this shift is -0.7 kcal for Ia and -2.0 kcal for Ib. These shifts were reduced to 0.0 for poly(vinylbenzophenone) and -0.7 for Ib when the spectra were recorded from their films, where all of the spectra are about 1–2 kcal lower than in organic glasses.

Quantum yields for the sensitized photoisomerization of *cis*- and *trans*-stilbene were measured in degassed benzene solutions using light of 366-nm wavelength. The results for the monomeric models have been reported elsewhere.[6] The results for the polymeric sensitizers are reported in Table III along with a summary of the monomer values. These results show that the polymers poly(vinylbenzophenone) and poly(β-naphthoylstyrene) sensitize the isomerization of stilbene with the same efficiency as do the corresponding models. However, poly(α-naphthoylstyrene) is less efficient than are its corresponding models in the case of the trans → cis process. Furthermore, the inefficiency for the α-naphthoyl polymer is related to the chain length of the polymer. Thus, when polystyrene of molecular weight 4700 was treated with α-naphthoyl chloride, the resultant polymer had a ϕ_t of 0.45 ± 0.01 while the polymer prepared by naphthoylation of a polystyrene with molecular weight 900 had ϕ_t of 0.49 ± 0.01.

The inefficiency of the α-naphthoylated polymers in sensitizing the trans → cis isomerization of stilbene could be explained on the basis of the steric requirements of the α-naphthoyl group. Such steric requirements could force the polymer into a configuration which would bury the internal chromophores and make them inaccessible to acceptor molecules. However, ϕ_c is normal for poly(α-naphthoylstyrene) and this implies that all of the excitation energy in this polymer is available for sensitization. Thus, it appears that the inefficiency in ϕ_t must be due to an induced inefficiency in the use of the excitation energy by the sensitized molecule of *trans*-stilbene. We believe this is the result of the positive volume of activation noted by Fischer[4] for the trans → cis process. Accordingly we envision the excited *trans*-stilbene molecules to be confined for a time in a polymeric cage which restricts their rotation. Thus, some of the excited stilbene molecules would decay to the ground state before proceeding to the twisted triplet, which is responsible for isomerization.[4] The fact that ϕ_c is not lower for poly(α-naphthoylstyrene) may be explained by the lack of a volume of activation for the cis → trans process.[4] It is believed that this explanation is more than just a local visocisty effect since the β-naphthoyl polymer would also be expected to show such an effect.

Aminimides. VIII.[1a] Synthesis and Homo- and Copolymerization Studies of 1,1,1-Trimethylacrylylhydrazinium Chloride and 1,1,1-Trimethylmethacrylylhydrazinium Chloride[1b]

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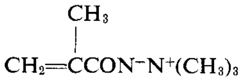
ABSTRACT: The monomers 1,1,1-trimethylacrylylhydrazinium chloride (II) and 1,1,1-trimethylmethacrylylhydrazinium chloride (III) were synthesized and shown to readily homo- and copolymerize with a variety of other vinyl monomers to produce copolymers containing pendent quaternary residues ($\text{-CONHNR}_3^+\text{X}^-$). The resultant polymers were treated with base to provide "reactive polymers" with pendent aminimide groups ($\text{CON}^-\text{N}^+\text{R}_3$). Since molecules with aminimide residues suffer a carbon–nitrogen migration reaction on heating, the aforesaid aminimide polymers were thermolyzed both in solution and the solid phase to provide unique, "reactive polymers" with pendent secondary or tertiary isocyanate groups. The reactivity ratios of each monomer (M_1) with styrene (M_2) were determined: monomer II, $r_1 = 0.46$, $r_2 = 0.58$; monomer III, $r_1 = 0.23$, $r_2 = 0.51$. The Alfrey–Price Q and e values were also calculated: $Q = 0.69$, $e = 0.34$ and $Q = 0.61$, $e = 0.66$, respectively.

Studies in several laboratories have shown that both aliphatic and aromatic compounds with ammonium acylimine residues of the type $\text{-CON}^-\text{N}^+\text{R}_3$ suffer a carbon–nitrogen migration reaction during pyrolysis,[2–4] yielding tertiary amines and isocyanates. In a prior publication,[1b] we described the preparation and polymerization properties of trimethylammonium-*N*-methacryloylimine (I, trimethylamine methacrylimide). The cited work demonstrated that monomers such as I



$$\text{CH}_2{=}\overset{\text{CH}_3}{\overset{|}{\text{C}}}\text{CON}^-\text{N}^+(\text{CH}_3)_3$$

I

are highly useful for preparing a wide variety of reactive polymers.

The present work was undertaken to prepare and to study some of the homo- and copolymerization characteristics of 1,1,1-trimethylacrylylhydrazinium chloride

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(1) (a) Presented in part to the Polymer Division at the 2nd Central Regional Meeting of the American Chemical Society, Columbus, Ohio, June 5, 1970; (b) for paper IV in this series, see B. M. Culbertson and R. C. Slagel, *J. Polym. Sci., Part A-1*, **6**, 363 (1968).

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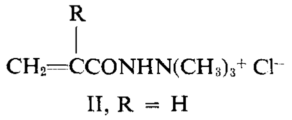
(II) and 1,1,1-trimethylmethacrylylhydrazinium chloride (III) and to compare the polymerization behavior of monomers II and III with I.



$$CH_2{=}\overset{R}{\overset{|}{C}}CONHN(CH_3)_3^+\ Cl^-$$

II, R = H
III, R = CH$_3$

Since molecules with residues of the type $-CONH-NR_3^+X^-$ may be treated with base to obtain compounds with the aminimide moiety ($-CON^-N^+R_3$),[2-4] it is readily apparent that monomers such as II and III should also have utility in the preparation of reactive polymers with pendent quaternary, aminimide, or isocyanate groups.

Experimental Section

The nmr spectra were obtained on a Varian A-60A spectrometer using tetramethylsilane as an internal standard, except with deuterium oxide as a solvent where 3-trimethylsilyl-1-propanesulfonic acid was used as a standard. The infrared spectra were recorded on a Perkin-Elmer 237B grating spectrophotometer. The melting points are uncorrected. Elemental analyses were determined by Huffman Laboratories, Inc., Wheatridge, Colo. Differential thermal and thermogravimetric analyses were obtained on the Du Pont 900 DTA and 950 TGA units, under nitrogen at a heating rate of 5°/min. Gel permeation chromatography (gpc) results were obtained on a Waters Model 200 unit using tetrahydrofuran solvent at room temperature and 4-ft columns of 10^6, 5×10^4, 10^3, 250, and 60 Å porosity Styragel resins. Inherent viscosities (η_{inh}) were determined at 30° using 0.5 g of polymer/100 ml of solvent. The thin layer chromatography (tlc) method employed silica gel coated plates, methanol solvent, and I_2 developer.

The basic ion exchange resin used was prepared from Fischer Scientific's Rexyn 201-resin. The resin, as received from Fisher, was treated with aqueous potassium hydroxide, washed with water until washings were neutral, and washed several times with the same solvent used in the ion exchange work, *i.e.*, acetone, methanol, tetrahydrofuran, or *N*,*N*-dimethylformamide. The expression wet acetone, wet methanol, etc., means the solvent used contained *ca.* 5% by weight of water.

The per cent isocyanate determinations were accomplished in the following manner. A polymer sample of known weight was treated in solution with an excess of alkylamine. After reaction at room temperature for a few minutes, during which time the amine reacted with the isocyanate moiety, the excess amine was titrated with a standard HCl solution, using bromocresol green indicator. Knowing the weight of polymer used, equivalents of amine added, and equivalents of HCl used, the weight per cent of NCO on the polymer backbone was calculated.

I. Monomers. 1,1,1-Trimethylacrylylhydrazinium Chloride (II). Methyl acrylate, 344 g (4.0 mol), was added with stirring to a 3-l. round-bottomed flask containing 900 ml of deionized water and 240 g (4.0 mol) of unsymmetrical dimethylhydrazine. The considerable exotherm was controlled by reflux condensers. After stirring for 12 hr the solution was evaporated to a pale yellow solid which was recrystallized from acetone–methanol to give a 437 g (92%) yield of 1,1-dimethylpyrazolinium 3-oxide (**1**), mp 89.5–90.5° (lit.[5] mp 90.5–91°). The carbonyl absorption in the infrared spectrum at 1585 cm^{-1} was consistent with reported[6] absorption for cyclic aminimides. The nmr spectrum (DMSO-*d*) showed a singlet at 6.85 ppm, triplets at 7.39 and 6.20 ppm in a ratio of 3:1:1, respectively.

Compound **1**, 114 g (1.0 mol), was placed in a flask and heated *in vacuo* at 250°. The material distilled at 120° (1.4 mm) and solidified upon cooling to afford a 70 g (62%) yield of 1,1-dimethyl-2-acrylhydrazine (**2**), mp 84° (lit.[7] mp 84°). Ir analysis showed absorption bands at 3220, 1675, 1640, and 1555 cm^{-1}.

A 2-l. glass-lined Parr bomb was charged with 650 ml of methyl alcohol, 100 g of **2**, and *ca.* 100 ppm of 2,2-diphenyl-1-picrylhydrazyl. Methyl chloride was charged until the bomb pressure was 55 psi. The bomb was heated overnight at 70°, cooled, and the volume reduced to *ca.* 200 ml. The product was precipitated with chloroform, washed with ether, and dried to obtain a 73 g (52%) yield of **3** (section II), mp 194–195° (lit.[7] mp 195–196°). Ir analysis (mineral oil mull) showed absorptions at 3140, 1680, 1630, and 1555 cm^{-1}. The nmr spectrum (D_2O) showed a singlet at 6.22 ppm and multiplets at 4.01 and 3.60 ppm in a ratio of 9:2:1, respectively (the nitrogen proton exchanged with D_2O).

1,1,1-Trimethylmethacrylylhydrazinium Chloride (III). To a solution of 1,1,1-trimethylammonium-*N*-methacryloylimine (I) in absolute methyl alcohol was added excess hydrogen chloride *via* a gas dispersion tube. The solution was stirred during the addition of the gas and the temperature maintained below 40° by an ice bath. The solution was reduced to nonvolatiles on the flash evaporator, redissolved in chloroform, and precipitated with benzene. Nearly quantitative yields of III were obtained: mp 139–139.5° (lit.[8] mp 139–139.5°); ir absorption bands at 3130, 1635, 1670, and 1550 cm^{-1}.

Comonomers. The monomers styrene and methyl methacrylate were purified by distillation under nitrogen through a 12-in. Vigreux column immediately before use. The monomers butyl acrylate and hydroxyethyl acrylate were used as received from Rohm and Haas and Dow Chemical.

II. Solvents and Initiators. All of the solvents used were purified according to standard procedures. Azobisisobutyronitrile (AIBN) was purified by recrystallization from methyl alcohol.

III. Polymerization. A. Polymerization of 1,1,1-Trimethylacrylylhydrazinium Chloride (II). 1. Homopolymerization. A 60-ml serum bottle was charged with 5.0 g of II, 10 ml of anhydrous methanol, and 5.0 mg of AIBN. The bottle was flushed with nitrogen, sealed, and placed in a shaker bath at 70 ± 1° for 20 hr. The viscous, alcoholic solution was poured into 300 ml of vigorously stirred acetone. The white precipitate was collected and washed several times with acetone to obtain a 3.5 g (70% yield) of polymer. After dissolving in methanol, reprecipitating with acetone, and drying *in vacuo*, the polymer was shown to be free of monomer by tlc. The polymer exhibited an inherent viscosity of 1.56 in methanol. The infrared spectrum (film) exhibited the expected strong amide absorption bands at 3400, 1700, and 1560 cm^{-1}.

A small sample of the polymer was dissolved in wet methanol and the solution fed through a column of basic ion exchange resin. The infrared spectrum (film) of the recovered and dried polymer exhibited the typical strong aminimide absorption band at 1570 cm^{-1} and no bands at 3400, 1700, and 1560 cm^{-1}. After heating in air at 150° (30 min), the infrared spectrum of the polymer exhibited a new strong band at 2260 cm^{-1} and no band at 1570 cm^{-1}.

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TABLE I
REACTIVITY STUDY OF MONOMER II

Run no.	Mol of II	Mol of styrene	Mol % of II monomer feed	N, %	Mol % of II in polymer	$F = M_1/M_2$ mole ratio of polymer
1	0.01	0.19	5.0	2.58	9.79	0.108
2	0.02	0.18	10.0	4.71	18.27	0.224
3	0.03	0.17	15.0	5.80	22.66	0.293
4	0.04	0.16	20.0	6.23	24.75	0.329
5	0.06	0.14	30.0	9.15	36.88	0.584
6	0.08	0.12	40.0	10.29	41.93	0.722
7	0.12	0.08	60.0	12.43	51.72	1.071
8	0.15	0.05	75.0	14.46	61.25	1.580
9	0.17	0.03	85.0	16.09	78.78	3.712

Differential thermal analysis and TGA curve also showed that the polymer lost 47% of its weight from 125–200° (theory, 46.1%).

2. Copolymer of II and Styrene. A 60-ml serum bottle was charged with 2.2 g of monomer II, 15 g of styrene, 0.2 g of AIBN, and 30 g of acetonitrile. The bottle was flushed with nitrogen, sealed, and placed in a shaker bath at 70 ± 1° for 20 hr. The viscous polymer solution was poured with stirring into 400 ml of ether. The precipitated polymer was collected and washed several times with ether to obtain a 13 g (80%) yield of crude polymer. The polymer was purified by dissolving it in methanol, precipitating into ether, washing with water, and drying *in vacuo*. Thin layer chromatography indicated the polymer to be free of monomer. The infrared spectrum (film) exhibited strong bands attributable to the styrene residue and additionally strong bands at 3400, 1700, and 1560 cm^{-1} attributable to amide monomer II. The polymer exhibited an inherent viscosity of 0.12 in chloroform. On the basis of nitrogen (2.68%) and chlorine (4.31%) analyses the polymer consists of 8.5 styrene units and 1.5 monomer II units (calcd N, 2.69%; Cl, 4.66%).

A sample of the polymer was dissolved in wet tetrahydrofuran and fed through a basic ion exchange column. The infrared spectrum (film) of the recovered polymer exhibited a strong absorption band at 1570 cm^{-1} and no amide bands. On the basis of nitrogen analysis (3.78%) the polymer checks for 8.5 styrene units to 1.5 aminimide units (calcd N, 3.90%). The infrared spectrum (thin film) of the polymer after thermolysis, 160° (30 min), exhibited a strong band at 2260 cm^{-1} and no band at 1570 cm^{-1}. The DTA curve exhibited a strong endotherm centered at *ca.* 172°. The TGA curve exhibited an 8.5% weight loss from 125 to 200° [calcd for $N(CH_3)_3$ loss, 8.22%].

3. Copolymer of II and Butyl Acrylate. A reaction flask was fitted with a stirrer, thermometer, nitrogen tube, and reflux condenser and charged with 57.6 g of *n*-butyl acrylate, 8.2 g of II, 1.0 g of AIBN and 75 ml of 95% ethanol. The polymerization was run at reflux for 20 hr under a slow nitrogen stream. The viscous polymer solution was diluted with tetrahydrofuran and fed through a basic ion exchange column. After removal of some solvent, a small sample of the polymer was isolated and purified. The sample polymer solution was added to ether and the precipitated polymer collected and washed several times with water. After drying, tlc indicated the polymer to be free of monomers. The infrared spectrum (film) of the polymer exhibited the expected strong band at 1730 and 1570 cm^{-1} and the polymer exhibited an inherent viscosity of 0.36 in chloroform. The TGA curve showed a 6.25% weight loss [$(CH_3)_3N$ evolution] from 125 to 200° and this indicates the polymer contains *ca.* 8.6 butyl acrylate units to 1.4 aminimide units [calcd for $N(CH_3)_3$ loss, 6.45%]. The infrared spectra of thin films of the polymer heated at 160° for 30 min exhibited a strong absorption band at 2260 cm^{-1} and no band at 1570 cm^{-1}.

A 500-ml flask was fitted with a stirred, thermometer, nitrogen tube, condenser, and distilling receiver and charged with 300 ml of xylene and the concentrated aminimide polymer solution. Under a slow nitrogen stream, 150 ml of mixed solvent was distilled from the reactor and the reactor temperature reached the reflux temperature of xylene. Distillation was discontinued and the contents of the flask were heated at reflux under a slow nitrogen stream for 3 hr. During thermolysis copious amounts of $(CH_3)_3N$ evolved from the reactor. The solution was cooled and the per cent nonvolatiles and isocyanate determined. The solution, with 24% solids, contained polymer with 2.76% NCO (calcd for 8.6 butyl acrylate to 1.4 vinyl isocyanate units, 4.20% NCO).

4. Copolymer of Methyl Methacrylate and II. Under a nitrogen atmosphere, 22.5 g of methyl methacrylate, 4.11 g of II, 0.4 g of AIBN, and 30 ml of ethyl Cellosolve were combined and sealed in a 100-ml serum bottle. After polymerization at 90° for 5 hr, the viscous polymer solution was cooled and poured into a large volume of ether. The precipitated crude polymer was dissolved in acetone, precipitated into water, collected, and dried *in vacuo* to obtain 22-g (83%) yield of purified polymer. The infrared spectrum (film) exhibited bands at 3440, 1730 (with shoulder at *ca.* 1700), and 1560 cm^{-1}, attributable to the two monomer residues. The polymer inherent viscosity was 0.12 in chloroform. On the basis of nitrogen analysis (1.67%) the polymer consists of *ca.* 9.4 methyl methacrylate units to 0.6 unit of II (calcd N, 1.63%).

A sample of the polymer was dissolved in wet acetone and the solution fed through a basic ion exchange column. The infrared spectrum (film) of the isolated polymer showed a strong band at 1570 cm^{-1} and no bands at 3440, 1700, and 1560 cm^{-1}. After thermolysis, 150° (30 min), the infrared spectrum of the film exhibited a strong band at 2260 cm^{-1} and no band at 1570 cm^{-1}. On the basis of nitrogen analysis (1.62%) the polymer was again shown to contain *ca.* 9.4 methyl methacrylate units to 0.6 aminimide unit (calcd N, 1.65%).

The DTA curve exhibited a reasonable sharp endotherm centered at *ca.* 172°. The TGA curve exhibited a 2.90% weight loss from 125 to 200° [calcd for $N(CH_3)_3$ loss, 2.77%].

5. Monomer II–Styrene Copolymerizations for the Alfrey–Price Q and e Values (Table I). The monomers, 70 ml of solvent mixture and AIBN initiator (1% by weight based on monomers total weight) were charged into 100-ml serum bottles. The solvent mixture was a 1:1 mixture of methyl alcohol and ethyl Cellosolve. After a brief nitrogen sparge, the bottles were sealed and shaken for a few minutes at room temperature to achieve homogeneous solutions. All polymerizations were run for 1 hr at 70 ± 1° to give 10% or less conversion.

The copolymers were isolated by pouring the solutions into a large excess of a 1:1 solvent mixture of diethyl ether and Skelly B. The polymers were washed several times with ether. Samples 1–5 were washed several times with warm water. Run 6 sample was treated with aqueous base (0.1 *N*) and washed with water until neutral. The aforesaid was performed on run 6 because the aminimide polymer was water insoluble and the quaternary polymer was water soluble. In runs 7–9 both the quaternary and aminimide polymers were soluble in water.

All quaternary polymers were converted to aminimide polymers prior to purification. Samples 1–5 were dissolved in wet acetone and fed through a column of basic ion exchange resin. The acetone solutions were filtered, concentrated, and poured into water, to precipitate the polymers. After collection and washing with water, the polymers were dried *in vacuo* to give analytical samples. The samples from runs 6–9 were also dissolved in wet methanol and fed through basic ion exchange columns. The filtered and concentrated solution from run 6 was poured into water to precipitate the polymer. After collection and washing with water, the purified polymer was dried *in vacuo*. All polymers from runs 1–6 were found free of monomer by tlc. The solutions for runs 7–9 were filtered, evaporated to dryness, and the polymers were purified by dialysis. For dialysis, the polymers were dissolved in 50 ml of distilled water, sealed in Visking seamless, regenerated cellulose tubing, and immersed at room temperature into 1 l. of distilled water. Periodically each polymer solution was checked for monomer by tlc. After *ca.* 3 hr, tlc indicated all four samples were free of monomers. The solutions were evaporated to dryness and the polymers dried *in vacuo* to obtain analytical samples. The infrared spectra (films) of the nine purified polymers exhibited strong bands at 1570 cm^{-1} and no amide bands.

6. Use of Monomer II to Prepare a Thermosetting Resin. Styrene (4.2 g), *N*-butyl acrylate (3.1 g), hydroxyethyl acrylate (1.0 g), monomer II (1.3 g), *n*-butyl alcohol (20 ml), and AIBN (0.15 g) were combined and polymerization achieved under nitrogen for 4 hr at 90°. Approximately 3 ml of the polymer solution was poured into ether, the precipitated polymer collected, washed several times with water, and dried *in vacuo* to obtain an analytical sample. Nitrogen analysis (3.70%) indicated the isolated polymer contained more than the expected amount of monomer II (calcd 2.33% N). The infrared spectrum (film) of the polymer exhibited bands attributable to the various monomer residues.

The remainder of the polymerization solution was diluted with wet tetrahydrofuran and the solution fed through a basic ion exchange column. After filtration and concentration, the solution was poured into ether to precipitate the polymer. The polymer was collected, dissolved in methanol, and again precipitated into ether. After collecting and washing with water, the polymer was dried *in vacuo* to obtain an analytical sample. Again, nitrogen analysis (3.62%) indicated more than the expected (2.35%) aminimide content. The infrared spectrum (free film) exhibited the expected strong absorption band at 1570 cm^{-1} (aminimide). Differential thermal and TGA indicated the polymer started losing $(CH_3)_3N$ at *ca.* 125° with the maximum rate at *ca.* 170°. The TGA curve exhibited a 7.50% weight loss from 125 to 200° [predicted $(CH_3)_3N$ weight loss from nitrogen determination 7.60%].

The aminimide polymer, with an inherent viscosity of 0.51 in chloroform, was dissolved in acetone (50% solids) and the solution was used to coat glass plates. The air-dried films (24 hr) were *ca.* 3 mil thick and exhibited an average Sward[9,10] of 26 and Tukon[9,10] of 5.7. Heating the films for 30 min at 60° caused evolution of $(CH_3)_3N$; the resulting films were found to have an average Sward of 18 and Tukon of 12.7. The infrared spectrum of the thermolyzed films exhibited a weak band at 2260 and *ca.* 1700 cm^{-1}, indicative of isocyanate and urethan residues and no band at 1570 cm^{-1}. The baked films were insoluble in chloroform, acetone, xylene, etc., and exhibited good adhesion to the glass.

B. Polymerizations of 1,1,1-Trimethylmethacrylylhydrazinium Chloride (III). 1. Homopolymerization. Monomer III, 5.0 g, was homopolymerized with AIBN in methanol and the polymer was isolated according to the same procedure used for monomer II (see section III.1). The polymer, which was obtained in a 4.2 g (80%) yield, exhibited an inherent viscosity of 0.39 in methanol. The infrared spectrum showed strong bands at 3400, 1700, and 1560 cm^{-1}. The polymer, after being dissolved in wet methanol and being treated with basic ion exchange resin, exhibited the expected strong band at 1565 cm^{-1} in the infrared spectrum. The TGA curve showed the polymer started losing $(CH_3)_3N$ at *ca.* 125° and that the theoretical amount of amine was lost from 125 to 200°.

2. Copolymer of III and Styrene. Styrene (20 g), monomer III (5.0 g), *N,N*-dimethylformamide (40 ml), and AIBN (0.2 g) were charged into a 100-ml serum bottle. After a brief nitrogen sparge, the bottle was sealed and placed in a shaker bath for 20 hr at 70 ± 1°. A small sample of the polymerization solution was poured into water, the polymer was collected, washed with water, and was dried *in vacuo*. The infrared spectrum contained strong bands indicative of the two monomer residues. The remainder of the viscous polymerization solution was divided into *ca.* two equal portions which were treated as follows.

The first portion of the polymerization solution was poured slowly into vigorously stirred, aqueous potassium hydroxide solution (0.5 *N*) and the precipitated polymer was collected, washed with water until neutral, and air dried to obtain a 12 g yield of crude polymer. The polymer was dissolved in acetone, filtered, precipitated into water, collected, and dried *in vacuo* to obtain purified polymer A with an inherent viscosity of 0.18 in chloroform. On the basis of nitrogen analysis (3.00%) the copolymer consists of *ca.* 8.8 styrene units to 1.2 aminimide (I) units. The infrared spectrum (film) of the polymer, with an inherent viscosity of 0.20 in chloroform, showed a strong band at 1565 cm^{-1}. After thermolysis (150°/30 min) the infrared spectrum of the film exhibited a strong band at 2260 cm^{-1} and no band at 1565 cm^{-1}. The DTA and TGA curves showed the polymer starts losing amine at *ca.* 125° and the TGA curve additionally showed a 6.62% weight loss from 125 to 200° (theory 6.52%).

The second half of the polymerization solution was diluted with wet *N,N*-dimethylformamide and the solution fed through a basic ion exchange column. After filtration, the solution was poured into water to precipitate the polymer. The precipitate was collected, washed with water, and dried *in vacuo* to obtain a 11.0 g yield of polymer B. The infrared spectrum, DTA, and TGA studies showed polymer A and B were identical.

Polymer A and B were combined and thermolyzed in 100 ml of refluxing xylene for 4 hr under a strong nitrogen stream. During thermolysis, copious amounts of amine evolved from the solution. The gpc curve for the polymer in solution, with $A_W = 732$ and $A_W/A_N = 1.98$, was sharp and without any indication of bimodal distribution. The infrared spectrum of a film of the polymer cast from solution showed a strong band at 2260 cm^{-1} and no band at 1565 cm^{-1}. The polymer in solution (28.5% solids) was titrated with amine and shown to contain 4.72% NCO (theory 4.96% NCO). A sample of the solution was concentrated and poured into Skelly B to precipitate the polymer. After collecting, washing with Skelly B, and drying *in vacuo*, the isolated polymer exhibited an inherent viscosity of 0.23

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TABLE II
REACTIVITY STUDY OF MONOMER III

Run no.	Mol of III	Mol of styrene	Mol % of III monomer feed	N, %	$(CH_3)_3N$,[a] lost %	Mol % of III in polymer from % N[b]	Mol % III in polymer from % $(CH_3)_3N$[c]	$F = M_1/M_2$ mol ratio of polymer[d]
1	0.01	0.19	5.0	2.53	5.30	9.78	9.85	0.108
2	0.02	0.18	10.0	4.24	8.27	16.69	16.20	0.200
3	0.03	0.17	15.0	5.57	12.02	22.38	22.10	0.288
4	0.04	0.16	20.0	6.82	13.50	27.95	26.50	0.387
5	0.06	0.14	30.0	7.67	16.75	31.10	32.50	0.451
6	0.08	0.12	40.0	9.42	19.65	40.11	39.20	0.686
7	0.12	0.08	60.0	11.49	23.14	50.55	47.50	1.022
8	0.15	0.05	75.0	12.73	27.36	57.02	57.00	1.327
9	0.17	0.03	85.0	14.76	32.10	68.50	70.00	2.174

[a] Determined by TGA (per cent weight loss from 125 to 200°). [b] Values used to determine r_1, r_2, and Q and e values. [c] Determined from column 6 [$(CH_3)_3N$ loss] values. [d] Calculated from per cent N data, column 5.

in chloroform. On the basis of nitrogen analysis (1.75%) the polymer contains *ca.* 8.8 styrene to 1.2 isopropenyl isocyanate residues (theory N 1.66%). The xylene solution of the poly(styrene-*co*-isopropenyl isocyanate) exhibits excellent shelf stability on storage in metal containers.

3. Copolymer of III and Methyl Methacrylate. Methyl methacrylate (11.3 g) and monomer III (2.25 g) were copolymerized in 20 ml of ethyl Cellosolve, using 0.2 g of AIBN initiator and the same procedure and conditions used to prepare the copolymer in section IIIA.4. After purification in the same manner (IIIA.4), the polymer was collected in a 12 g (88%) yield. The infrared spectrum of the polymer exhibited bands at 3440, 1730 (shoulder at *ca.* 1700), and 1560 cm^{-1}, attributable to the two monomer residues. The polymer inherent viscosity was 0.14 in chloroform. On the basis of nitrogen analysis (2.47%) the polymer consists of *ca.* nine methyl methacrylate units to each unit of III (calcd N 2.60%).

The polymer was dissolved in wet acetone, fed through a basic ion exchange column, and isolated. The infrared spectrum (film) exhibited a strong band at 1565 cm^{-1}. After thermolysis (150°/30 min), the infrared spectrum (film) exhibited a strong band at 2260 cm^{-1} and no band at 1565 cm^{-1}. On the basis of nitrogen analysis (2.46%) the polymer was again shown to contain *ca.* nine methyl methacrylate units to aminimide units (calcd N 2.76%). The TGA curve exhibited a 5.50% weight loss from 125 to 200° [calcd for $N(CH_3)_3$ loss 5.66%].

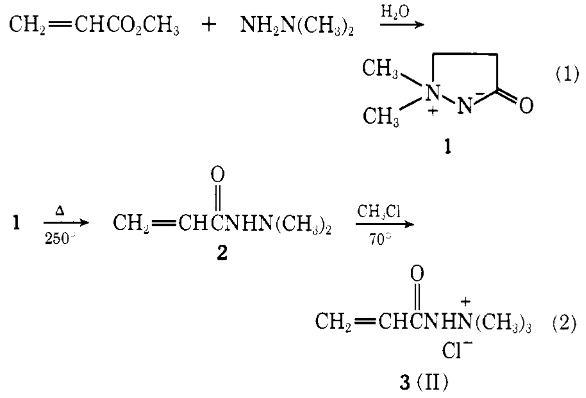
4. Monomer III-Styrene Copolymerizations for the Alfrey-Price *Q* and *e* Values (Table II). All copolymerizations were run at 70° in 70 ml of ethyl Cellosolve by the same procedure used for monomer II (see section IIIA.5) and conversions for all runs were <10%.

All polymerization solutions were poured into a large excess of a 1:1 solvent mixture of diethyl ether and Skelly B and the collected crude polymers were washed several times with ether.

The quaternary polymers were converted to aminimide polymers prior to purification, conversion determinations, and analyses. The crude polymers from runs 1-8 were washed several times with 0.1 *N* sodium hydroxide solution and water until the washings were neutral. Infrared spectra indicated that all polymers still contained some quaternary residues. The polymers were dissolved in acetone (runs 1-6) or methanol (runs 7-8) and the concentrated solutions poured into vigorously stirred 0.1 *N* sodium hydroxide solution. The precipitated polymers were collected, washed with water until neutral, dried, and were shown to be free of monomer by tlc. Within detectable limits, the infrared spectra indicated that the quaternary residues were absent from all eight polymers, *i.e.*, all spectra exhibited only aminimide absorption band at 1565 cm^{-1}. The crude polymer from run 9 was dissolved in wet methanol and the solution fed through a basic ion exchange column. The acetone solution was filtered, evaporated to dryness, and the product was rubbed with acetone. The fine divided by product was collected, washed several times with acetone, air dried, and was shown to be free of monomers by tlc. All polymers (runs 1-9) were dried *in vacuo* (0.1 mm) at 65° before nitrogen and data of thermogravimetric analyses were obtained.

Results and Discussion

A. Monomer Synthesis and Properties. Monomer II was prepared according to eq 1 and 2.



Briefly, the reaction scheme employs the fact that methyl acrylate will react with 1,1-dimethylhydrazine in polar solvents to give an excellent yield of 1,1-dimethylpyrazolinium 3-oxide **1**.[5] When heated, cyclic compounds of type **1** ring open[5,6] to give fair to good yields of the corresponding linear α,β-unsaturated hydrazines (**2**). Compound **2** (1,1-dimethyl-2-acrylhydrazine) may be quaternized readily with methyl chloride to obtain excellent yields of monomer **II**.[7]

Monomer III was readily prepared in approximately quantitative yield by dissolving trimethylamine methacrylimide (I)[1b] in absolute methanol and saturating the solution with hydrogen chloride gas.[8]

Both monomers II and III have similar solubility characteristics, *i.e.*, they are both soluble in alcohols, water, acetonitrile, *N,N*-dimethylformamide, ethyl Cellosolve, and chloroform. They are insoluble in

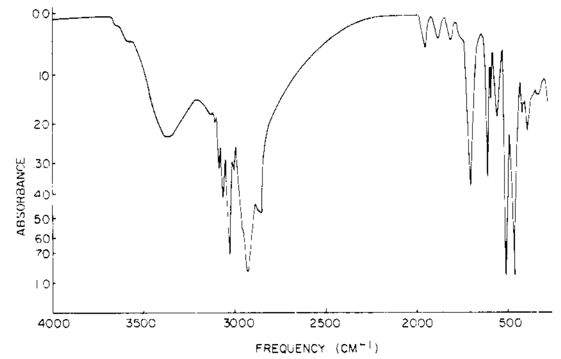


Figure 1. Infrared spectrum (film) of poly[styrene-*co*-(1,1,1-trimethyl-2-methacrylylhydrazinium chloride)] containing *ca.* 12 mol % of monomer III.

acetone, benzene, dioxane, carbon tetrachloride, and ether. The thermal stability of each monomer is good up to at least 100°. The shelf stability seems to be fair when the monomer is pure and when stored in the dark in sealed containers. Both monomers are strongly acidic and very hygroscopic.

B. Polymerizations of II. The homopolymerization of II was carried out in methanol, using AIBN as initiator, to obtain high molecular weight polymer. The infrared spectrum exhibited the expected amide absorption bands. A sample of the polymer was dissolved in methanol and treated with basic ion exchange resin to obtain the respective poly(trimethylamine acrylimide). The infrared spectrum with a strong absorption band at 1570 cm^{-1} and no amide bands supported the polymer structure. Differential thermal analysis and TGA indicated that the aminimide polymer starts losing trimethylamine at *ca.* 125°. Further, elimination of amine approached the theoretical amount when the polymer was heated from 125 to 200°. The infrared spectrum of the heat-treated polymer showed a strong isocyanate band at 2250 cm^{-1}.

In this initial work, it was demonstrated that monomer II can be copolymerized with styrene, butyl acrylate, and methyl methacrylate to low molecular weight polymers. The presence of the quaternary [$-CONHN(CH_3)_3 + Cl^-$] and other monomer residues in the copolymers were well established by elemental and infrared analysis.

The three copolymers of II and styrene, butyl acrylate, and methyl methacrylate were dissolved in tetrahydrofuran or acetone and treated with a basic ion exchange resin to obtain the respective copolymers with pendent aminimide [$-CON^-N^+(CH_3)_3$] residues. Elemental analysis, DTA, TGA, and infrared spectra studies confirmed the fact that the pendent quaternary residues were converted to aminimide moieties. Differential thermal analysis curves showed that all the copolymers started losing trimethylamine at *ca.* 125° and that the maximum rate of amine evolution occurs at *ca.* 170°. The TGA curves showed that the aminimide copolymers lost approximately the theoretical amount of amine when heated from 125 to 200°. The infrared spectra of the three copolymers exhibited the strong aminimide carbonyl absorption band. In contrast, the infrared spectra of the polymer films after thermolysis, 150° (30 min), exhibited only the strong isocyanate absorption band.

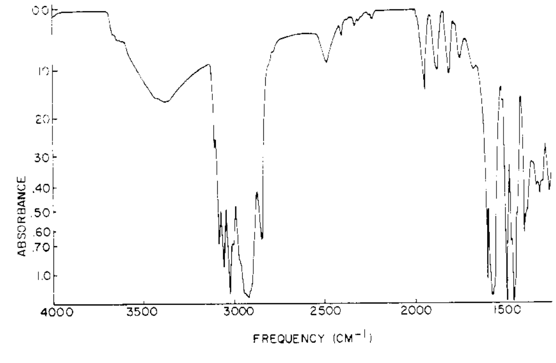


Figure 2. Infrared spectrum (film) of poly(styrene-*co*-trimethylamine methacrylimide) containing *ca.* 12 mol % of monomer I.

It was demonstrated that the copolymers with pendent aminimide residues could also be heated in solution to obtain soluble polymers with pendent secondary isocyanate moieties. For example, poly(butyl acrylate-*co*-trimethylamine acrylimide) was heated in refluxing xylene to obtain poly(butyl acrylate-*co*-vinyl isocyanate).

Monomer II was used to prepare a thermosetting resin. The formulation consisted of monomers II, styrene, butyl acrylate, and hydroxyethyl acrylate in the polymerization mixture. The polymer was treated with base to convert the quaternary residues to aminimide moieties. Infrared analysis indicated that the base-treated polymer contained all four monomer residues. Further, nitrogen analysis and TGA also demonstrated the presence of the aminimide functional group. It was shown that the polymer could be deposited as a coating and cross-linked with heat. Changes in the infrared spectra of the heated films supported the assumption that cross-linking occurred by formation of urethan bonds. The same type of approach was used earlier to demonstrate that the aminimide derived from monomer III (I, trimethylamine methacrylimide) could be used to prepare thermosetting resins.[1b]

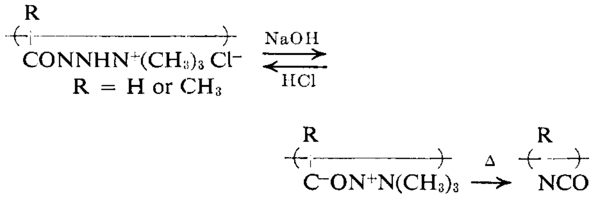
C. Polymerization of III. Monomer III was homopolymerized with AIBN in methanol to a high yield of a low molecular weight polymer. The infrared spectrum exhibited absorption bands indicative of the monomer III residue. After being dissolved in methanol and being treated with a basic ion exchange resin, the isolated polymer was shown to be identical by infrared studies, DTA, TGA, etc., with the previously prepared poly(trimethylamine methacrylimide).[1b] Thermogravimetric analysis and DTA showed the polymer started losing trimethylamine at *ca.* 125° and the TGA curve also showed the polymer lost theoretical amount of amine over the range 125–200°.

Monomer III was copolymerized with styrene in high conversion to a low molecular weight copolymer. The infrared spectrum (film) of the purified polymer gave evidence that the copolymer contained both monomer moieties (see Figure 1). In contrast, trimethylamine methacrylimide (I) will not copolymerize with styrene.[1b] It was found that poly[styrene-*co*-(1,1,1-trimethylmethacrylylhydrazinium chloride)] could be treated with aqueous base or passed over a basic ion exchange resin to obtain the corresponding poly(styrene-*co*-trimethylamine methacrylimide). The infrared spectra of the two polymers treated in this way were identical, containing a strong absorption band indicative of the monomer I residue (see Figure 2). Nitrogen analysis and TGA indicated the polymer consisted of *ca.* 8.8 styrene units to 1.2 monomer I units, in excellent agreement with the 9:1 ratio of monomers charged for polymerization. The infrared spectrum of a free film, after thermolysis at 150° for 30 min, showed that the new polymer was poly(styrene-*co*-isopropenyl isocyanate).

A sample of the poly(styrene-*co*-trimethylamine methacrylimide) was heated in refluxing xylene to obtain poly(styrene-*co*-isopropenyl isocyanate) (see Figure 3). The xylene solution of isocyanate polymer, which was free of any gel particles, exhibited excellent shelf stability. Gel permeation chromatography studies indicated that the isocyanate polymer was of low molecular weight and had a narrow molecular weight distribution. The results of nitrogen analysis and per cent NCO determinations were in good agreement with the values calculated for a copolymer containing 8.8 styrene units to 1.2 isopropenyl isocyanate units.

Monomer III was copolymerized with methyl methacrylate and the analytical results of the purified polymer were in good agreement with the moles of monomers charged for the polymerization. The low molecular weight copolymer was also readily converted with base to poly(methyl methacrylate-*co*-trimethylamine methacrylimide). The infrared spectrum, per cent nitrogen, and TGA results were in excellent agreement with the structure proposed for the aminimide polymer. Infrared spectra indicated that poly(methyl methacrylate-*co*-isopropenyl isocyanate) was formed when thin films of the polymer were heated at 150° for 30 min.

From these brief studies, it is clear that both monomers II and III have potential for modification of vinyl polymers to prepare a wide variety of polymers with pendent quaternary, aminimide, secondary, or tertiary isocyanate residues. The aforesaid potential use of these monomers for preparing "reactive vinyl polymers" may be represented schematically as



D. Determination of Momoner Reactivity Ratios. The reactivity ratios of II and III were determined in the same manner as previously reported for monomer I.[1b] The compositions of the monomer feeds and the copolymers obtained for the styrene–II or styrene–III system are summarized in Tables I and II. From these results the monomer reactivity ratios were obtained by the method of Fineman and Ross:[11] $r_1 = 0.46$, $r_2 = 0.58$ for II and $r_1 = 0.23$, $r_2 = 0.51$ for III.

In Figure 4 the mole fraction of II and III in the monomer feeds are plotted against the corresponding mole fraction of II and III in the copolymer. Strong alternation occurs in the II–styrene and III–styrene copolymers predicted by the r_1 and r_2 values and supported by the cross-over on the copolymer composition curves. This is expected for two monomers, one of which can give rise to a radical of high electron density and one having a double bond of low electron density.

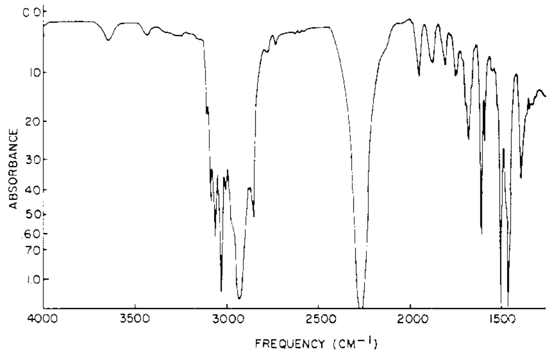


Figure 3. Infrared spectrum (film) of poly(styrene-*co*-isopropenyl isocyanate) containing *ca.* 12 mol % of isopropenyl isocyanate.

The Alfrey–Price Q and e values[12] for II and III were obtained from the monomer reactivity ratios: $Q = 0.69$, $e = 0.34$ for II and $Q = 0.61$, $e = 0.66$ for III. The Q and e values of styrene used in the calculations were $Q = 1.0$ and $e = -0.80$.[13]

From the Q and e values of trimethylamine methacrylimide[1b] (I, $Q = 0.18$; $e = 0.60$), 1,1-dimethyl-1-(2-hydroxypropyl)amine methacrylimide ($Q = 0.12$; $e = 2.45$), and 1,1-dimethyl-1-(2,3-dihydroxypropyl)amine methacrylimide ($Q = 0.24$; $e = -1.24$) previously determined,[14] one can see that the quaternary monomers II and III are much more reactive than the same general class of aminimide monomers. The switch from a negative e value for monomer I to a plus e value for monomer II and III is in the direction one would predict for substituted acrylamide or methacrylamide monomers.[13]

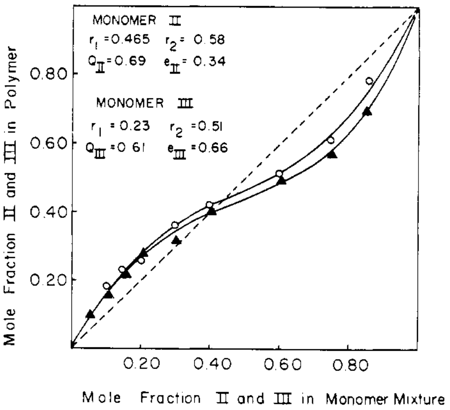


Figure 4. Copolymer composition curves for the copolymerization of II (○) and III (▲) with styrene.

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[11] M. Fineman and S. D. Ross, *J. Polym. Sci.*, **5**, 269 (1950).

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[13] L. J. Young, *ibid.*, **54**, 444 (1961).

[14] B. M. Culbertson, E. A. Sedor, and R. C. Slagel, *Macromolecules*, **1**, 254 (1968).

The marked change in the copolymerization characteristics of monomers such as I and III is highly useful for preparing a variety of polymers with either the quaternary, aminimide, or isocyanate pendent groups. This was readily demonstrated in this work when it was shown that monomer III readily copolymerizes with styrene and by earlier work which had demonstrated that monomer I would not copolymerize with styrene.

Acknowledgment. The authors are indebted to M. R. Hallwachs, P. J. Menardi, and D. L. Gregerson for excellent technical assistance during this work.

Syntheses of Ladder Polymers. II.[1] Poly(isoindoloquinazolinediones)

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ABSTRACT: Two thermally stable isoindoloquinazolinedione polymers have been prepared by the cyclopolycondensation reaction of the aromatic diaminodiamides and 5,5′-bis(2-aminobenzamide) and 5,5′-methylenebis(2-aminobenzamide) with pyromellitic dianhydride in N-methylpyrrolidone at 22°. All of the polymers obtained were completely soluble in fuming nitric acid and concentrated sulfuric acid. TGA weight losses of less than 10% at 550° in nitrogen and at 530° in air were observed. The structure and polymerization route of poly(isoindoloquinazolinedione) were studied by the infrared spectral and ultraviolet spectral method, and it was established that the polymerization proceeded through the formation of tractable poly(amic acid amide) of high molecular weight ($\eta_{\text{inh}} = 2.9$), followed by cyclodehydration, yielding poly(imide amide); on subsequently being heated, this undergoes intramolecular rearrangement along the polymer chain, giving the thermodynamically stable poly(isoindoloquinazolinedione) with the structure of isoindolo[1,2-*b*]quinazoline-10,12-dione. In previous publications,[1,2] it was shown that polymer containing the isoindoloquinazolinedione ring has the thermodynamically stable structure with the isoindolo[1,2-*b*]quinazoline-10,12-dione ring and the model reaction of anthranilamide with phthalic anhydride afforded the kinetically stable isoindolo[2,1-*a*]quinazoline-5,11-dione and the thermodynamically stable isoindolo[1,2-*b*]quinazoline-10,12-dione. 5,11-Dione is thermally rearranged to 10,12-dione. In this paper, the detailed syntheses and structure of poly(isoindoloquinazolinediones) by the cyclopolycondensation reaction of aromatic diaminodiamides with pyromellitic dianhydride are disclosed.

Discussion

The preparation of a new type of ladder polymer, poly(isoindoloquinazolinediones) with an isoindoloquinazoline[2,1-*b*]quinazoline-10,12-dione ring was first reported by Gaudemaris, *et al.*[3] In a previous paper[1] the structure of thermodynamically stable poly(isoindoloquinazolinedione) with an isoindolo[1,2-*b*]quinazoline-10,12-dione ring was reported.

In order to confirm the possibility of the formation of the kinetically stable poly(isoindoloquinazolinedione) and the correct structure of thermodynamically stable poly(isoindoloquinazolinedione), new model compounds were synthesized as described in Scheme I. The reaction of anthranilamide with pyromellitic dianhydride in N-methylpyrrolidone (NMP) affords bis(*o*-carbamoylphenylcarbamoyl)benzenedicarboxylic acid (I) quantitatively at room temperature. When I is heated at 140–210°, the first intramolecular cyclodehydration takes place to afford bis(carbamoyl-2-phenyl)-N,N′-pyromellitimide (II) in quantitative yield. 7H,16H-Benzo[1′′,2′′:3,4:4′′,5′′:3′,4′]dipyrrolo[2,1-*b*:2′,1′-*b*′]diquinazoline-7,9,16,18-tetrone (IV) is obtained by heating II at 230–400°. The changing of I by heating was followed by ir (Figure 1), uv (Figure 2), and elemental analyses. Compound I had a strong carbonyl absorption band due to the carboxyl group at 1715 cm^{-1}, an amide carbonyl absorption band at 1660 cm^{-1}, NH stretching vibration bands at 3450 and 3350 cm^{-1} (A in Figure 1), and λ_{max} at 260, 303, and 315 mμ (A in Figure 2). The ir spectrum B in Figure 1 and the uv spectrum C in Figure 2 are interpreted as being due to compound II because of the imide carbonyl absorption bands at 1780 and 1720 cm^{-1}, the amide carbonyl absorption band at 1650 cm^{-1}, the characteristic absorption of the imide ring at 720 cm^{-1}, and further the λ_{max} at 250 and 310 mμ. The possibility of the formation of III was followed by observing the changes in the ir (Figure 1) and uv (Figure 2) spectra. Spectrum C in Figure 1 shows carbonyl absorption bands at 1780 cm^{-1} (five-membered ring carbonyl), 1700 cm^{-1} (six-membered ring carbonyl), and 1650 cm^{-1} (amide carbonyl), which are explained as a mixture of II and IV. The distinct spectral change of the uv spectrum due to the change from II to III was not observed in Figure 2. The formation of IV was confirmed by the appearance of new strong carbonyl absorption bands at 1780, 1700, and new absorption band at 1640 cm^{-1} (C=N double bond), and the disappearance of NH absorption peaks (3450, 3350 cm^{-1}) and amide carbonyl peaks (1650 cm^{-1}). New λ_{max} absorption peaks appear at 320 and 390 mμ due to the isoindoloquinazolinedione ring (Figure 2). Although Gaudemaris, *et al.*, have reported that III was obtained by heating

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