermogravimetric analysis, with 10% weight loss occurring between 318 and 350 °C in helium. The polymers were soluble in N,N-dimethylacetamide and chlorinated solvents. Creasable films were obtained by solution casting from chloroform. The chemistry and physical properties of the monomers and polymers are discussed.

Introduction

Aromatic polyimides are a class of high-performance polymers which exhibit good thermal stability and mechanical properties.[1] These polymers are usually synthesized by a two-step condensation process. First, a precursor poly(amic acid) is prepared by the reaction of an aromatic dianhydride with an aromatic diamine followed by cyclodehydration (either thermal or chemical) to the polyimide.[1−4] Frequently, the final imide polymer is insoluble, infusible, and intractable. Consequently, research is now being conducted to improve polyimide solubility and melt processability.

The Diels−Alder reaction of bis(1,3-diene)s with bismaleimides is a viable synthesis of aromatic polyimides.[5] Moderate to high molecular weight polymers have been prepared from the reaction of bismaleimides with biscyclopentadienes[6] and bisfulvenes.[7] Pseudo bisdienes such as substituted thiophenes[8] and cyclopentadienones[9,10] have been reacted with the maleimide group to form an initial Diels−Alder adduct which contained a sulfone or ketone bridging group, respectively. The thermal elimination of sulfur dioxide or carbon monoxide from the adduct afforded a new 1,3-diene *in situ* which then further reacted with another maleimide functionality. The repetition of these reactions resulted in high molecular weight polymers. Tan *et al.*[11,12] have prepared masked bis(1,3-diene)s, such as benzocyclobutene. The 1,3-diene *o*-benzocyclobutene quinodimethane was generated *in situ* by the thermal electrocyclic ring opening of benzocyclobutene which readily reacted with maleimide dienophiles by the Diels−Alder reaction.[11−12]

A novel bis(1,3-diene) system, bis(3,4-dimethylenepyrrolidyl)arylenes, prepared in our laboratory, was found to be highly reactive and readily formed self-Diels−Alder products.[13−15] Consequently, the purification and storage of the monomer were difficult and the resultant polyimides formed were inconsistent.

The high reactivity was attributed to the 1,3-diene being held in the active cisoid conformation. These self-Diels−Alder adducts contributed to the formation of cross-linked oligomeric products which caused gelation during the early stages of polymerization. To decrease the self-Diels−Alder reaction, the bis(exocyclic 1,3-diene) monomer in which the pyrrolidyl ring holds the 1,3-diene in the reactive cisoid conformation was modified to an acyclic 1,3-diene monomer. This allowed the 1,3-diene to assume an equilibrium between the inactive transoid and the active cisoid conformations. The monomer designed and synthesized was a bis[*N*-(butadienyl-2−methyl)-*N*-ethylamino]arylene.[16,17] This acyclic bis(1,3-diene) system was stable and did not undergo a self-Diels−Alder reaction in the solid state at room temperature or when heated in solution. Thus, the purification and storage of this less active monomer system were possible. The molecular weights of the polymers prepared from the monomer system, however, were relatively low as evident from the inherent viscosity data ($\eta_{\mathrm{inh}} < 0.2$ dL/g).

The decrease in activity was attributed to the 1,3-diene group existing, for the most part, in the inactive transoid conformation. To increase the activity of the 1,3-diene so as to enhance the molecular weights of these polymers, methyl groups were introduced in the ortho positions of the aromatic amine functionality. According to molecular model representations, these groups sterically favor the cisoid form of the acyclic 1,3-diene system. Bis[4-(*N*-(butadienyl-2-methyl)amino)-arylene]s were prepared and subsequently reacted with bismaleimides to afford soluble polyimides.[17] The inherent viscosity of the polymers ($\eta_{\mathrm{inh}} = 0.18{-}0.46$ dL/g) was significantly increased, which indicated that these were higher molecular weight materials than those prepared from bis[*N*-(butadienyl-2-methyl)-*N*-ethylamino]arylenes. The films obtained from this polymer, however, failed the double-crease test. It was also found from dynamic thermogravimetric analysis that the polymers were easily oxidized in air above 200 °C. This oxidation was attributed to the conversion of the secondary amine group present in the polymer backbone to the corresponding amine oxide.

In this study, the secondary amine group of the monomer was amidated to obviate the oxidation problem. It was also anticipated that the amide group would provide additional steric bulk to the 1,3-diene system, which should favor the reactive cisoid conformation. This amidated monomer was designed to provide a more

---

[⊗] Abstract published in *Advance ACS Abstracts,* January 15, 1996.

active 1,3-diene system for the Diels–Alder reaction and a more thermally stable high molecular weight polymer.

Experimental Section

Starting Materials. The 3-methyl-2,5-dihydrothiophene 1,1-dioxide, 3-(bromomethyl)-2,5-dihydrothiophene 1,1-dioxide, 2-(bromomethyl)-1,3-butadiene, and 1,4-[*N,N*′-bis(butadienyl-2-methyl)diamino]-2,3,5,6–tetramethylbenzene were prepared as previously described.[17] Propylene oxide (Aldrich Chemical Co.) was used as received. Benzene was obtained from commercial sources, purified by washing with sulfuric acid followed by distillation, and subsequently stored over molecular sieves prior to use. Acetyl chloride, 4-benzoyl chloride, 2-naphthoyl chloride, 4-phenylbenzoyl chloride, 4-nitrobenzoyl chloride, 2-phenoxybenzoic acid, *N*-phenylmaleimide, and hydroquinone (Aldrich) were used as received. 2-Phenoxybenzoyl chloride was prepared following a known procedure.[18] 1,1,2,2,-Tetrachloroethane (Aldrich) was vacuum distilled prior to use. Bis(4-maleimidylphenyl)methane (Aldrich) was purified on a silica gel column which was eluted with chloroform. Bis(3-maleimidyphenyl)sulfone, 1,4-dimaleimidylbenzene, and 1,2-dimaleimidylbenzene were obtained from Aldrich.

1,4-[*N,N*′-Bis(butadienyl-2-methyl)diacetamido]-2,3,5,6-tetramethylbenzene (1). Into a 100 mL three-necked, round-bottomed flask equipped with a magnetic stirrer were placed 1,4-[*N,N*′-bis(butadienyl-2-methyl)diamino]-2,3,5,6-tetramethylbenzene (2.44 g, 8.23 mmol), 45 mL of dry benzene, and 1.5 mL of propylene oxide. To the stirred solution was added 3.8 mL (4.20 g, 53.44 mmol) of acetyl chloride. The reaction was stirred for 4 days at room temperature. During this time, a white precipitate formed. Approximately 25 mL of 95% ethanol was added to the mixture to destroy the excess acid chloride and dissolve the precipitate. The solvent was removed by rotoevaproation to afford a yellow oil. The oil was taken up in 95% ethanol, and distilled water was added dropwise to precipitate the product. The bis(amide-1,3,-diene) product was collected by filtration and dried under vacuum at room temperature. Recrystallization from aqueous ethanol (40–50% v/v) afforded 2.10 g (67%) of an off-white granular powder. No melting point was observed below 270 °C by DSC (heating rate of 10 °C/min). IR (KBr): 1647 cm^{-1} (C=O). ^1H NMR ($CDCl_3$): δ 1.72 (d, 3H), 2.07 (s, 6H), 4.39 (d, 2H), 4.63–5.60 (m, 4H), 6.33 (dd, 1H). ^{13}C ($CDCl_3$): 15.84, 15.89, 22.18, 22.33, 47.58, 115.65, 115.83, 121.34, 133.81, 133.87, 137.32, 137.44, 139.45, 139.66, 141.66, 141.71, 170.52, 170.54 ppm. Anal. Calcd for $C_{24}H_{32}N_2O_2$: C, 75.75, H, 8.48, N, 7.36. Found: C, 74.37, H, 8.41, N, 7.26.

1,4-[*N,N*′-Bis(butadienyl-2-methyl)dibenzamido]-2,3,5,6-tetramethylbenzene (2). The title compound was prepared in a similar manner to **1** using an excess of benzoyl chloride. Recrystallization from aqueous ethanol (40–50% v/v) afforded white needles in 58% yield. No melting transition was observed below 270 °C by DSC. IR(KBr): 1626 cm^{-1} (C=O). UV (methanol, $\lambda_{max} = 217$ nm, $\epsilon = 35506$ L/(mol cm), $\lambda_{max} = 221.7$ nm, $\epsilon = 35123$ L/(mol cm). ^1H NMR ($CDCl_3$): δ 1.92 (s, 6H), 4.48 (s, 2H), 4.60–5.45 (m, 4H), 6.25 (dd, 1H), 7.05–7.24 (m, 5H). ^{13}C NMR ($CDCl_3$): 16.62, 48.41, 115.73, 122.02, 127.25, 129.33, 133.53, 136.55, 137.40, 139.39, 140.98, 170.08 ppm. Anal. Calcd for $C_{34}H_{36}N_2O_2$: C, 80.92, H, 7.19, N, 5.55. Found: C, 80.73, H, 7.19, N, 5.61.

1,4-[*N,N*′-Bis(butadienyl-2-methyl)bis(2-naphthamido)]-2,3,5,6-tetramethyl benzene (3). Into a 100 mL three-necked, round-bottomed flask equipped with a magnetic stirrer were placed 1,4-[*N,N*′-bis(butadienyl-2-methyl)diamino]-2,3,5,6-tetramethylbenzene (1.99 g, 6.73 mmol), 50 mL of dry benzene, and 1.2 mL of propylene oxide.

2-Naphthoyl chloride (3.09 g, 16.19 mmol) was added to the stirred solution by a powder funnel, followed by the addition of 25 mL of dry benzene. The reaction was stirred for 2 days at room temperature; during this time the product precipitated from solution. To the reaction mixture approximately was added 25 mL of 95% ethanol to destroy the excess acid chloride. The crude bis(amide-1,3-diene) product was collected by filtration, washed with 95% ethanol, and subsequently dried under vacuum at room temperature. Recrystallization from 95% ethanol:chloroform (8:1) afforded a white powder in 80% yield. No melting point was observed below 270 °C by DSC. IR (KBr): 1633 cm^{-1} (C=O). ^1H NMR ($CDCl_3$): δ 1.95 (s, 6H), 4.39 (d, 2H), 4.63–5.49 (m, 4H), 6.12 (dd, 1H), 7.20–7.75 (m, 7H). ^{13}C NMR ($CDCl_3$): 16.75, 48.53, 115.55, 121.84, 124.01, 126.23, 126.88, 127.01, 127.07, 127.42, 128.43, 131.91, 133.32, 133.59, 133.92, 137.28, 139.49, 140.83, 170.27 ppm. Anal. Calcd for $C_{42}H_{40}N_2O_2$: C, 83.41, H, 6.67, N, 4.63. Found: C, 83.25, H, 6.61, N, 4.65.

1,4-[*N,N*′-Bis(butadienyl-2-methyl)bis(4-phenylbenzamido)]-2,3,5,6-tetramethylbenzene (4). The title compound was prepared in a similar manner to **3** using 4-phenylbenzoyl chloride. Recrystallization from a 95% ethanol:chloroform (2:1) mixture afforded white platelets in 55% yield. No melting transition was observed below 270 °C by DSC. IR (KBr): 1640, 1626 cm^{-1} (C=O). ^1H NMR ($CDCl_3$): δ 1.99 (s, 6H), 4.50 (s, 2H), 4.64–5.47 (m, 4H), 6.25 (dd, 1H), 7.22–7.49 (m, 9H). ^{13}C NMR ($CDCl_3$): 16.67, 48.56, 115.72, 121.90, 125.88, 126.82, 127.66, 127.74, 128.83, 133.67, 135.36, 137.43, 139.57, 139.88, 141.04, 142.00, 169.81 ppm. Anal. Calcd for $C_{46}H_{44}N_2O_2$: C, 84.11, H, 6.75; N, 4.26. Found: C, 83.48, H, 6.68, N, 4.23.

1,4-[*N,N*′-Bis(butadienyl-2-methyl)bis(4-nitrobenzamido)-2,3,5,6-tetramethylbenzene (5). The title compound was prepared in a similar manner to **3** using 4-nitrobenzoyl chloride. Recrystallization from a 95% ethanol:chloroform (1.5:1) mixture afforded yellow needles in 70% yield. No melting point was observed below 270 °C by DSC. IR (KBr): 1633 (C=O), 1513, 1344 cm^{-1} (NO_2). ^1H NMR ($CDCl_3$): δ 1.96 (s, 6H), 4.53 (d, 2H), 4.95–5.41 (m, 4H), 6.25 (dd, 1H), 7.96 (d, 2H). ^{13}C ($CDCl_3$): 16.74, 48.44, 115.73, 122.10, 122.58, 127.89, 133.96, 137.32, 139.05, 140.64, 142.53, 147.86, 167.91 ppm. Anal. Calcd for $C_{34}H_{34}N_4O_6$: C, 68.67, H, 5.76; N, 9.42. Found: C, 68.13, H, 5.70, N, 9.33.

1,4-[*N,N*′-Bis(butadienyl-2-methyl)bis(4-aminobenzamido)]-2,3,5,6-tetramethylbenzene (6). The title compound was prepared by the reduction of **5** following a reported procedure.[19] A 250 mL round-bottomed flask equipped with a magnetic stirrer was charged with 0.36 g (0.61 mmol) of **5**, 75 mL of absolute ethanol, 15 mL of distilled water, 0.17 g of calcium chloride, and 2.79 g of powdered zinc. The reaction mixture was refluxed for 2 days. The hot mixture was filtered through a Celite filter bed. The product was precipitated by the addition of distilled water, collected by filtration, and subsequently dried under vacuum at room temperature. Recrystallization from aqueous ethanol (40–50% v/v) afforded 0.31 g (95%) of a white powder. No melting transition was observed below 270 °C by DSC. IR (KBr): 3451, 3359 (NH_2), 1612 cm^{-1} (C=O). ^1H NMR (DMSO-d_6): δ 1.89 (s, 6H), 3.40 (s, 1H), 4.41 (d, 2H), 4.70–4.75 (m, 1H), 5.00–5.59 (m, 5H), 6.20–6.40 (m, 3H), 6.85 (d, 2H). ^{13}C NMR (DMSO-d_6): 16.31, 16.35, 48.36, 48.56, 112.10, 112.12, 115.47, 115.66, 121.75, 122.23, 122.61, 122.66, 129.73, 133.17, 133.25, 138.10, 139.10, 139.87, 140.04, 141.33, 141.54, 150.36, 150.55, 168.74, 168.86 ppm. Anal. Calcd for $C_{34}H_{38}N_4O_2$: C, 76.38, H, 7.16; N, 10.48. Found: C, 75.83, H, 7.02, N, 10.34.

1,4-[*N,N*′-Bis(butadienyl-2-methyl)bis(2-phenoxybenzamido)]-2,3,5,6- tetramethylbenzene (7). The title compound was prepared in a similar manner to **3** using 2-phenoxybenzoyl chloride. Recrystallization from an ethanol:water: chloroform (4:1:0.3) mixture afforded a white powder in 18–31% yield, melting transition (DSC) 186.5–189.0 °C. IR (KBr): 1640 (C=O), 1232 cm^{-1} (C–O–C). ^1H NMR ($CDCl_3$): δ 1.93 (s, 6H), 4.50 (s, 2H), 4.54–5.43 (m, 4H), 6.27 (dd, 1H), 6.54–7.36 (m, 2H). ^{13}C NMR ($CDCl_3$): 17.27, 48.00, 115.78, 116.97, 119.58, 121.51, 121.63, 123.75, 127.70, 128.62, 129.60, 129.65, 133.92, 137.30, 138.40, 141.32, 153.59, 156.23, 168.26 ppm. Anal. Calcd for $C_{46}H_{44}N_2O_4$: C, 80.21, H, 6.44; N, 4.07. Found: C, 80.09, H, 6.30, N, 4.09.

***N*-(Butadienyl-2-methyl)-2,6-dimethylaniline (8).** A 250 mL round-bottomed flask was charged with 2,6-dimethylaniline (14.47 g, 0.12 mol), 2-(bromomethyl)-1,3-butadiene (8.78 g, 0.06 mol), sodium carbonate (6.33 g, 0.06 mol), and 100 mL of methanol. The reaction mixture was stirred for 2 days. After removal of the solvent by rotoevaporation, 150 mL of ethyl acetate was added to precipitate the inorganic salts, which were then collected by filtration. The product was isolated by removal of the solvent and dried under vacuum at room temperature. The crude material was purified by column chromatography; 4 × 60 cm, silica gel 230−400 mesh, petroleum ether/ethyl acetate) to afford a white powder in 61% yield ($R_{\times a6}$ = 0.45, 6/4 petroleum ether/ethyl acetate). ^{1}H NMR ($CDCl_3$): δ 2.53 (s, 6H), 3.32 (s, 1H), 5.02 (s, 2H), 5.37 (J = 11 Hz) and 5.55 (J = 18 Hz) (d,d, 1H, 1H), 5.42 and 5.61 (s,s, 1H, 1H), 6.40 (dd, 1H), 7.09 (t, 1H), 7.25 (d, 2H).

***N*-(Butadienyl-2-methyl)-2,6-dimethylphenylacetamide (9).** Into a 50 mL round-bottomed flask cooled in an ice bath was placed 2.0 g (10.68 mmol) of *N*-(butadienyl-2-methyl)-2,6-dimethylaniline and 15 mL of dry benzene. To the solution was added 1.45 mL (1.25 g, 21.43 mmol) of propylene oxide as an acid scavenger. Acetyl chloride (2.28 mL, 2.52 g, 32.06 mmol) was added dropwise to the solution, and the mixture was stirred at room temperature for 30 h. Excess acid chloride was destroyed by the addition of 5 mL of 95% ethanol to the reaction. The solution was concentrated on a rotoevaporator, and the remaining liquid was collected and placed under vacuum for 50 h. The crude material was eluted through a silica gel column (1 × 50 cm, silica gel 230−400 mesh) with 6/4 petroleum ether/ethyl acetate, and white crystals ($R_{\times a6}$ = 0.48, 6/4 petroleum ether/ethyl acetate) were obtained in 34% yield after the removal of the eluent, mp 67.0−68.4 °C. ^{1}H NMR ($CDCl_3$): δ 1.74 (s, 3H), 2.18 (s, 6H), 4.41 (s, 2H), 5.11 (J = 11 Hz) and 5.57 (J = 18 Hz) (d,d, 1H, 1H), 4.79 and 5.08 (s,s, 1H, 1H), 6.35 (dd, 1H), 7.10 (m, 3H).

***N*-(Butadienyl-2-methyl)-2,6-dimethylphenylbenzamide (10).** The title compound was prepared analogously to **9** using benzoyl chloride. The purified product was obtained in 47% yield. ($R_{\times a6}$ = 0.46, 6/4 petroleum ether/ethyl acetate). ^{1}H NMR ($CDCl_3$): δ 2.17 (s, 6H), 4.60 (s, 2H), 5.09 (J = 11 Hz) and 5.49 (J = 18 Hz) (d,d, 1H, 1H), 5.00 and 5.16 (s,s, 1H, 1H), 6.39 (dd, 1H), 6.92 (d, 3H), 7.00−7.20 (m, 5H).

***N*-(Butadienyl-2-methyl)-2,6-dimethylphenyl-4-nitrobenzamide (11).** The title compound was prepared analogously to **9** using 4-nitrobenzoyl chloride. The crude product was recrystallized from methanol to afford a 63% yield of white needles, mp 125.5−127.0 °C. ^{1}H NMR ($CDCl_3$): δ 2.18 (s, 6H), 4.61 (s, 2H), 5.12 (J = 11 Hz) and 5.49 (J = 18 Hz) (d,d, 1H, 1H), 4.49 and 5.19 (s,s, 1H, 1H), 6.39 (dd, 1H), 6.95 (d, 2H), 7.05 (t, 1H), 7.39 (d, 2H), 7.98 (d, 2H).

Model Diels−Alder Adduct Synthesis. Into a 10 mL round-bottomed flask equipped with a magnetic stirrer were charged the bis(amide-1,3-diene), *N*-phenylmaleimide, and chloroform to afford a ~25% (w/w) solution. Hydroquinone (0.1 g) was added as a radical scavenger. The reaction mixture was stirred at room temperature for 96 h. The adduct was precipitated by dropwise addition of the reaction mixture into 100 mL of rapidly stirred anhydrous diethyl ether, collected by filtration, and subsequently dried under vacuum.

Kinetic Procedure. Into two NMR tubes, 0.25−0.40 mmol of 1,3-diene and 0.45−0.75 mmol of *N*-phenylmaleimide were weighed separately and 0.5 g of deuterated chloroform was added to each tube. The proton NMR spectrum of the pure 1,3-diene was obtained prior to the reaction. The probe temperature of the NMR was 21 °C. The reaction time was monitored after the addition of the 1,3-diene solution to the NMR tube containing the *N*-phenylmaleimide solution. The reaction rate was determined by integration of the appropriate NMR signals with the accuracy of the NMR integrations being ±5%. The average of seven to eight NMR integrations were obtained at specific time intervals. The reaction was monitored to 60−80% completion.

Poly(amide imide) Synthesis. Into a three-necked 10 mL round-bottomed flask equipped with a nitrogen inlet, a condenser, and a mechanical stirrer were added stoichiometric quantities of the bis(amide-1,3-diene) and bismaleimide. Hydroquinone was added as a radical scavenger. 1,1,2,2-Tetrachloroethane was added to afford a ~25% (w/w) solution, which was stirred at room temperature under a nitrogen atmosphere for 24 h. The reaction temperature was then increased to 100−130 °C and maintained for 30 h. The polymer solution was cooled to room temperature and diluted to approximately 10% solids by the addition of chloroform. The polymer was precipitated by dropwise addition of the reaction mixture into rapidly stirred anhydrous diethyl ether, collected by filtration, and dried under vacuum. Reprecipitation from a chloroform solution into diethyl ether afforded the poly(amide imide).

Film Formation. Chloroform solutions (15−20% w/w/) of the polymers were cast onto clean, dry plate glass and air-dried to a tack-free form. The films on glass were dried under vacuum at 100 °C for 12 h.

Other Characterization Techniques. Inherent viscosities (η_{inh}) were obtained on 0.3% (w/v) chloroform solutions at 30 °C. Melting points were determined using either a Thomas-Hoover melting point apparatus or Perkin-Elmer DSC-4 differential scanning calorimeter (heating rate of 10 °C/min) and are uncorrected. Differential scanning calorimetry (DSC) was performed under a nitrogen atmosphere at a heating rate of 20 °C/min on a Perkin-Elmer DSC-4 scanning calorimeter with the glass transition temperature (T_g) taken as the inflection point of the T vs temperature curve. Dynamic thermogravimetric analysis (TGA) was performed on as-isolated polymer powders on a Perkin-Elmer TGS-2 thermogravimetric system at a heating rate of 2.5 °C/min in air and helium. Infrared spectra were obtained on either a Perkin-Elmer 283 spectrophotometer or a Nicolet 740 FTIR spectrometer as KBr disks or polymer thin films. Proton NMR and ^{13}C NMR were obtained on a General Electric QE-300 spectrometer. The chemical shifts are reported as δ values (ppm) downfield from tetramethylsilane (TMS). Ultraviolet spectra were obtained using methanol solutions on a Shimadzu UV-265 UV−visible spectrophotometer. Elemental analyses were performed at A. H. Robins Co., Richmond, VA.

Results and Discussion

Bis(amide-1,3-diene)s. Based on our experience with the bis[4-(*N*-(butadienyl-2-methyl)amino)arylene] polymers, it was expected that further modification of the monomer could enhance the ensuing polymer properties. Due to the sensitivity of the secondary amine group of the bis[4-(*N*-(butadienyl-2-methyl)amino]arylene system to oxidation at temperatures >200 °C,[17] it was proposed to alter the amine group either of the monomer or of the resultant polymer. We chose to derivatize the monomer since a quantitative conversion of the secondary amine group in the polymer may not be possible. It was also considered that the conversion of the secondary amine to a corresponding bulky amide group may provide additional steric effects in the monomer. Based on molecular modeling studies, the amide groups contained in the bis(amide-1,3-diene)s should sterically hinder the transoid conformation of the 1,3-diene group and thus favor the cisoid conformation and, as a consequence, enhance the reactivity.

The conversion of the secondary amine was achieved by amidation of the amine function of bis[4-(*N*-(butadienyl-2-methyl)aminoarylene] with acetyl chloride (Scheme 1). Subsequently, a series of bis(amide-1,3-diene)s (**1**−**5**, **7**) were prepared by the reaction of 1,4-[*N*,*N*′-bis(butadienyl-2-methyl)diamino]-2,3,5,6-tetramethylbenzene with several acid chlorides to afford the bis(amide-1,3,-diene)s in 30−80% yield (Table 1).

The 4-nitrobenzoyl-containing bis(amide-1,3-diene) (**5**) provided a functional nitro group which was reduced to an amine prior to polymerization. The usual chemical reduction methods of the nitro group could also hydrolyze the amide. Consequently, a very mild reduction method for aromatic nitro substituents, which involved refluxing the compound containing the nitro group in aqueous ethanol with zinc powder, was employed. This reaction afforded yields >95% of the bis(amide-1,3-diene) (**6**). Infrared and NMR spectra confirmed that the nitro group was reduced to the amine and that the 1,3-diene was unaffected by the reaction conditions.

Scheme 1

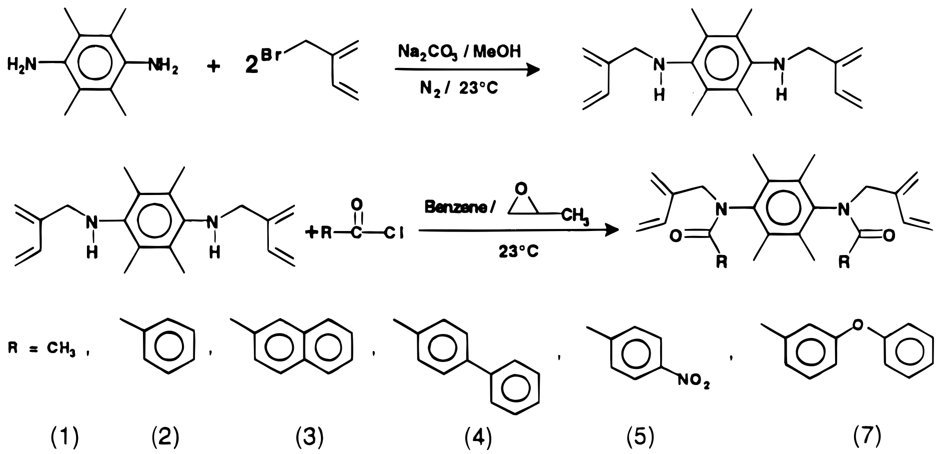
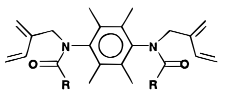
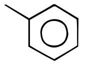
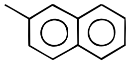
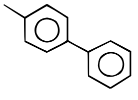
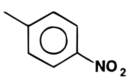
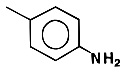
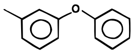


Table 1. Characterization of Bis(amide-1,3-diene)s



		SOLUBILITY[1]			THERMAL TRANSITIONS, °C[2]	
R	ID	A	B	C	ENDO	EXO
CH_3	(1)	S	S	S	----[3]	152,158, 174
	(2)	S	S	S	----[3]	195
	(3)	S	S	I	----[3]	237
	(4)	S	S	S	207	212
 NO_2	(5)	P	I	S	----[3]	190
 NH_2	(6)	P	P	I	168	233
	(7)	S	S	S	189	191

1. Solubility determined on ~0.1g/1 mL. I: Insoluble, P: Partly Soluble, S: Soluble. A: 1,1,2,2-Tetrachloroethane, B: Chloroform, C: Benzene.
2. Thermal transitions detected by DSC at a heating rate of 10°C/min.
3. No transition detected by DSC.

Most of the bis(amide-1,3-diene) monomers were soluble in benzene and chlorinated solvents (Table 1). The 4-nitrophenyl-containing bis(amide-1,3-diene) (**5**) was only partially soluble in 1,1,2,2-tetrachloroethane and insoluble in chloroform, while the 4-aminophenyl-containing bis(amide-1,3-diene) (**6**) exhibited only partial solubility in chlorinated solvents. The 2-naphthyl-containing bis(amide-1,3-diene) (**3**) was insoluble in benzene.

None of these monomers exhibited melting points below 270 °C. Several exothermic transitions were observed in all cases during the initial DSC scan to 300 °C (Table 1). After quenching to room temperature, these transitions were not reproducible upon subsequent rescanning of the same sample. The exothermic transitions (152−133 °C) in the DSC curves were attributed to the polymerization of the 1,3-diene. A melting endotherm at 189 °C was observed for the 2-phenoxyphenyl-containing bis(amide-1,3-diene) (**7**), which was immediately followed by an exothermic transition at 191 °C. This transition was attributed to the thermal reaction of the 1,3-diene group.

Previously, the dimerization of bis(3,4-dimethylenepyrrolidyl)arylenes had been observed to occur both in solution and in the solid state which was attributed to the formation of self-Diels−Alder adducts.[13−15] For example, the bis(3,4-dimethylenepyrrolidyl)arylenes dimerized readily due to the 1,3-diene group being held in the highly reactive cisoid conformation and thereby increasing the probability of a self-Diels−Alder reaction. The low-temperature stability of the (amide-1,3-diene) system was determined for a 20% w/w/ deuterated chloroform solution of 1,4-[*N*,*N*′-bis(butadienyl-2-methyl)dibenzamido]-2,3,5,6-tetramethylbenzene (**2**) heated at 50 °C and monitored by proton NMR. After 24 h, no detectable evidence of self-Diels−Alder adducts was observed. Similar results were obtained for other acyclic bis(amine-1,3-diene)s,[17] which indicated that this diene system is relatively resistant to homo-Diels−Alder reactions.

Model Diels−Alder Adducts. Model adducts were prepared by the Diels−Alder reaction of *N*-phenylmaleimide with the bis(amide-1,3-diene)s in 70 to >95% yields. The adducts were soluble in chlorinated solvents and N,N-dimethylacetamide (DMAc). Characteristic infrared absorptions of the imide group were observed at 1774, 1704, and 1380 cm^{-1}. The amide 1 band for the adducts occurred between 1647 and 1619 cm^{-1}. Both the proton NMR and IR spectra of the corresponding polymers were remarkably similar in many respects (Figures 1 and 2).

The (amide imide) adducts did not exhibit well-defined melting points by DSC; however, several endo and exothermic transitions were observed. These transitions suggest that the Diels−Alder adducts were undergoing a retrocycloaddition reaction at elevated temperatures (endothermic transitions) with a subsequent thermal addition reaction of the regenerated 1,3-diene and dienophile reactants (exothermic transitions). Similar behavior had been observed for model compounds prepared from bis(amine-1,3-diene)s and *N*-phenylmaleimide.[16,17]

To determine the relative rates of reaction for the amine and the various amide-derivatized 1,3-dienes, model mono(1,3-diene)s were used. The mono[amide-1,3-diene]s were prepared from *N*-(butadienyl-2-methyl)-2,6-dimethylaniline (**8**) and concomitant acid chlorides (Scheme 2). The 1,3-diene compounds examined contained acetyl, benzoyl and 4-nitrobenzoyl amide

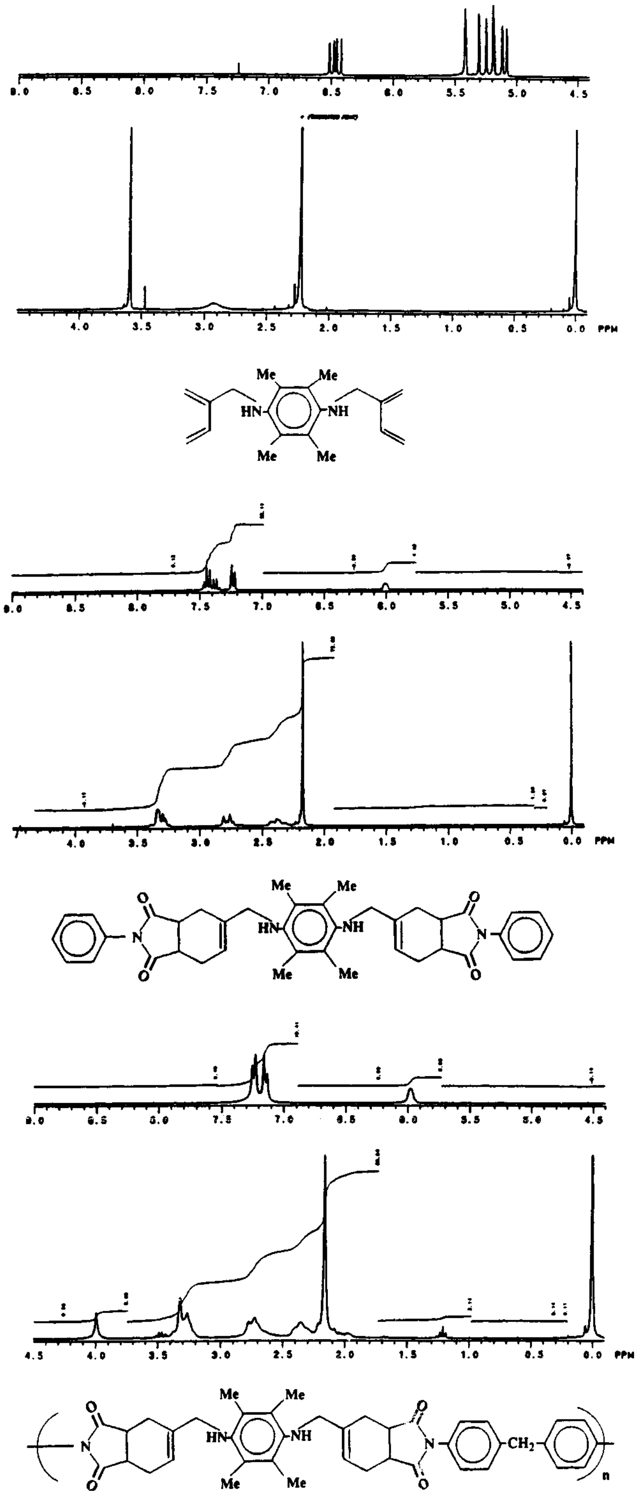


Figure 1. ^{1}H NMR spectra of bis(1,3-diene)s 1,4-[*N*,*N*′-bis(butadienyl-2-methyl)diamino]-2,3,5,6-tetramethylbenzene, the corresponding Diels–Alder model adduct compound, and the polymer.

groups (**9**–**11**). The relative rates of reaction were determined by monitoring the proton NMR for chemical shift changes for the vinyl proton (C=CH) of the 1,3-diene structure of the reactant at 6.3–6.4 ppm to that of the cyclohexenyl structure of the Diels–Alder adduct at 5.5–5.7 ppm. A linear relationship was obtained for the log([maleimide]/[1,3-diene]) vs time. The reaction kinetics were determined to be second order overall: first order for 1,3-diene and maleimide, respectively. The rate constants, reported in Table 2, were determined by eq 1:

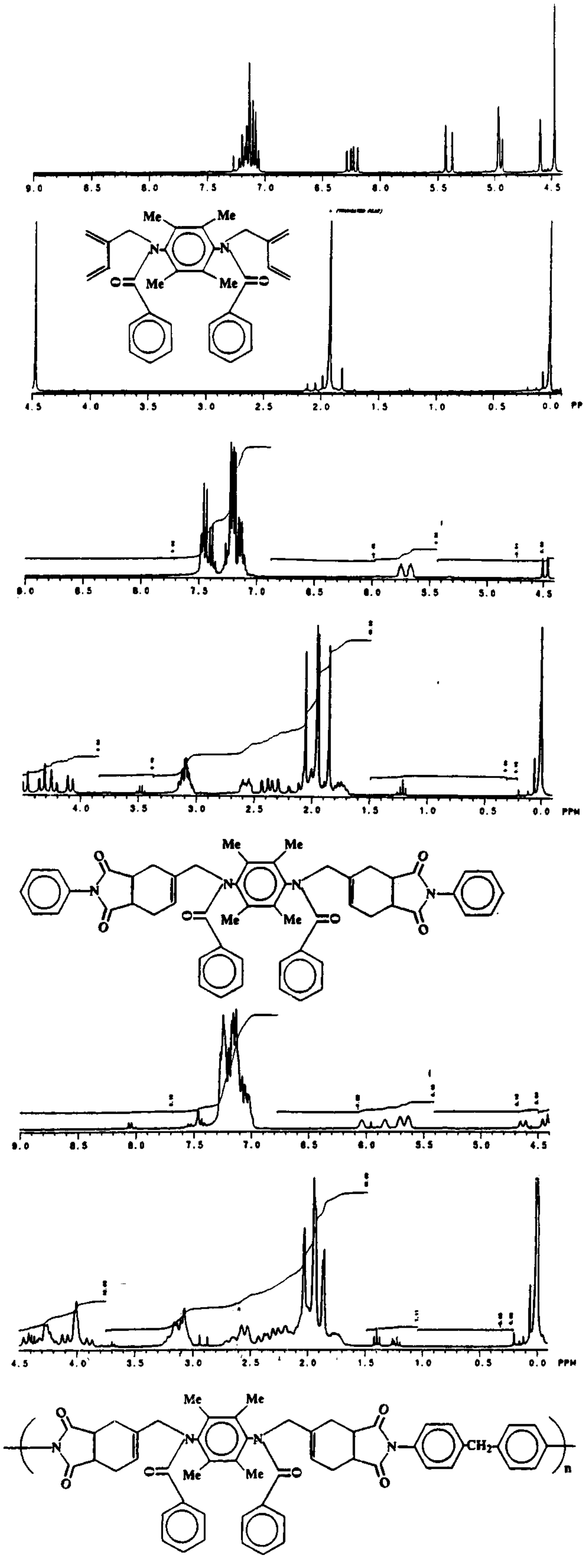
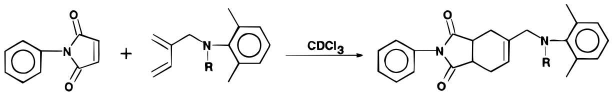


Figure 2. ^{1}H NMR of 1,4-[*N*,*N*′-bis(butadienyl-2-methyl)-dibenzamido]-2,3,5,6-tetramethylbenzene, the corresponding Diels–Alder model adduct compound, and the polymer.

$$\text{rate constant} = \frac{2.303 \times \text{slope}}{[\text{maleimide}]_{t=0} - [1,3\text{-diene}]_{t=0}} \quad (1)$$

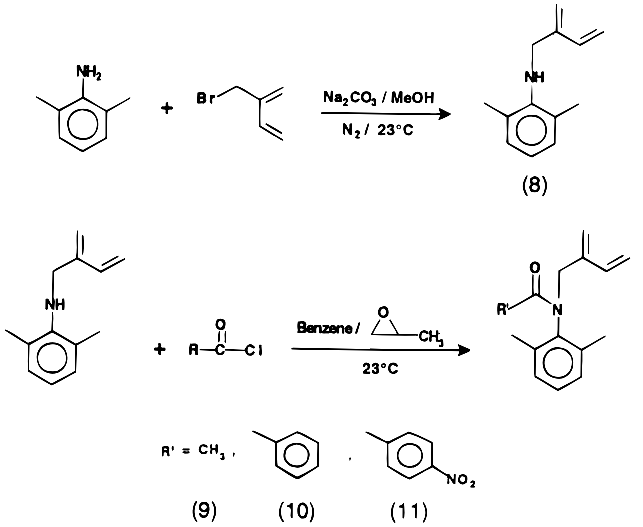
Based on these results, it was concluded that the structure of the amide substituent had a significant

Table 2. Relative Rates in Deuterated Chloroform at 23 °C



R	ID	k, mol/(L min) X 10^{-2}	RELATIVE RATE
CH_3CO--	(9)	1.27	0.54
p-$NO_2C_6H_4CO$--	(11)	1.88	0.79
H--	(8)	2.36	1.00
C_6H_5CO--	(10)	2.68	1.14

Scheme 2



effect on the reactivity of the 1,3-diene. Both electronic and steric effects of the pendant groups play a significant role on the reactivity of the 1,3-diene systems. The 1,3-diene group was affected by the electron-withdrawing effect of the carbonyl group since the acetyl group was less reactive than the unsubstituted 1,3-diene (0.54 to 1). However, the steric effects of the benzoyl group favor the cisoid conformation which enhances reactivity relative to the carbonyl electron-withdrawing effects seen for the acetyl group, thereby affording a more reactive 1,3-diene than even the unsubstituted 1,3-diene (1.14 to 1). It was further determined that electronic effects were also important since the *p*-nitrobenzoyl group decreased the reactivity relative to the unsubstituted benzoyl group; however, although the *p*-nitrobenzoyl group is more electron withdrawing than the acetyl group, its bulk enhanced the reactive cisoid diene conformation more relative to the latter group. This combined contribution of steric and electronic effects made the benzoyl-containing amide-1,3-diene more reactive than the *N*-unsubstituted 1,3-diene, even though the benzoyl group is generally regarded as an electron-withdrawing group.

Poly(amide imide)s. A series of poly(amide imide)s, (PAI)s, were prepared by the Diels–Alder reaction of stoichiometric quantities of the bis(amide-1,3-diene) with bismaleimides in 1,1,2,2-tetrachloroethane containing hydroquinone (Scheme 3). The polymerizations were performed at room temperature for approximately 12 h with a subsequent increase in temperature to 100–130 °C, which was maintained for the duration of the reaction time (15–30 h).

The PAIs were isolated as either a powder or a fibrous material. The inherent viscosities of polymers prepared from bis(4-maleimidylphenyl)methane (BMPM) ranged from 0.48 to 0.81 dL/g (Table 3). A series of polymers prepared from 1,4-[*N*,*N*′-bis(butadienyl-2-methyl)dibenzamido]-2,3,5,6-tetramethylbenzene (**2**) and 4,4′-bis(maleimidylphenyl)methane (BMPM), bis(3-maleimidyl phenyl)sulfone (BMPS), 1,2-dimaleimidylbenzene (1,2-DMB), and 1,4–dimaleimidylbenzene (1,4-DMB) had inherent viscosities of 0.21–0.81 dL/g (Table 3).

The polymers were soluble in DMAc and chlorinated solvents (Table 3). An exception was the polymer prepared with the 4–aminophenyl amide group, which was insoluble in all organic solvents. This insolubility was observed to be inversely related to the solution temperature: increasing the temperature of the solution caused the polymer to precipitate, while upon cooling the polymer redissolved.

^{1}H NMR Analysis of Model Compounds and Polymer. The ^{1}H NMR spectra of the bis(amine-1,3-diene) and the bis(amide-1,3-diene) monomers, the corresponding model compounds from the Diels–Alder reaction with *N*-phenylmaleimide, and the correspond-

Scheme 3

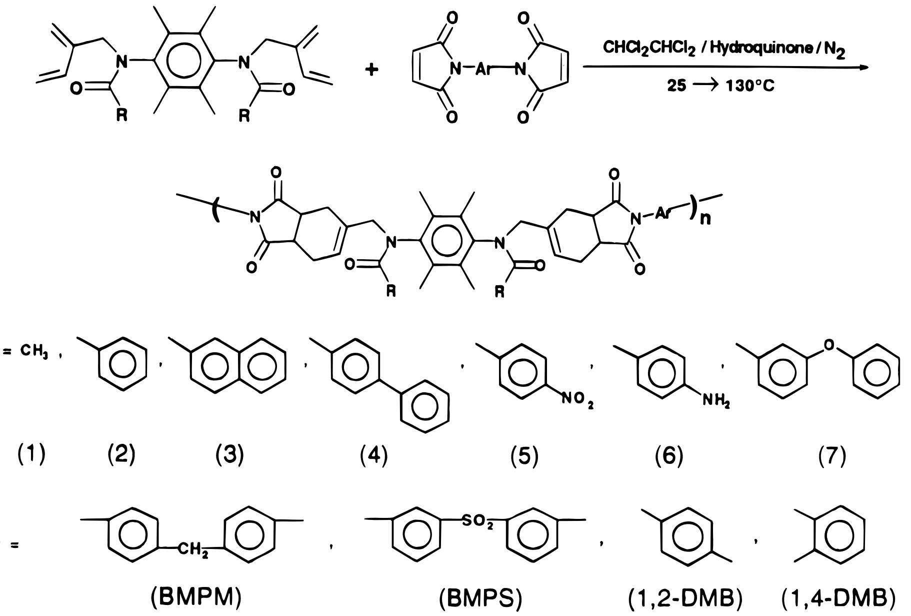
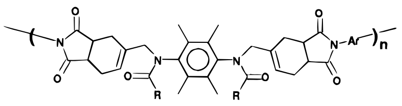
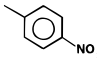
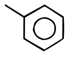
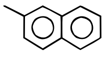
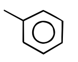
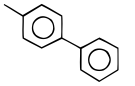
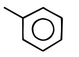
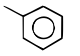
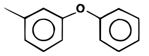
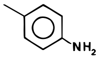


Table 3. Poly(amide imide) Characterization



R	Ar¹	η_{inh},² dL/g	SOLUBILITY³ A	B	C	D
	BMPM	0.52⁴	S	P	I	S
	1,2-DMB	0.26	S	S	I	S
	BMPM	0.64	S	S	I	S
	1,4-DMB	0.21	S	S	I	S
CH_3	BMPM	0.55	S	S	I	S
CH_3	BMPS	0.24	S	S	I	S
	BMPM	0.63	S	S	I	S
	BMPM	0.81	S	S	I	S
	BMPS	0.22	S	S	I	S
	BMPM	0.48	S	S	I	S
	BMPM	---	I	I	I	I

1. BMPM: 4,4'-bis(maleimidylphenyl)methane, BMPS: 3,3'-bis(maleimidylphenyl) sulfone, 1,2-DMB: 1,2-dimaleimidylbenzene, 1,4-DMB: 1,4-dimaleimidylbenzene
2. Inherent viscosities determined on 0.3% chloroform solutions at 30°C.
3. Solubility determined on ~0.1g/1 mL of solvent. I: Insoluble, P: Partly Soluble, S: Soluble. A: 1,1,2,2-Tetrachloroethane, B: Chloroform, C: Benzene, D: N,N-Dimethylacetamide.
4. Inherent viscosity determined on 0.3% dimethylformamide solution at 30°C.

ing polymers with bis(4-maleimidyl)methane are shown in Figures 1 and 2. From a comparison of the spectra of **2** and the precursor bis(amine-1,3-diene), several changes were observed after the addition of the pendant benzoyl moiety. The protons attributed to the methyl protons on the phenyl ring shifted upfield to 1.92 ppm as compared to 2.24 ppm for that of the precursor bis(amine-1,3-diene), which implies that these protons are located in the shielding zone of the amide carbonyl. The protons associated with the methylene group located between the 1,3-butadienyl and amine functionalities shifted downfield to 4.48 ppm as compared to 3.60 ppm for the precursor bis(amine-1,3-diene). This indicates that the methylene group is situated in the deshielding zone of the amide carbonyl. The absorption pattern attributed to the methylene protons located on the C-1 and C-4 positions of the 1,3-butadienyl system became more complex after the introduction of the amide functionality (**2**). The vinylic proton located at the C-3 position of the 1,3-diene system shifted upfield from 6.45 ppm for the bis(amine-1,3-diene) to 6.25 ppm for **2** in that this proton is in the shielding zone of the amide carbonyl. Similar results were observed for all the other bis(amide-1,3-diene) monomers prepared in this study.

The formation of a cyclohexene ring system by Diels–Alder reactions of bis(amine-1,3-diene) and bis(amide-1,3-diene) (**2**), respectively, with *N*-phenylmaleimide is evident from the corresponding ^{1}H NMR spectra. The protons attributed to the methyl groups attached to the phenyl ring for the bis(amine-1,3-diene) appeared unaffected after the conversion to the Diels–Alder adduct. The multiplet at 3.23–3.42 ppm was attributed to the methylene protons located at the C-4 and C-7 positions of the isoindole type system. The vinylic proton at the C-6 position appear as a broad singlet at 6.00 ppm for the model compound.

Comparing the respective ^{1}H NMR spectra of the cycloadducts of the precursor bis(amine-1,3-diene) and bis(amide-1,3-diene), the splitting pattern of the protons assigned to the isoindole system is more complex. After introduction of the amide functionality, these protons could reside in both the shielding and deshielding zones of the amide carbonyl. The vinylic proton located at the C-6 position of the isoindole type system shifted upfield to 5.63–5.79 ppm and appear as a doublet as compared to the model compound of the precursor bis(amine-1,3-diene), implying that this proton is located in the shielding zone of the amide carbonyl. Also, the protons attributed to the methyl groups attached to the phenyl ring of the model compound of bis(amide-1,3-diene appear as a multiplet compared to that of monomer. While the peak is centered at 1.95 ppm, approximately 25% of this absorption appears at 1.82 ppm and ~25% appears at 2.10 ppm, implying that these protons are located in the shielding and deshielding zones of the amide carbonyl, respectively.

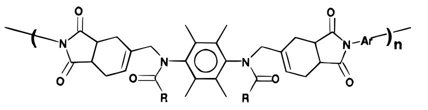
Similar results were observed for the ^{1}H NMR spectra of the respective polymers of the bis(1,3-diene)s. The spectra of the model compound and polymer from the bis(amine-1,3-diene) monomer were quite similar and differed only in the absorption attributed to the proton associated with the methylene group form the bis(4-maleimidyl)methane monomer. However, the spectrum of the polymer from bis(amide-1,3-diene) became even more complex compared to that obtained for the model compound. The vinylic proton located at the C-6 position of the isoindole type system of the polymer appears as a quartet at 5.60–6.09 ppm compared to the doublet at 5.63–5.79 ppm observed for the model compound. The downfield shift suggests that this proton exists in the deshielding region of the amide carbonyl. The model compounds and polymers prepared form the other bis(amide-1,3-diene)s afforded similar results.

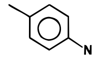
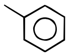
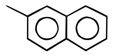
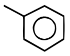
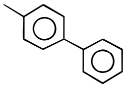
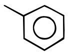
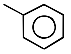
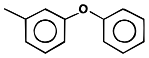
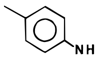
Polymer Characterization. The glass transition temperature (T_g) of the polymers prepared from BMPM ranged from 202–269 °C and were dependent on the amide group (Table 4). The order of increasing T_g was 2-phenoxybenzoyl < benzoyl < 4-phenylbenzoyl < acetyl < 2-naphthoyl < 4-nitrobenzoyl. The polymer prepared from the 4-aminobenzoyl-containing bis(amide-1,3-diene) and BMPM did not exhibit a T_g. The T_g for the poly(amide imide)s prepared from 1,4-[*N*,*N*′-bis(butadienyl-2-methyl)dibenzamido]-2,3,5,6-tetramethylbenzene (**2**) and bismaleimides ranged from 208 to 236 °C, with the order of increasing T_g being BMPS < BMPM < 1,4-DMB < 1,2-DMB (Table 4). The polymer prepared from BMPS exhibited a lower T_g than the BMPM-containing PAIs, presumably due to its lower molecular weight.

Polymer powders examined by TGA exhibited 10% weight loss from 318 to 350 °C in air and from 324 to 381 °C in helium (Table 4). These results are similar to the PAIs previously reported.[17]

The films cast from chloroform of the polymers prepared from the bis(amide-1,3-diene)s and BMPM were flexible and creasable and only lightly colored. A brittle film was obtained from the naphthoyl system, even though the inherent viscosity was comparable to that of the 4-phenylbenzoyl system. This may be due to the more rigid nature of the 2-naphthoyl pendant group. The 2–phenoxybenzoyl system also provided a

Table 4. Poly(amide imide) Thermal Characterization



R	Ar[1]	T_g,[2] °C	TGA 10% WT. LOSS[3], °C	
			AIR	N_2
	BMPM	260	335	359
	1,2-DMB	236	323	335
	BMPM	222	342	365
	1,4-DMB	220	318	334
CH_3	BMPM	219	330	332
CH_3	BMPS	218	356	316
	BMPM	218	333	371
	BMPM	215	321	348
	BMPS	208	350	357
	BMPM	202	318	381
	BMPM	---	338	324

1. BMPM: 4,4'-bis(maleimidylphenyl)methane, BMPS: 3,3'-bis(maleimidylphenyl) sulfone, 1,2-DMB: 1,2-dimaleimidylbenzene, 1,4-DMB: 1,4-dimaleimidylbenzene
2. Glass transition temperatures determined by DSC at a heating rate of 20°C/min.
3. Dynamic TGA determined on powdered samples at a heating rate of 2.5°C/min.

brittle film which may be due to either the low molecular weight or to the bulkiness of the amide group.

The polymers prepared from BMPM and the bis(amide-1,3-diene)s were examined for liquid crystalline characteristics by polarized light microscopy. No detectable liquid crystalline textures were observed at temperatures up to 300 °C for any of these materials. Presumably there is more flexibility in the polymer backbone than anticipated, thus preventing the formation of liquid crystalline mesophases.

The PAIA prepared from 1,4-[*N*,*N*′-bis(butadienyl-2-methyl)dibenzamido]-2,3,5,6-tetramethylbenzene (**2**) and BMPM was examined by dynamic mechanical analysis from −150 to +220 °C under a nitrogen atmosphere. The modulus was 8.48×10^9 dyn/cm^2 (123 ksi) at 23 °C. Two transitions were observed for this material. The onset of the first transition was 129 °C with values for the loss tangent (tan δ), storage modulus (E'), and loss modulus (E'') of 7.7×10^{-2}, 8.63×10^9 dyn/cm^2 (125 ksi), and 6.64×10^8 dyn/cm^2 (9.6 ksi), respectively. The second transition occurred at 193 °C with values for the loss tangent (tan δ), storage modulus (E'), and loss modulus (E'') of 4.52×10^{-1}, 2.12×10^9 dyn/cm^2 (30.7 ksi), and 9.57×10^8 dyn/cm^2 (13.9 ksi), respectively.

Conclusions

A series of new poly(amide imide)s were prepared by the Diels−Alder reaction between several new bis(amide-1,3-diene)s and bismaleimides. The polymers exhibited good solubility in organic solvents and moderate thermal stability in air and helium. Lightly colored, flexible and creasable films were obtained for several of the polymers by solution casting from cholorform.

Acknowledgment. The authors wish to thank NASA Langley Research Center for their financial support of this research (NAG-1-672), Dr. Terry Bluhm at Xerox (Canada) for his analysis of the polymers for potential liquid crystallinity, and Dr. Thomas Haas at Virginia Commonwealth University for his mechanical analysis of the poly(amide imide) film.

References and Notes

(1) Cassidy, P. E. *Thermally Stable Polymers: Synthesis and Properties*; Marcel Dekker: New York, 1980.
(2) Sroog, C. E. *Prog. Polym. Sci.* **1991**, *16*, 561.
(3) Harries, F. W.; Feld, W. A.; Lavier, L. H. *J. Polym. Sci., Polym. Lett. Ed.* **1975**, *13*, 283.
(4) Hergenrother, P. M.; Wakelyn, N. T.; Havens, S. J. *J. Polym. Sci., Polym. Chem. Ed.* **1987**, 25, 1093.
(5) Bailey, W. J. In Diels−Alder *Polymerization-Step Growth Polymerization*; Solomon, D. H., Ed.: Marcel Dekker: New York, 1972; Vol. 3, pp 279−332.
(6) Stille, J. K.; Plummer, L. *J. Org. Chem.* **1961**, *26*, 4026.
(7) Reeder, J. E. (to E. I. du Pont de Nemours and Co.) U.S. Patent 3,344,071, Aug 1, 1967; *Chem. Abstr.* **1967**, *67*, 74026t.
(8) Kraiman, E. A. (to Union Carbide Corp.) U.S. Patent 2,890,-206, June 9, 1959; *Chem. Abstr.* **1959**, *53*, 17572e.
(9) Kraiman, E. A. *Macromol. Synth.* **1966**, *2*, 110.
(10) Chow, S. W. (to Union Carbide Corp.) U.S. Patent 3,074,-915, Jan 22, 1963; *Chem. Abstr.* **1963**, *58*, 10358a.
(11) Tan, L. S. *J. Polym. Sci., Polym. Chem. Ed.* **1987**, *25*, 3159.
(12) Tan, L. S., Soloski, E. J.; Arnold, F. E. In ACS Symp. Ser. 367; Dickie, R. A., Labana, S. S., Bauer, R. S., Eds.; American Chemical Society: Washington, DC, 1988; pp 349−365.
(13) Ottenbrite, R. M.; Yoshimatsu, A.; Smith, J. G., Jr. *Polym. Prepr.* **1987**, *28* (2), 280.
(14) Ottenbrite, R. M.; Smith, J. G., Jr. *Polym. Prepr.* **1988**, *29* (1), 263.
(15) Ottenbrite, R. M.; Yoshimatsu, A.; Smith, J. G., Jr. *Polym. Adv. Tech.* **1990**, *1*, 117.
(16) Ottenbrite, R. M.; Smith, J. G., Jr. *Polym. Prepr.* **1989**, *30* (1), 199.
(17) Ottenbrite, R. M.; Smith, J. G., Jr. *Polym. Prepr.* **1989**, *30* (1), 213; *Polym. Adv. Tech.* **1992**, *3*, 373.
(18) Detar, D. F.; Hlynsky, A. J. *Am. Chem. Soc.* **1955**, *77*, 4411.
(19) Kuhn, W. E. *Organic Syntheses*; John Wiley and Sons: New York, 1943; Collect. Vol. 2, p 447.

MA9464332