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Novel Synthesis of Aromatic Polyamides by Palladium-Catalyzed Polycondensation of Aromatic Dibromides, Aromatic Diamines, and Carbon Monoxide

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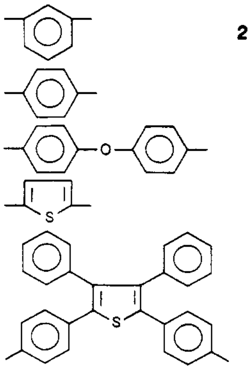
ABSTRACT: A novel and facile method for the synthesis of aramids has been developed by the carbonylation polymerization of aromatic dibromides and aromatic diamines with carbon monoxide in the presence of a palladium catalyst. A variety of aramids having inherent viscosities between 0.2 and 0.8 dL·g^{-1} were prepared readily under ordinary pressure. The effects of reaction variables such as kinds and amounts of catalyst and acid acceptor, reaction medium, and reaction temperature and time on the polycondensation were discussed in detail.

Introduction

Synthetic organometallic chemistry has made rapid progress in the past two decades, and by using organometallic catalysts many highly reactive and highly selective reactions have been achieved. In the field of synthetic polymer chemistry, however, few works have been reported to date on the synthesis of condensation polymers using organometallic catalysts. Recently Yamamoto et al.[1] reported the nickel-catalyzed C–C coupling polymerization of the Grignard reagent of *p*-dibromobenzene yielding poly-*p*-phenylene. The use of palladium catalysts in the synthesis of poly(arylene–acetylenes) through the C–C coupling polymerization of aromatic dibromides with aromatic diacetylenes was described independently by Havens and Hergenrother[2] and by Trumbo and Marvel.[3] Murahashi et al.[4] presented the ruthenium-catalyzed polycondensation of dinitriles with diamines leading to aliphatic polyamides.

It has been known for many years that the palladium-catalyzed reaction of aromatic bromides, aromatic amines, and carbon monoxide yielded readily aromatic amides.[5] It was thought that this route may constitute another promising polymer-forming reaction. Therefore, the palladium-catalyzed carbonylation was extended to that with bifunctional monomer pairs. We report herein a novel successful synthesis of aromatic polyamides (aramids) by the polycondensation of aromatic dibromides and aromatic diamines with carbon monoxide in the presence of palladium catalysts (eq 1).

$$\underset{1}{\mathrm{BrArBr}} + \mathrm{CO} + \underset{2}{\mathrm{H_2NAr'NH_2}} \xrightarrow[\text{solvent}]{\text{Pd cat. tert amine}} \underset{3}{[\text{-}\mathrm{C(O)ArC(O)NHAr'NH}]_n\text{-}} \quad (1)$$



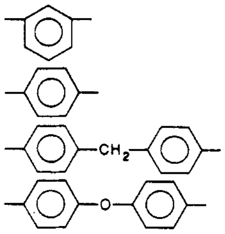
1a, Ar =

b, Ar =

c, Ar =

d, Ar =

e, Ar =



2a, Ar′ =

b, Ar′ =

c, Ar′ =

d, Ar′ =

Experimental Section

Materials. *m*-Dibromobenzene (**1a**), 2,5-dibromothiophene (**1d**), *m*-phenylenediamine (**2a**), *p*-phenylenediamine (**2b**), tributylamine, and 1,8-diazabicyclo[5.4.0]-7-undecene (DBU) were purified by vacuum distillation. *p*-Dibromobenzene (**1b**), bis(4-bromophenyl) ether (**1c**), bis(4-aminophenyl)methane (**2c**), and 1,4-diazabicyclo[2.2.2]octane (DABCO) were purified by recrystallization from ethanol. Bis(4-aminophenyl) ether (2d) was recrystallized from tetrahydrofuran. 2,5-Bis(4-bromophenyl)-3,4-diphenylthiophene (**1e**) was synthesized by the bromination of tetraphenylthiophene, which was prepared from benzyl chloride and sulfur,[6] with bromine in dichloromethane, and purified by recrystallization from dichloroethane, mp 250–252 °C (lit.[7] 242 °C). Anal. Calcd for $C_{28}H_{18}Br_2S$: C, 61.56; H, 3.32; Br, 29.25; S, 5.87. Found: C, 61.55; H, 3.26; Br, 29.48; S, 5.84.

Palladium acetate [$Pd(OAc)_2$] and palladium chloride ($PdCl_2$) were obtained commercially and used without further purification. Dichlorobis(triphenylphosphine)palladium(II) [$PdCl_2(PPh_3)_2$],[8] dichlorobis(benzonitrile)palladium(II) [$PdCl_2(PhCN)_2$],[9] and tetrakis(triphenylphosphine) palladium(0) [$Pd(PPh_3)_4$][10] were prepared by the reported procedure.

Triphenylphosphine (PPh_3) was purified by recrystallization from hexane. Lithium chloride was dried at 150 °C in vacuo. All solvents such as pyridine, *N*,*N*-dimethylformamide (DMF), *N*,*N*-dimethylacetamide (DMAc), *N*-methyl-2-pyrrolidone (NMP), dimethyl sulfoxide (DMSO), hexamethylphosphoramide (HMPA), and 1,3-dimethyl-2-imidazolidone (DMI) were purified by vacuum distillation.

Polymerization. Polymer 3ad from 1a and 2d. In a three-necked flask equipped with a stirrer, a carbon monoxide inlet, and a reflux condenser were placed 0.5898 g (2.5 mmol) of **1a**, 0.5106 g (2.55 mmol) of **2d**, 0.1053 g (0.15 mmol) of $PdCl_2(PPh_3)_2$, 0.0787 g (0.30 mmol) of PPh_3, and 7.5 mL of DMAc. The flask was purged several times with carbon monoxide and warmed with stirring at 115 °C in an oil bath. To the mixture 0.9 mL (6 mmol) of DBU was added with a syringe. The reaction mixture was stirred at 115 °C until the consumption of carbon monoxide stopped. The reaction solution was diluted with 20 mL of DMAc and poured into 400 mL of methanol. The precipitated polymer was filtered, washed successively with hot methanol and chloroform, and dried at room temperature in vacuo. The yield was 0.961 g (110%). The inherent viscosity of the polymer in concentrated sulfuric acid was 0.55 dL·g^{-1}, measured at a concentration of 0.5 g·dL^{-1} at 30 °C. The IR spectrum (film) exhibited absorptions at 3300 cm^{-1} (N—H) and 1650 cm^{-1} (C=O). Anal. Calcd for $(C_{20}H_{14}N_2O_3)_n$: C, 72.72; H, 4.27; N, 8.48. Found: C, 70.24; H, 4.20; N, 8.67; Br, 0.83.

Other polymers were prepared by analogous procedures.

Measurements. IR spectra were recorded on a Hitachi EP-G3 spectrophotometer. Thermogravimetry (TG) was performed with a Shimadzu TGA-30M thermal analyzer. Number-average molecular weight (M_n) and weight-average molecular weight (M_w) were determined by means of gel permeation chromatography (GPC) on the basis of a polystyrene calibration on a JASCO HPLC BIP-I apparatus (column, Shodex GPC AD-80M/S polystyrene gel; eluent, DMF containing 0.01 mol·L^{-1} of lithium bromide).

Results and Discussion

The carbonylation polymerization of *m*-dibromobenzene (**1a**) and bis(4-aminophenyl) ether (**2d**) with carbon monoxide in the presence of a palladium catalyst and a

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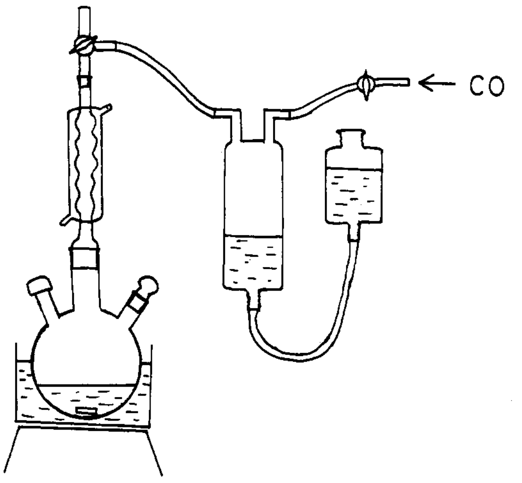

Figure 1. Polymerization apparatus.

Table I
Synthesis of Aramid 3ad with Various Tertiary Amines[a]

tert amine	reactn time, h	polym η_{inh},[b] dL·g^{-1}
tri-*n*-butylamine	22.5	0.08
triethylenediamine	2.5	0.17
4-(dimethylamino)pyridine	3	0.14
DBU	2	0.33

[a] Polymerization was carried out with 2.5 mmol of **1a**, 2.5 mmol of **2d**, 5.5 mmol of the tertiary amine, 0.17 mmol of $PdCl_2(PPh_3)_2$, and 0.33 mmol of PPh_3 in 10 mL of DMAc at 100 °C under carbon monoxide. [b] Measured at a concentration of 0.5 g·dL^{-1} in concentrated sulfuric acid at 30 °C.

tertiary amine as a hydrogen bromide acceptor in an organic solvent leading to aramid **3ad** was investigated in detail. An ordinary catalytic reduction apparatus with a gas burette was used to carry out the polymerization (Figure 1). The polymerization was continued with stirring the reaction mixture under ordinary pressure until the consumption of carbon monoxide in the gas burette stopped.

During the polymerization, we often encountered the problem of palladium black separation as it lacks catalytic activity and remains as a contaminant in the resulting polymer. This problem was effectively suppressed by the addition of a 4-fold excess of PPh_3 to a palladium catalyst by mole to the reaction mixture in addition to already coordinated PPh_3, and consequently the reaction mixture remained in homogeneous solution throughout the polymerization.

Aromatic amines did not react with aromatic bromides and carbon monoxide in the absence of a tertiary amine that was a strong enough base to neutralize the hydrogen bromide formed in the carbonylation.[5] Accordingly, the effect of tertiary amines on the polymerization was examined (Table I). Among four tertiary amines used, DBU was the most effective base judging from the shortest reaction time and the highest viscosity value of the resulting aramid. Compared to the other tertiary amines used, DBU swells the aramid apart from acting as an acid acceptor, thereby enhancing the propagation reaction.

Figure 2 shows the effect of amount of DBU on the inherent viscosity of the aramid. A minimum of 2 equiv of the tertiary amine based on the bifunctional monomers is required for the polymerization. The highest inherent viscosity was obtained when a slight excess of DBU was used.

The influence of reaction temperature on the inherent viscosity of the aramid was examined between 75 and 150 °C (Figure 3). The polymerization was found to be highly dependent on temperature and the highest viscosity was attained at 115 °C. At a lower temperature of 75 °C, the reaction rate was so slow judging from the uptake of carbon monoxide that the polymer remained in low molecular weight. The apparent reaction rate should increase rapidly with increasing temperature; however, the volume of carbon monoxide dissolved in the reaction mixture decreased gradually. Consequently, at a temperature higher than 150 °C, the actual reaction rate was too slow to obtain a high molecular weight aramid.

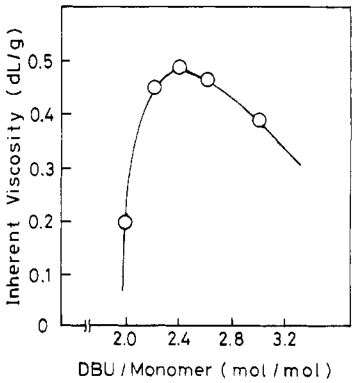

Figure 2. Effect of amount of DBU on inherent viscosity of aramid **3ad** formed by the polycondensation of **1a** with **2d** under carbon monoxide at 115 °C for 1.5–4 h. Monomers, 2.5 mmol; $PdCl_2(PPh_3)_2$, 0.17 mmol; PPh_3, 0.33 mmol; DMAc, 7.5 mL.

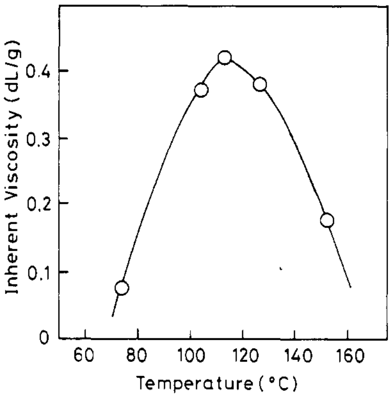

Figure 3. Effect of reaction temperature on inherent viscosity of aramid **3ad** formed by the polycondensation of **1a** with **2d** under carbon monoxide for 1.5–7 h. Monomers, 2.5 mmol; DBU, 5.5 mmol; $PdCl_2(PPh_3)_2$, 0.17 mmol; PPh_3, 0.33 mmol; DMAc, 10 mL.

Table II
Synthesis of Aramid 3ad in Various Solvents[a]

solvent	reactn time, h	polym η_{inh},[b] dL·g^{-1}	solvent	reactn time, h	polym η_{inh},[b] dL·g^{-1}
DMF	2.0	0.44	HMPA	4.0	0.32
DMAc	1.5	0.43	DMSO	1.5	0.42
NMP	0.8	0.27	pyridine	4.0	0.44
DMI	1.0	0.21			

[a] Polymerization was carried out with 2.5 mmol of **1a**, 2.5 mmol of **2d**, 5.5 mmol of DBU, 0.17 mmol of $PdCl_2(PPh_3)_2$, and 0.33 mmol of PPh_3 in 10 mL of the solvent at 115 °C under carbon monoxide. [b] See footnote *b* of Table I.

Table II summarizes the solvent effect on the inherent viscosity of the aramid. Among these polar solvents, most of which are good solvents for the aramid, DMF, DMAc, DMSO, and pyridine produced the polymer with the higher inherent viscosity. Taking into account the reaction time based on the consumption rate of carbon monoxide, DMAc and DMSO were the most suitable solvents. Therefore, subsequent polymerizations were carried out by using DMAc as the reaction medium.

Table III
Synthesis of Aramid 3ad with Various Catalysts[a]

catalyst	reactn time, h	polym η_{inh},[b] dL·g^{-1}
$PdCl_2(PPh_3)_2/2PPh_3$	2.0	0.49
$Pd(PPh_3)_4$	1.2	0.49
$PdCl_2/4PPh_3$	2.0	0.44
$Pd(OAc)_2/4PPh_3$	2.0	0.47
$PdCl_2(PhCN)_2/4PPh_3$	2.0	0.45

[a] Polymerization was carried out with 2.5 mmol of **1a**, 2.5 mmol of **2d**, 6.0 mmol of DBU, and 0.17 mmol of the catalyst in 7.5 mL of DMAc at 115 °C under carbon monoxide. [b] See footnote *b* of Table I.

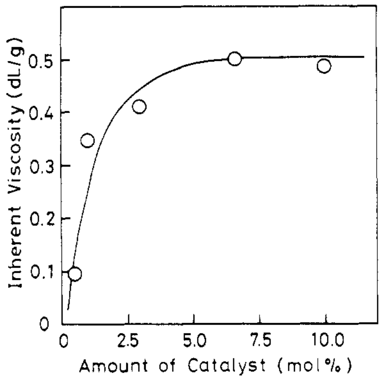

Figure 4. Effect of amount of $PdCl_2(PPh_3)_2$ on inherent viscosity of aramid **3ad** formed by the polycondensation of **1a** with **2d** under carbon monoxide at 115 °C for 1.5–7 h. Monomers, 2.5 mmol; DBU, 6.0 mmol; $PdCl_2(PPh_3)_2/PPh_3$, 1/2 (molar ratio); DMAc, 7.5 mL.

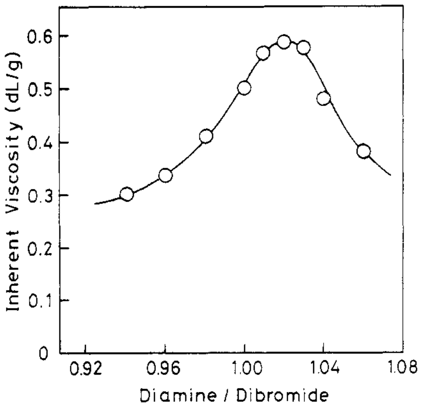

Figure 5. Effect of molar ratio of diamine **2d** to dibromide **1a** on inherent viscosity of aramid **3ad** by polycondensation under carbon monoxide at 115 °C for 2–4 h. Dibromide, 2.5 mmol; DBU, 6.0 mmol; $PdCl_2(PPh_3)_2$, 0.17 mmol; PPh_3, 0.33 mmol; DMAc, 7.5 mL.

Table III lists the catalytic effect of palladium compounds on the polymerization. These five palladium catalysts had almost the same effect, affording the aramid with inherent viscosities in the range 0.44–0.49 dL·g^{-1}. Figure 4 shows the influence of the amount of $PdCl_2(PPh_3)_2$ on the inherent viscosity of the polymer. To obtain the aramid having sufficiently high inherent viscosity, more than 5 mol % of the catalyst based on the monomers was required.

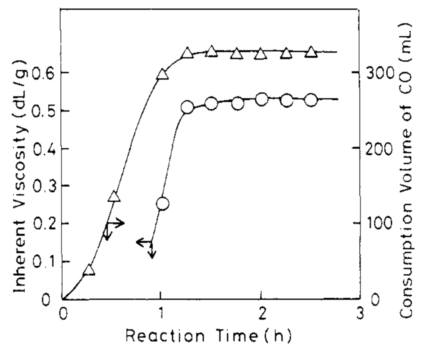

Figure 6. Time dependence of inherent viscosity of aramid **3ad** formed by the polycondensation of **1a** with **2d** under carbon monoxide at 115 °C. Monomers, 7.5 mmol; DBU, 18.0 mmol; $PdCl_2(PPh_3)_2$, 0.50 mmol; PPh_3, 1.0 mmol; DMAc, 22.5 mL.

Table IV
Inherent Viscosities of Various Aramids[a]

dibromide	diamine 2a	2b	2c	2d
1a	0.25	0.36	0.43	0.55
1b	0.43	0.30[b]	0.41[b]	0.61[b]
1c	0.46	0.60[b]	0.63	0.71[b]
1d	0.21	0.25	0.31	0.47
1e	0.49	0.81	0.62	0.78

[a] Polymerization was carried out with 2.5 mmol of the dibromide, 2.55 mmol of the diamine, 6.0 mmol of DBU, 0.15 mmol of $PdCl_2(PPh_3)_2$, and 0.30 mmol of PPh_3 in 7.5 mL of DMAc at 115 °C for 1.5–5 h under carbon monoxide. Inherent viscosity was measured at a concentration of 0.5 g·dL^{-1} in concentrated sulfuric acid at 30 °C. [b] To the polymerization mixture 0.38 g of lithium chloride was added.

Figure 5 gives the effect of molar ratio of the diamine to the dibromide on the inherent viscosity of the aramid. The highest viscosity was attained when a 2 mol % excess of the diamine to the dibromide was used. According to the results of the elemental analysis, the aramid had both bromine and amino groups on its terminals. Normally, for the preparation of the condensation polymers with the highest molecular weight, the condensing monomer components should be equimolar to each other. Therefore, it is difficult to explain the above result.

Figure 6 shows the time dependence on the inherent viscosity of the polymer and on the consumption of carbon monoxide. The polymerization proceeded rapidly at 115 °C in DMAc along with the rapid consumption of carbon monoxide, and was almost complete within 1.5 h.

The polymer thus obtained was confirmed to be the corresponding aramid **3ad** by means of infrared spectroscopy and elemental analysis. The IR spectrum exhibited absorptions at 3300 cm^{-1} (N—H) and 1650 cm^{-1} (C=O), which are the characteristic absorptions of amide bonds. The elemental analysis values were in good agreement to the calculated values with no trace of metallic ash. The thermal behavior of aramid **3ad** was compared with that of the aramid having the same chemical structure prepared by the conventional low-temperature solution polycondensation of isophthaloyl chloride with aromatic diamine **2d**. The thermogravimetry curves in air were found to be almost the same as each other. The molecular weight of aramid **3ad** having an inherent viscosity of 0.55 dL·g^{-1} was determined by means of GPC. The chromatogram indicated that the M_n and M_w values were 48 000 and 77 000, respectively, for standard polystyrene, and the ratio of M_w/M_n was 1.6.

A variety of aramids **3aa–ed** were successfully prepared from combinations of aromatic dibromides **1a–e** and aromatic diamines **2a–d** under the optimum reaction conditions obtained for aramid **3ad**. The results are summarized in Table IV. In the case of the polymerizations which proceeded with the precipitation of aramids, lithium chloride was added to the reaction solution to prevent the formation of polymer precipitates. However, the addition of an excess amount of lithium chloride resulted in the lowering of the inherent viscosity of aramids. Since lithium

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chloride could interact with the catalyst and the interaction might reduce the catalytic activity, lithium chloride should be used at an amount low enough to prevent precipitation except for aramid **3bd**.

All the aramids obtained had inherent viscosities in the range 0.2–0.8 $dL \cdot g^{-1}$. Since some of the aramids had poor solubility in the reaction media, they were obtained in relatively low viscosity values. It is noteworthy that the tetraphenylthiophene-containing aramids had better solubility in organic solvents, and thereby the inherent viscosities of the resulting aramids were 0.5–0.8 $dL \cdot g^{-1}$. These viscosity values were almost equal to those of the aramids prepared from 2,5-bis(4-chloroformylphenyl)-3,4-diphenylthiophene and aromatic diamines through low-temperature solution polycondensation.[11]

Thus, we have developed a novel and facile method for the synthesis of aramids from aromatic dibromides, aromatic diamines, and carbon monoxide through palladium-catalyzed polycondensation. Aramids are conventionally prepared by the polycondensation of aromatic diacids or acid chlorides with aromatic diamines. Generally, most of aromatic diacids and their acid chlorides are obtained with difficulty through many steps of reactions, whereas some of aromatic dibromides are synthesized simply by the bromination of aromatic compounds. (Exceptional examples are isophthaloyl and terephthaloyl chlorides which are commercially available.) Therefore, the present method had advantages over the conventional diacid chloride–diamine route due to ready availability of aromatic dibromides and is applicable to the synthesis of various types of aramids.

Registry No. (**1a**)(**2a**)(CO) (copolymer), 114492-48-7; (**1a**)(**2b**)(CO) (copolymer), 114492-49-8; (**1a**)(**2c**)(CO) (copolymer), 114492-50-1; (**1a**)(**2d**)(CO) (copolymer), 114492-47-6; (**1b**)(**2a**)(CO) (copolymer), 114492-51-2; (**1b**)(**2b**)(CO) (copolymer), 114492-52-3; (**1b**)(**2c**)(CO) (copolymer), 114492-53-4; (**1b**)(**2d**)(CO) (copolymer), 114492-54-5; (**1c**)(**2a**)(CO) (copolymer), 114492-55-6; (**1c**)(**2b**)(CO) (copolymer), 114504-80-2; (**1c**)(**2c**)(CO) (copolymer), 114492-56-7; (**1c**)(**2d**)(CO) (copolymer), 114492-57-8; (**1d**)(**2a**)(CO) (copolymer), 114492-58-9; (**1d**)(**2b**)(CO) (copolymer), 114492-59-0; (**1d**)(**2c**)(CO) (copolymer), 114492-60-3; (**1d**)(**2d**)(CO) (copolymer), 114492-61-4; (**1e**)(**2a**)(CO) (copolymer), 114492-62-5; (**1e**)(**2b**)(CO) (copolymer), 114492-63-6; (**1e**)(**2c**)(CO) (copolymer), 114492-64-7; (**1e**)(**2d**)(CO) (copolymer), 114532-24-0; $PdCl_2(PPh_3)_2$, 13965-03-2; PPh_3, 603-35-0; $Pd(PPh_3)_4$, 14221-01-3; $PdCl_2$, 7647-10-1; $Pd(OAc)_2$, 3375-31-3; $PdCl_2(PhCN)_2$, 14220-64-5.

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Synthesis and Characterization of 1,2-Cyclobutenedicarboxamides: Thermally Generated Polymers and Diels–Alder Adducts

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ABSTRACT: A series of model diamides were synthesized from mono- and disubstituted amines with the diacid chloride of cyclobutene-1,2-dicarboxylic acid. Yields ranged from 30 to 70%. Melting points of the purified diamides ranged from less than 23 °C for *N*-alkyl and *N,N*-dialkyl species to 204 °C for the *N*-phenyl model. Relative rates of thermolysis (by DSC) with maxima from 208–224 °C at 10 °C/min were dependent on the number and type of substituents and on intramolecular hydrogen bonding. Thermolysis products were Diels–Alder dimers for N-monosubstituted materials and for bulky tetrasubstituted models and spontaneously formed polymers for two tetrasubstituted models with at least one methyl group on each nitrogen. Thermal imidization of cycloadducts was possible in some cases with concomitant oxidation to tetrasubstituted aromatic diimides.

Introduction

2,3-Disubstituted cyclobutenes and their thermally generated butadiene derivatives undergo a rich variety of reactions. The cyclobutenes can behave as dienophiles in cycloaddition reactions with appropriate dienes and thermally ring-open to the corresponding substituted butadienes.[1,2] The resulting dienes in turn have been found to spontaneously dimerize and polymerize[3,4] and to react with dienophiles in typical [4 + 2] cycloadditions.[4] We are currently exploring these compounds for synthesis of polybutadienes and for curing of thermosetting polymers and composites. The latter application involves the incorporation of a relatively nonreactive functionality into tough composite matrix polymers for potential use as one-pot, thermally activated curing systems. The former provides a synthetic pathway to a unique family of 2,3-disubstituted poly-1,4-butadienes which may be converted to the head-to-head polyacrylamides not readily available by other synthetic routes.

We previously described our initial results on the thermal reactions of several model diamides and polyamides.[5] Of three derivatives with two or four nitrogen substitutents (**1**–**3**), only compound **2** spontaneously polymerized while the others cyclodimerized. In an effort to further understand the factors controlling the spontaneous reactions of the butadienes generated by thermal

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