Specialty Polyurethane Soft Segments. IV. Reactions of Aminated Poly(Propylene Glycols) with Isatoic Anhydride

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SYNOPSIS

Although it has been reported that aminated poly(propylene glycols) react with isatoic anhydride to cleanly yield the corresponding *o*-aminophenyl amide (**II**), this paper shows that a competing reaction leads to the formation of about 10% of the corresponding urea carboxylic acid (**III**). This impurity (unreactive toward polyisocyanates) limits the usefulness of (**II**) in urethane/urea polymers. A procedure has been developed to quantify (**II**) and (**III**). Based on the insight gained, a process has been developed to produce the corresponding *o*-aminophenyl amide derivatives of aminated poly(propylene glycols) in a state of high purity (~ 100%). A given aminated poly(propylene glycol) is added dropwise to a slurry of isatoic anhydride in an inert fluid (such as toluene or a previously prepared product) at a temperature (60–100°C) at which reaction is rapid. Local excesses of unreacted amine are minimized to prevent formation of urea carboxylic acid impurities. This process has been applied to the preparation of the corresponding derivatives of a variety of aminated poly(propylene glycols). © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Work in this laboratory has continued for several years to study the effects of hydrogen-bonding moieties in the soft segments of urethane/urea polymers.[1–13] Many monomers and polymers containing urea, amide, biuret, and thiourea moieties in the soft-segment backbone of the polymers have been reported based on aminated poly(propylene glycols).[8–13] Most of these monomers reported to date have contained primary, aliphatic amino end groups and, therefore, are extremely reactive with polyisocyanates. One phase of this study is to prepare and evaluate monomers having the same hydrogen-bonding backbone characteristics but having end groups that provide a full range of reactivities: primary aliphatic amines, secondary aliphatic amines, aromatic amines, and alcohols. A recent article described results with monomers containing aliphatic, secondary amino end groups.[12] This article describes results in the synthesis of monomers containing *o*-aminophenyl end groups based on isatoic anhydride.[13]

EXPERIMENTAL

Starting Materials

Isatoic anhydride and *sec*-butylamine were obtained from the Aldrich Chemical Co. Jeffamine™ D-2000 [an aminated poly(propylene glycol) of about 2000 molecular weight], Jeffamine D-400 [an aminated poly(propylene glycol) of about 400 molecular weight], Jeffamine M-600 (a 2-methoxyethanol-initiated propylene oxide adduct of about 600 molecular weight that had been aminated), Jeffamine T-403 (a trimethylolpropane-initiated propylene oxide-based triol of about 440 molecular weight that has been aminated), and Jeffamine T-5000 (a glycerine-initiated propylene oxide-based triol of about 5000 molecular weight that had been aminated) were manufactured by Texaco.

Analytical Procedures

Samples for HCl (0.1*N*) and NaOH (0.1*N*) titrations were dissolved in methanol (200 mL) and ti-

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trated potentiometrically using a Brinkmann 636 Titroprocessor equipped with an E-635 Dosimat. Samples for $HClO_4$ (0.1*N*) titrations were dissolved in glacial acetic acid and titrated on the same equipment. NMR spectra (5 wt % in DMSO-d_6) were obtained on a Varian Gemini 300 instrument (300 MHz for proton and 75 MHz for carbon).

Reaction of Jeffamine D-2000 with Isatoic Anhydride: Marquis and Yeakey Procedure[14]

Jeffamine D-2000 (203.1 g, 0.100 mol) was placed in a 500 mL, three-necked reactor equipped with a stirrer, thermometer, condenser, and temperature controller and maintained under a nitrogen atmosphere. The flask was heated to 30°C and solid isatoic anhydride (32.62 g, 0.200 mol) was added in small batches over a 15 min period. Reaction temperature increased to 40°C during addition and gas evolution occurred. Reactor temperature was maintained at 40°C for 2 h after addition, then heated at 50°C for 16 h and finished at 100°C for 5 h. The product was a dark amber liquid, 226.0 g; 0.0541 meq/g by HCl titration; 93.9% amine conversion; 0.788 meq/g by $HClO_4$ titration; and 0.112 meq/g by NaOH titration.

Preparation of *o*-Aminophenyl Amide (IV)

sec-Butylamine (7.32 g, 0.100 mol) was weighed into a 500 mL wide-mouth bottle equipped with a stirrer. Water (250 mL) was added to give a solution about 0.4*M* in amine. Isatoic anhydride (16.31 g, 0.100 mol) was added batchwise over a 2 min period. The resultant gray slurry was stirred for 30 min at ambient temperature and then filtered through sintered glass. After air-drying overnight, the filter cake was slurried in methanol (250 mL) and filtered to remove the bulk of unreacted isatoic anhydride. The filter cake was washed with methanol. The combined methanol solutions were stripped on a rotary evaporator and the crude product was slurried in water (500 mL) for 5 h to remove unreacted *sec*-butylamine. The product was recovered by filtration and drying as a light gray solid.

Preparation of Urea Carboxylic Acid (V)

sec-Butylamine (73.14 g, 1.00 mol) was weighed into the same reactor used above. Water (167 mL) was added to give a solution about 6.0*M* in amine. Isatoic anhydride (16.31 g, 0.100 mol; 10 : 1 molar ratio of *sec*-butylamine : isatoic anhydride) was added batchwise over a 2 min period. The temperature rose to 38°C during addition. The resultant dark amber solution was stirred at ambient temperature for 30 min and then acidified with dilute (1*N*) sulfuric acid to convert unreacted *sec*-butylamine to its salt and to convert the *sec*-butylamine salt of urea carboxylate to the free carboxylic acid. The crude insoluble solid product separated and was removed by filtration. Titration with HCl and NaOH indicated the presence of some amine salt. The crude solid was slurried in water (800 mL, pH about 4) and further reacted with 1*N* sulfuric acid until the pH was < 2. After filtration and air-drying, NaOH titration indicated traces of sulfuric acid and amine salt. The crude product was stirred vigorously with water (2 × 500 mL) and recovered after filtering and air-drying as a light gray solid.

Reaction of Jeffamine M-600 with Isatoic Anhydride

Jeffamine M-600 (60.3 g, 0.100 mol) was weighed into the 500 mL reactor used above. Isatoic anhydride (1.63 g, 0.010 mol, 10%) was added at one time with stirring (24–30°C). After 15 min, a small sample of the resultant clear solution was taken for NMR analysis. Additional isatoic anhydride (2.44 g, 0.025 mol, 25%) was added at one time with stirring (30–34°C). After an additional 30 min, a small sample of the resultant clear solution was taken for NMR analysis. Additional isatoic anhydride (4.08 g, 0.050 mol, 50%) was added at one time with stirring (28–32°C). After an additional 30 min, a small sample of the resultant clear solution was taken for NMR analysis. Additional isatoic anhydride (4.08 g, 0.075 mol, 75%) was added at one time (24–28°C). After stirring overnight (16 h), a small sample of the resultant clear solution was taken for NMR analysis. Additional isatoic anhydride (4.08 g, 0.100 mol, 100%) was added at one time (24–27°C) and stirred for an additional 40 h. The resultant dark amber liquid product was analyzed by NMR and titrations.

Reaction of Jeffamine D-2000 with Isatoic Anhydride: Isatoic Anhydride Dispersed in Toluene

Isatoic anhydride (32.60 g, 0.200 mol) was placed in the 500 mL reactor used above (except an addition funnel was added to the stoppered port) and was slurried in toluene (77.3 g). Jeffamine D-2000 (203.1 g, 0.100 mol) was placed in the addition funnel. The reactor was heated to 60°C and the D-2000 was added dropwise over a period of 90 min. After ad-

dition, the reactor was heated at 60°C for 1 h; then, the toluene was removed by heating under reduced pressure, finishing at 125°C for 2 h at 1 mmHg pressure. After heating at 150°C for an additional 3 h, the product (227.6 g) was obtained as a dark red liquid: 0.0379 meq/g by HCl titration, which corresponds to a 95.7% amine conversion; 0.874 meq/g by $HClO_4$ titration, which corresponds to 95.1 mol % amine amide; and 100 : 0 molar ratio of *o*-aminophenyl amide : urea carboxylic acid (and salt) by proton NMR analysis; carbon-13-NMR shows only the *o*-aminophenyl amide carbonyl (168.7 ppm, amide). The urea carboxylic acid (and salt) was not detected by proton or carbon-13-NMR.

Reaction of Jeffamine D-2000 with Isatoic Anhydride: Isatoic Anhydride Dispersed in Previously Made Product

Isatoic anhydride (97.8 g, 0.600 mol) was placed in the same reactor setup used above (except a 2 L reactor was used) and was slurried in a portion of previously prepared product (250 g). Jeffamine D-2000 (609.33 g, 0.300 mol) was placed in the addition funnel. The reactor was heated to 60°C and the D-2000 was added dropwise over a period of 227 min. After addition, the reactor was heated at 150°C for an additional 3 h. The product (937.5 g) was obtained as a dark red liquid: 0.0410 meq/g by HCl titration, which corresponds to a 96.2% amine conversion; 0.885 meq/g by $HClO_4$ titration, which corresponds to 95.2 mol % *o*-aminophenyl amide; and 100 : 0 molar ratio of *o*-aminophenyl amide : urea carboxylic acid (and salt) by proton NMR analysis; carbon-13-NMR shows only the *o*-aminophenyl amide carbonyl (168.7 ppm, amide). The urea carboxylic acid (and salt) was not detected by proton or carbon-13-NMR.

RESULTS AND DISCUSSION

Introduction

A series of patents to Texaco[14-16] reported that aminated poly(propylene glycols) react with isatoic anhydride to yield the corresponding *o*-aminophenyl amide (Fig. 1). These materials are claimed to be useful as both soft-segment components and chain extenders in reaction injection molding (RIM)-fabricated urethane/urea polymers. However, the application examples in these patents are very limited.

In light of this work by Texaco, a study was undertaken to study the reaction of backbone-modified

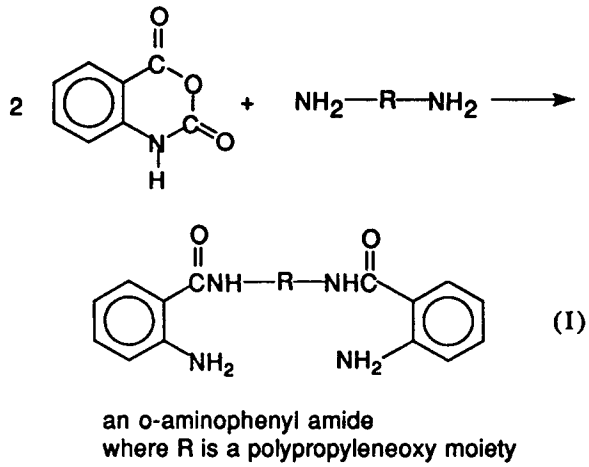


Figure 1 Reaction of aminated poly(propylene glycols) with isatoic anhydride as described by Marquis and Yeakey.

polyamines with isatoic anhydride, since on the surface, this appeared to be a way of converting primary aliphatic amines to the corresponding materials with *o*-aminophenyl end groups. Isatoic anhydride is relatively inexpensive since it is used in the production of saccharin. It would only be used in small amounts to modify end groups.

The first reaction studied was the reaction of 1 mol of Jeffamine D-2000 with 2 mol of isatoic anhydride following the conditions used by Marquis and Yeakey.[14] Although the reaction appeared to proceed as described, product analysis (titration and carbon-13-NMR) indicated that at least 10% of the Jeffamine D-2000 had been converted to an unexpected product. The carbon-13-NMR spectrum (see Fig. 2) has a series of lines consistent with the anticipated product. However, the spectrum also contains a series of smaller lines consistent with a related, but different, structure.

A more detailed search of the literature indicated that a clean reaction to the corresponding *o*-aminophenyl amide (**II**) as taught by Marquis and Yeakey[14] should not be expected.[17-20] The isatoic anhydride ring can open in two ways, depending on which carbonyl is attacked by amine (Fig. 3). The structure around the amino moieties of Jeffamine D-2000 predicts[18] that an appreciable amount of the corresponding urea carboxylic acid (**III**) should also be formed. Urea carboxylic acid (**III**) should have a carbon-13-NMR spectrum somewhat similar to *o*-aminophenyl amide (**II**).

Although the *o*-aminophenyl amide (**II**) should be very useful in its reactions with polyisocyanates, the urea carboxylic acid (**III**) is a chain stopper un-

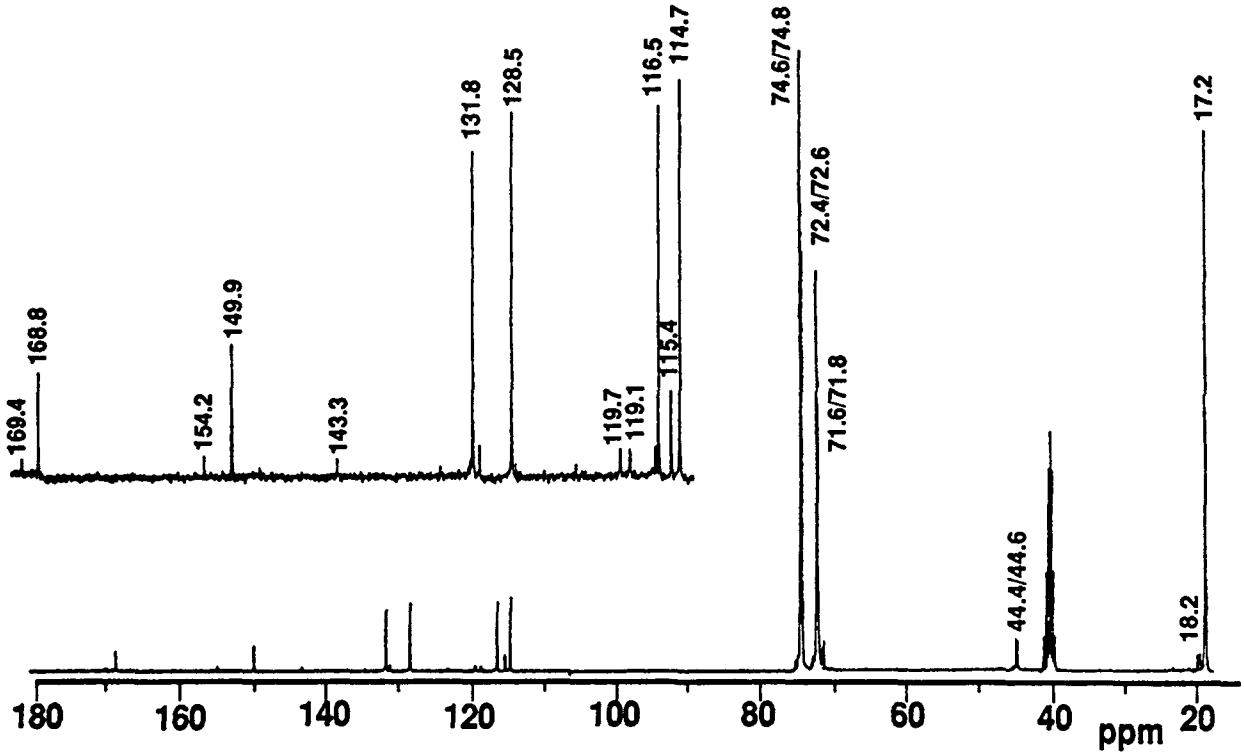
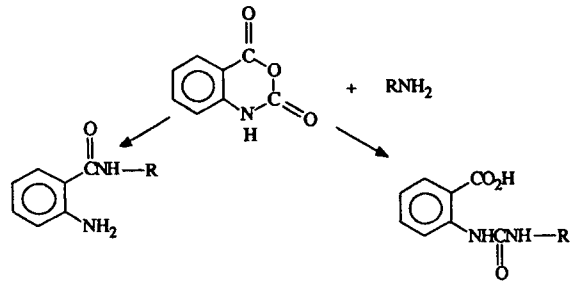


Figure 2 Carbon-13-NMR spectrum of Jeffamine D-2000 and isatoic anhydride adduct using conditions of the Marquis and Yeakey patent.

less very specific conditions are employed. A 10% urea carboxylic acid impurity (**III**) negates the usefulness of *o*-aminophenyl amide (**II**) in reactions with polyisocyanates. Therefore, it was important to learn how to eliminate the formation of this impurity and, if successful, to extend this technology to a series of aminated poly(propylene glycols). Polymers based on derivatives of aminated poly(propylene glycols) and polyisocyanates have potential utility in high modulus automotive body panel applications.



o-Aminophenyl Amide (II) Urea Carboxylic Acid (III)

Figure 3 Dependence of reaction products on reaction site.

Model System Based on *sec*-Butylamine

A method needed to be developed to quantitatively differentiate between these two possible structures (**II** and **III**). At the same time, a model needed to be used that closely resembled the structural features around the amino moiety of aminated poly(propylene glycols). Secondary butylamine has these structural features and is readily available:

Aminated poly(propylene glycol) sec-Butylamine

Staiger[18] has shown that the major product of the reaction of isatoic anhydride with *sec*-butylamine is the corresponding *o*-aminophenyl amide (**IV**) using a 1 : 1 stoichiometry, whereas the major product is the urea carboxylic acid (**V**) using a 1 : 10 stoichiometry. Both of these compounds were made, pu-

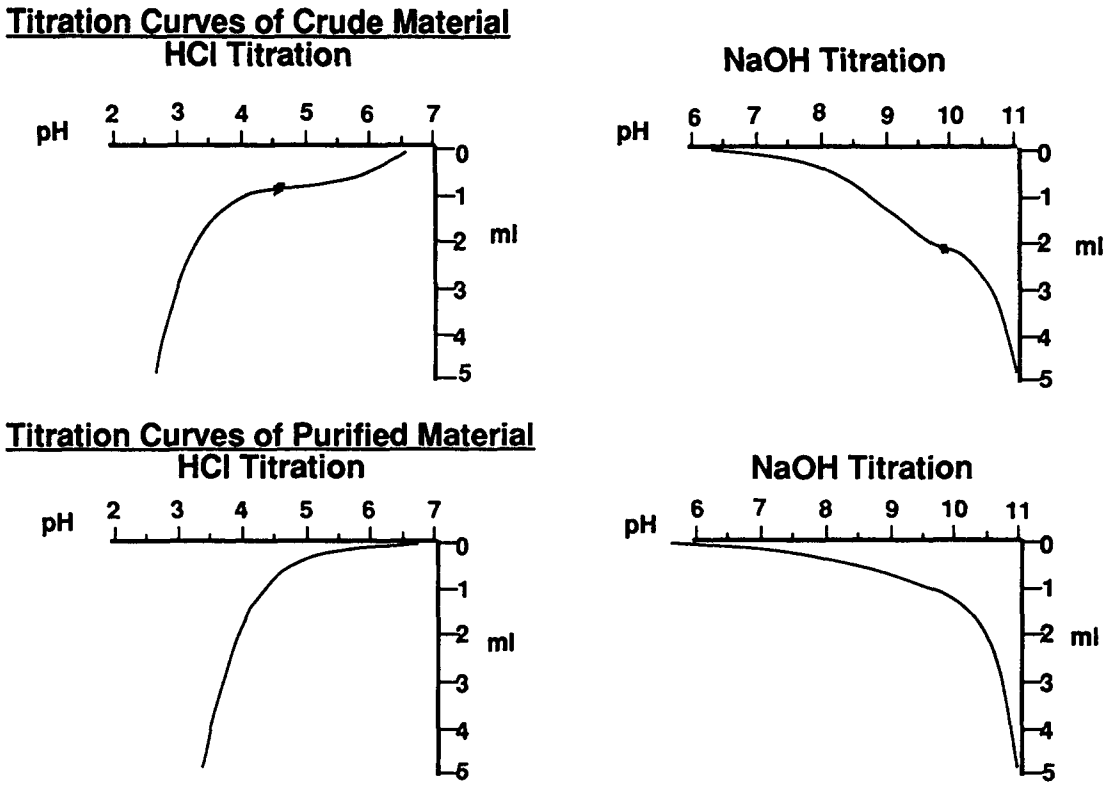
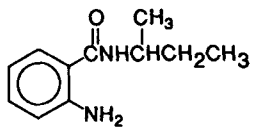
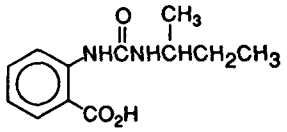


Figure 4 Titration curves showing purification of *o*-aminophenyl amide (**IV**).

rified, and characterized by titration (HCl, $HClO_4$, and NaOH) and by proton and carbon-13-NMR:



o-Aminophenyl Amide (IV)



Urea Carboxylic Acid (V)

Synthesis and Characterization of o-Aminophenyl Amide (IV)

The *o*-aminophenyl amide (**IV**) was prepared by adding isatoic anhydride to an equivalent amount of *sec*-butylamine in water (0.4 *M*) at ambient temperature. After filtration and drying, the product (**IV**) was obtained as a light gray solid. Titration with HCl showed that all *sec*-butylamine had been removed. Titration with NaOH showed that all isatoic anhydride had been removed. These titration curves are given in Figure 4.

A summary of the carbon-13-NMR spectral results of *o*-aminophenyl amide (**IV**) in DMSO-d_6 is given in Table I. An APT (attached proton test) spectrum was also run to help in carbon-13-NMR line assignments. Carbon atoms having an even number of attached protons give positive (up) lines, while carbon atoms having an odd number of attached protons give negative (down) lines. The *o*-aminophenyl amide (**IV**) structure was also approximated from an STN International database.† Agreement is very good except for the C-4 ring carbon atom. The exact structure (**IV**) was not in the database.

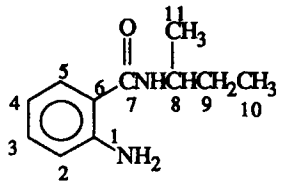
A summary of the proton NMR spectral results of *o*-aminophenyl amide (**IV**) is given in Table II. The line splittings were used, in part, to make line assignments.

Synthesis and Characterization of Urea Carboxylic Acid (V)

The urea carboxylic acid (**V**) was prepared by adding isatoic anhydride to a 10-fold excess of *sec*-butylam-

† Carbon-13-NMR line assignments were approximated using the SPECAL calculation package of SPECINFO database in STN International, Division of American Chemical Society, Columbus, Ohio.

Table I Carbon-13 NMR Structural Assignments for *o*-Aminophenyl Amide (IV):

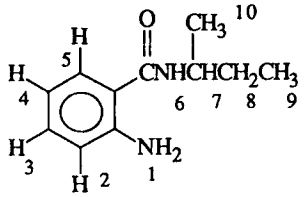


Carbon Atom	Line Assignment[a] (ppm)	APT Spectrum	STN International Assignment[a] (ppm)
1	149.4	Up	149.2
2	115.1	Down	115.2
3	131.7	Down	133.0
4	116.5	Down	122.2
5	128.3	Down	128.3
6	115.9	Up	115.7
7	168.7	Up	167.0
8	46.2	Down	46.3
9	29.1	Up	29.0
10	10.9	Down	10.3
11	20.4	Down	20.1

[a] ppm from tetramethylsilane (TMS = 0); DMSO-d_6 as solvent.

ine in water (6.0*M*) at ambient temperature (see Experimental section). The purification procedure was followed by titration. Figure 5 gives NaOH titration curves for (1) the crude product after first acid treatment, (2) after slurrying in water with pH adjusted to < 2, and (3) the final product after additional water washing. The urea carboxylate (**V**) was prepared as its *sec*-butylamine salt (**VI**). The first titration curve in Figure 5 clearly shows that a considerable amount of salt (**VI**) is present after the first acid wash (material is titrated between first and second break of titration curve).[9] The center titration curve in Figure 5 shows that the amine salt (**VI**) has been removed but indicates a small amount of sulfuric acid present (first break). The third titration curve in Figure 5 shows the purified urea carboxylic acid (**V**) with all base titratable impurities removed.

Table II Proton NMR Structural Assignments for *o*-Aminophenyl Amide (IV)



Hydrogen Atom	Relative Area	Line Assignment[a] (ppm)
1	1.75	3.65 (singlet)
2	1.00	7.46 (doublet)
3	1.05	7.10 (triplet)
4	1.04	6.49 (triplet)
5	1.05	6.67 (doublet)
6	1.01	7.87 (doublet)
7	1.02	3.88 (multiplet)
8	1.98	1.48 (multiplet)
9	2.91	0.85 (triplet)
10	2.95	1.09 (doublet)

[a] ppm from tetramethylsilane (TMS = 0); DMSO-d_6 as solvent.

Since the urea carboxylic acid (**V**) will be present as its *sec*-butylamine salt (**VI**) under basic reaction conditions, a small portion of (**V**) was converted to (**VI**) with *sec*-butylamine. A summary of the carbon-13-NMR spectral results of (**V**) and (**VI**) are given in Table III. The carbon-13-NMR spectra of both materials were compared to an STN International database.[†] Only fair agreement was obtained. Neither compound was present in the database. An APT spectrum of compound (**V**) was also run to help in carbon-13-NMR line assignments.

A summary of the proton NMR spectral results of (**V**) and (**VI**) are given in Table IV. The line

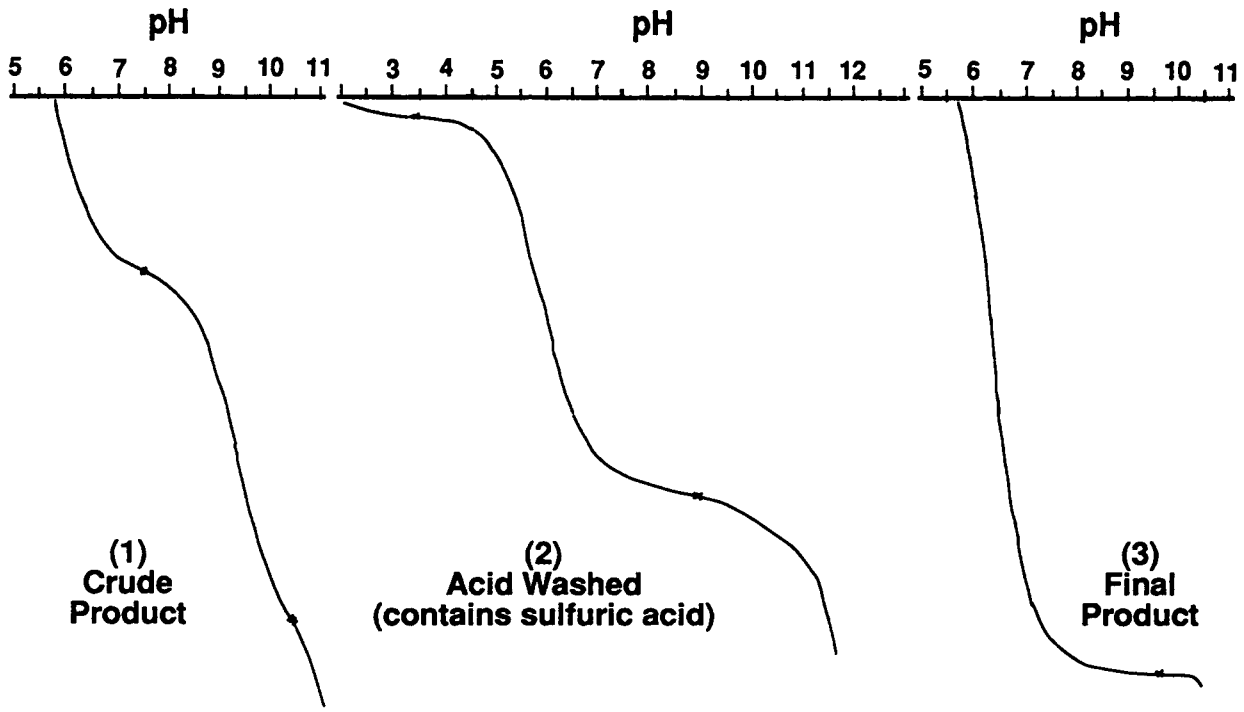
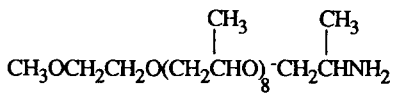


Figure 5 Sodium hydroxide titration curves showing purification stages of urea carboxylic acid (**V**).

splittings were used, in part, to make line assignments.

Effect of Reaction Parameters on Formation of the Corresponding *o*-Aminophenyl Amide and Urea Carboxylic Acid from Jeffamine M-600

The proton NMR spectra provide a quantitative method of obtaining the relative quantities of compounds (**IV**), (**V**), and (**VI**). This technique was used to better understand the effect of selected reaction parameters on the formation of the corresponding *o*-aminophenyl amide (**VII**), urea carboxylic acid (**VIII**), and Jeffamine M-600 salt of the urea carboxylic acid (**IX**) formed by the reactions of Jeffamine M-600 with isatoic anhydride. Jeffamine M-600 much more closely represents the structure of the Jeffamine D-2000 structure, but since it is a monofunctional amine, it is somewhat easier to study:



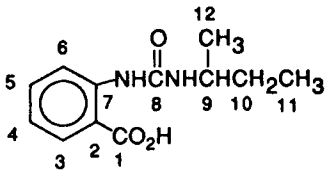
Jeffamine™ M-600

A reaction was set up using a 10 : 1 molar ratio of Jeffamine M-600 to isatoic anhydride. After the isatoic anhydride had reacted, a sample was taken for NMR analysis. Then, additional isatoic anhydride was added batchwise to adjust the Jeffamine M-600-to-isatoic anhydride molar ratio to 4 : 1. This stepwise reaction sequence and NMR sampling procedure was continued through 2 : 1, 1.33 : 1, and 1 : 1 Jeffamine M-600 to isatoic anhydride molar ratios.

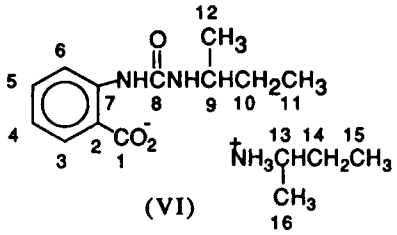
Each sample was analyzed by proton NMR for the relative amounts of (**VII**), (**VIII**), and (**IX**). Figure 6 shows the proton NMR spectrum of the aromatic protons for the product distribution at the 1.33 : 1 molar ratio stage. *o*-Aminophenyl amide (**VII**) is clearly the major product as evidenced by the strong lines centered at 7.45 (doublet), 7.10 (triplet), 6.67 (doublet), and 6.48 (triplet) ppm. The Jeffamine M-600 salt of the urea carboxylic acid (**IX**) is clearly present as evidenced by the weaker lines centered at 8.24 (doublet), 7.90 (doublet), 7.14 (triplet), and 6.73 (triplet) ppm. The urea carboxylic acid (**VIII**) is absent at this reactant ratio (see Table IV).

The data from this reaction series are summarized in Table V. Clearly, the relative amount of *o*-aminophenyl amide (**VII**) increases as the Jeffamine M-600 : isatoic anhydride molar ratio decreases

Table III Carbon 13-NMR Structural Assignments for Urea Carboxylic Acid (V) and Its *sec*-Butylamine Salt (VI):



(V)



(VI)

Carbon Atom	(V) APT Spectrum	Line Assignments[a] (ppm) Compound (V)	STN Int[b]	Compound (VI)	STN Int
1	Up	169.4	169.3	170.8	176.2
2	Up	114.4	116.0	120.9	111.8
3	Down	138.8	130.7	130.7	130.7
4	Down	119.7	121.7	119.0	121.7
5	Down	133.5	134.8	130.9	134.8
6	Down	119.1	120.0	118.2	120.0
7	Up	143.3	149.0	142.7	149.0
8	Up	154.2	154.2	154.8	154.2
9	Down	46.5	46.6	46.6	46.6
10	Up	29.1	29.8	29.3	29.8
11	Down	10.5	10.3	10.6	10.3
12	Down	20.5	20.8	20.6	20.8
13				47.9	nd
14				27.2	nd
15				9.7	nd
16				17.7	nd

[a] ppm from tetramethylsilane (TMS = 0); DMSO-d_6 as solvent; nd = not determined.

through the range studied. It is easier to see these changes if the data are recalculated to show the concentration and changes in concentration of each species under the changing reaction conditions (see Table VI). These changes in concentrations are plotted in Figure 7. Clearly, the Jeffamine M-600 salt of the urea carboxylate (**IX**) is formed early in the reaction sequence at high amine : isatoic anhydride molar ratios and highly basic conditions. There are essentially no additional amounts of (**VIII**) and/or (**IX**) formed after the 2 : 1 molar ratio sample.

The final product in the above study (1 : 1 molar ratio) was studied in greater detail by a series of titration curves (see Fig. 8):

(a) $HClO_4$ 1.2030 meq/g
(b) HCl 0.0792 meq/g
(c) NaOH 0.1288 meq/g (first break)
0.0876 meq/g (second break)

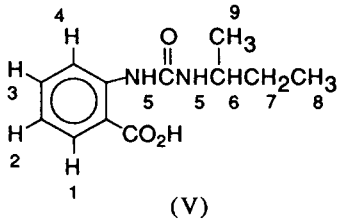
The $HClO_4$ titration gives the total amine present. The HCl titration gives only the aliphatic amine as free Jeffamine M-600 and/or the Jeffamine M-600 salt of the urea carboxylic acid (**IX**):

1.2030 meq/g $HClO_4$ titration
−0.0792 meq/g HCl titration
1.1240 meq/g *o*-aminophenyl amide (**VII**)

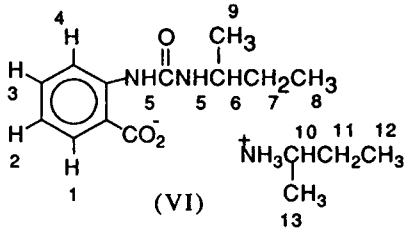
$$\frac{(1.124 \text{ meq/g})(722)(100)}{(1000 \text{ mg/g})} = 81.1 \text{ wt \% (VII)}$$

The NaOH titration shows two breaks: The first break represents titration of the carboxylic acid moiety on the urea carboxylic acid (**VIII**). The second break represents titration of residual isatoic anhydride and/or the Jeffamine M-600 salt (**IX**) by the displacement of a weaker base with a stronger base in a salt. Since the proton NMR indicates that most of the carboxylic acid derivative is present as

Table IV Proton NMR Structural Assignments for Urea Carboxylic Acid (V) and Its *sec*-Butylamine Salt (VI):



(V)



(VI)

Hydrogen Atom	Relative Area (V)	(V) Line Assignment[a] (ppm)	(VI) Line Assignment[a] (ppm)
1	1.02	7.89 (doublet)	7.91 (doublet)
2	1.00	7.44 (triplet)	7.24 (triplet)
3	1.04	6.91 (triplet)	6.80 (triplet)
4	0.99	8.39 (doublet)	8.28 (doublet)
5	0.88	7.22 (doublet)	6.75 (doublet)
6	1.07	3.59 (multiplet)	3.58 (multiplet)
7	1.95	1.42 (multiplet)	1.41 (multiplet)
8	2.89	0.89 (triplet)	0.88 (triplet)
9	2.91	1.05 (doublet)	1.04 (doublet)
10			3.11 (multiplet)
11			1.65 (multiplet)
12			0.84 (triplet)
13			1.17 (doublet)

[a] ppm from tetramethylsilane (TMS = 0); DMSO-d_6 as solvent.

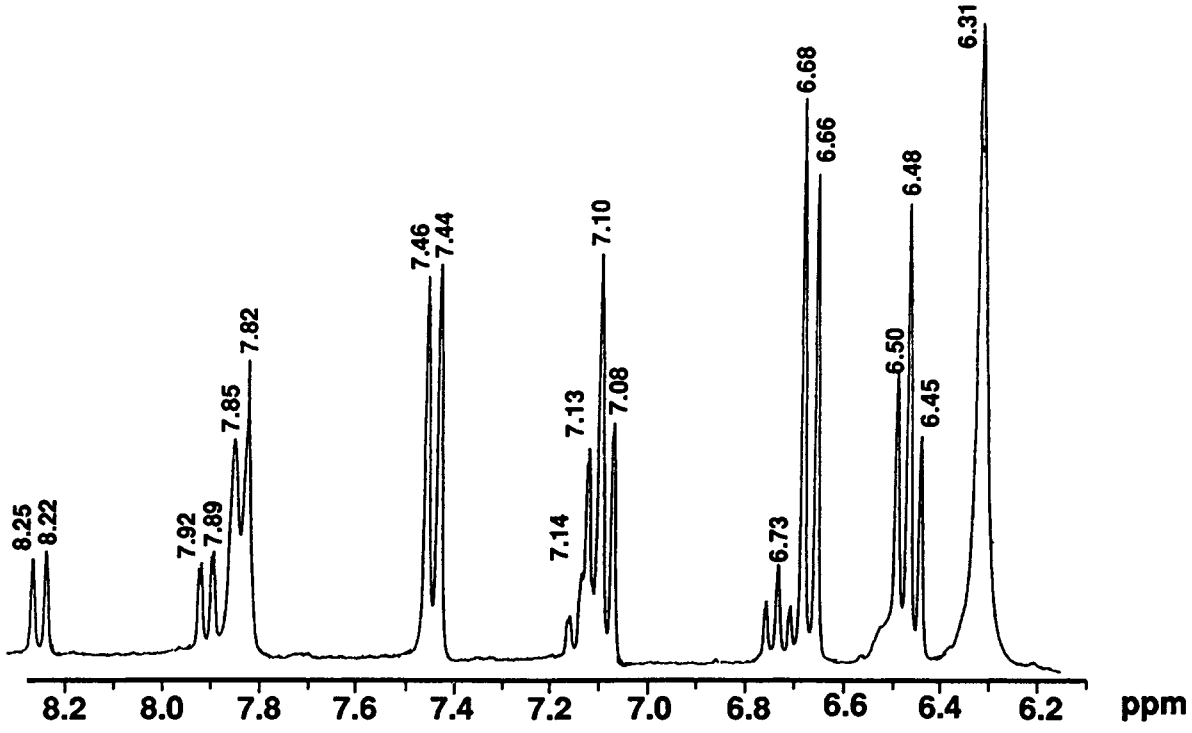


Figure 6 Proton NMR spectrum of Jeffamine M-600 and isatoic anhydride adduct using 1.33 : 1 molar ratio.

Table V Effect of Reaction Parameters on Formation of (VII), (VIII), and (IX)

Sample No.	% Isatoic Anhydride Added	M-600 : IA Molar Ratio	Reaction Temp. (°C)	Time before Next Addition	% Product (by Proton NMR) (VII)	(VIII)	(IX)
A	10	10 : 1	24–30	15 min	53.6	0	46.4
B	25	4 : 1	30–34	30 min	62.4	0	37.6
C	50	2 : 1	28–32	30 min	74.2	0	25.8
D	75	1.33 : 1	24–28	16 h	82.7	0	17.3
E	100	1 : 1	24–27	40 h	87.0	← 13.0 →	

(**VIII**), the second break is calculated as isatoic anhydride:

$$\frac{(0.1288 \text{ meq/g})(766)(100)}{(1000 \text{ mg/g})} = 9.9 \text{ wt \% (VIII)}$$

$$\frac{(0.0876 \text{ meq/g})(163)(100)}{(1000 \text{ mg/g})}$$

$$= 1.4 \text{ wt \% isatoic anhydride}$$

The HCl titration determines any free Jeffamine M-600 and/or the amine salt (**IX**):

$$\frac{(0.0792 \text{ meq/g})(603)(100)}{(1000 \text{ mg/g})} = 4.8 \text{ wt \% M-600}$$

Summary:

	Wt %
o-Aminophenyl amide (**VII**)	81.1
Urea carboxylic acid (**VIII**)	9.9
Jeffamine M-600	4.8
Isatoic anhydride	1.4
Total	97.2

The carbon-13-NMR spectrum of this reaction product (1 : 1 molar ratio) is given in Figure 9 and the proton NMR spectrum is given in Figure 10. They are consistent with the expected spectra based on the above analysis. The ratio of (**VII**) to (**VIII**) by titration is 81.1 : 9.9 (normalized to 89.1 : 10.9). The same ratio by proton NMR is 87.0 : 13.0. This is very good agreement and further substantiates the validity of proton NMR as an analytical tool.

Product Using Process of Texaco Patents[14–16]

Now that an analytical understanding has been developed for the reactions of (1) *sec*-butylamine with isatoic anhydride and (2) Jeffamine M-600 with isatoic anhydride, the product formed using the Marquis and Yeakey[14] procedure can be reexamined with much more detailed understanding.

A second appraisal of the carbon-13-NMR spectrum of a 1 : 1 equivalent ratio of the reactions of Jeffamine D-2000 with isatoic anhydride made by the Marquis and Yeakey process (Fig. 2) shows that the larger line pattern represents the corresponding *o*-aminophenyl amide product, whereas the smaller line pattern represents the corresponding urea carboxylic acid and/or its amine salt.

Table VI Effect of Reaction Parameters on Changes in (VII), (VIII), and (IX) Concentrations

Sample No.	% Isatoic Anhydride Added	Mol M-600 Converted[a]	Mol Product (VII)	Mol Products (VIII) and (IX)	Changes in Mol of Products (VII)	(VIII) and (IX)
A	10	0.010	0.0054	0.0046	0.0054	0.0046
B	25	0.025	0.0156	0.0094	0.0102	0.0048
C	50	0.050	0.0371	0.0129	0.0215	0.0035
D	75	0.075	0.0620	0.0130	0.0249	0.0001
E	100	0.100	0.0870	0.0130	0.0250	0.0000

[a] Assumes complete M-600 conversion.

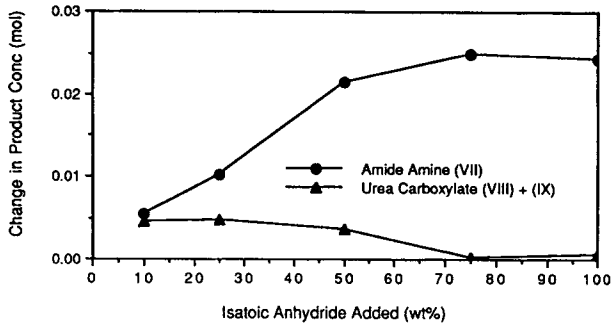


Figure 7 Change in product distribution with added isatoic anhydride.

The proton NMR spectrum of the aromatic region is given in Figure 11. All lines are consistent with the above analysis. The integrated spectrum indicates an *o*-aminophenyl amide : urea carboxylic acid molar ratio of 86.8 : 13.2. Therefore, the Marquis and Yeakey process does not produce *o*-aminophenyl amides with sufficient selectivities to be of general use for urethane/urea polymers.

Improved Process for making *o*-Aminophenyl Amides of Aminated Poly(propylene glycols)

The results suggest that it should be possible to minimize (or eliminate) the amount of urea carboxylic acid and/or its salt formed by adding the aminated poly(propylene glycol) to the isatoic anhydride. However, this represents a serious handling and mixing problem since isatoic anhydride is a fluffy solid that decomposes at its melting point (233°C). It is much easier to add the solid isatoic anhydride to the well-stirred, liquid aminated poly(propylene glycol) as done in the Texaco process.

One way to work with a solid is to disperse it in an inert fluid. In this way, a well-defined quantity of solid isatoic anhydride can be dispersed under conditions of good mixing and temperature control and the aminated poly(propylene glycol) can be added at a controlled rate. By balancing the reaction temperature and addition rate, the majority of the aminated poly(propylene glycol) can be reacted as it is added and thereby never produce a condition where a local excess of the polyamine is present.[13]

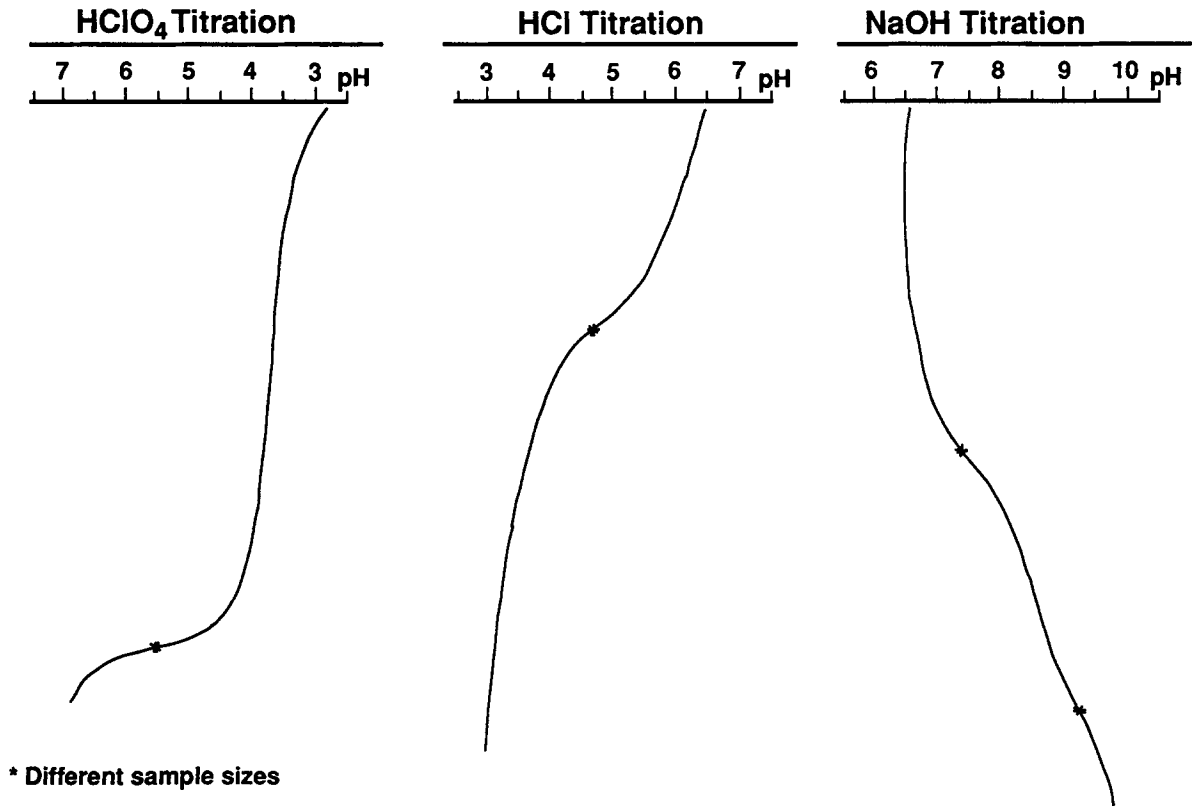


Figure 8 Titration analysis of Jeffamine M-600 and isatoic anhydride adduct using 1 : 1 molar ratio.

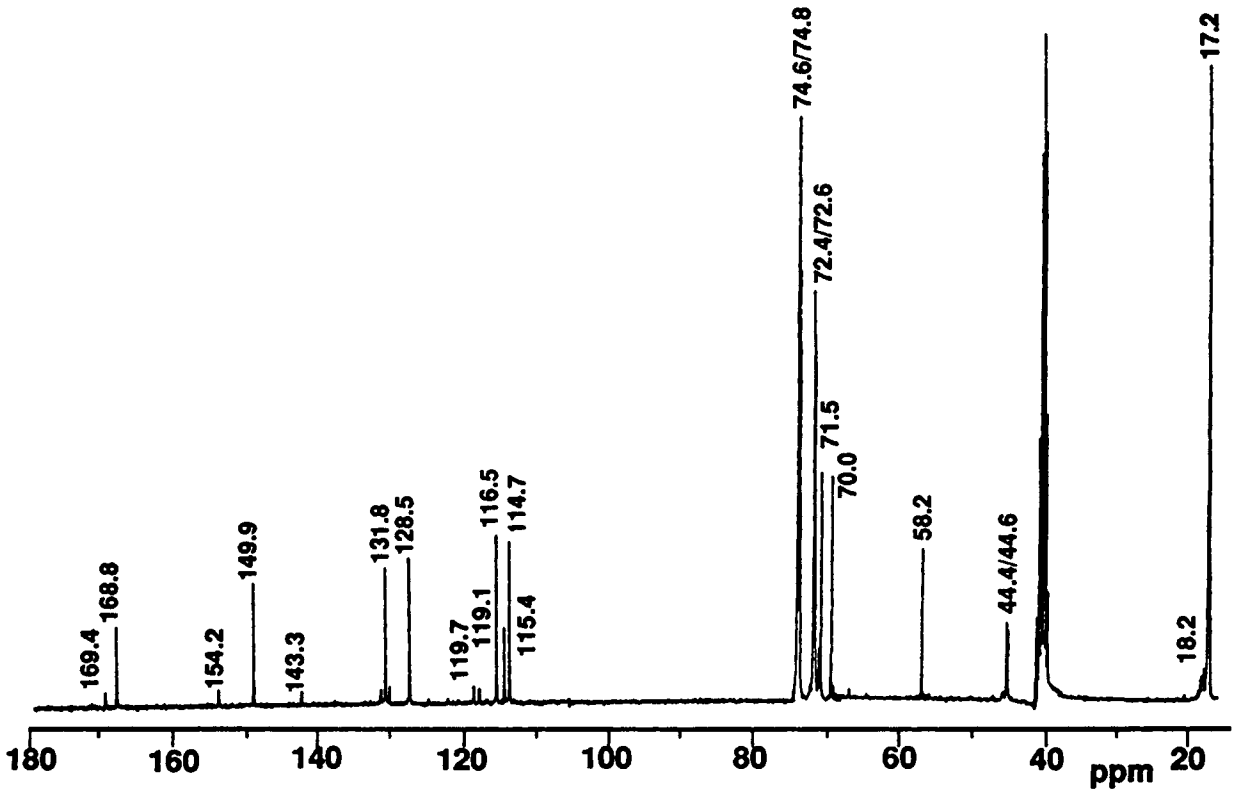


Figure 9 Carbon-13 NMR spectrum of Jeffamine M-600 and isatoic anhydride adduct using 1 : 1 molar ratio.

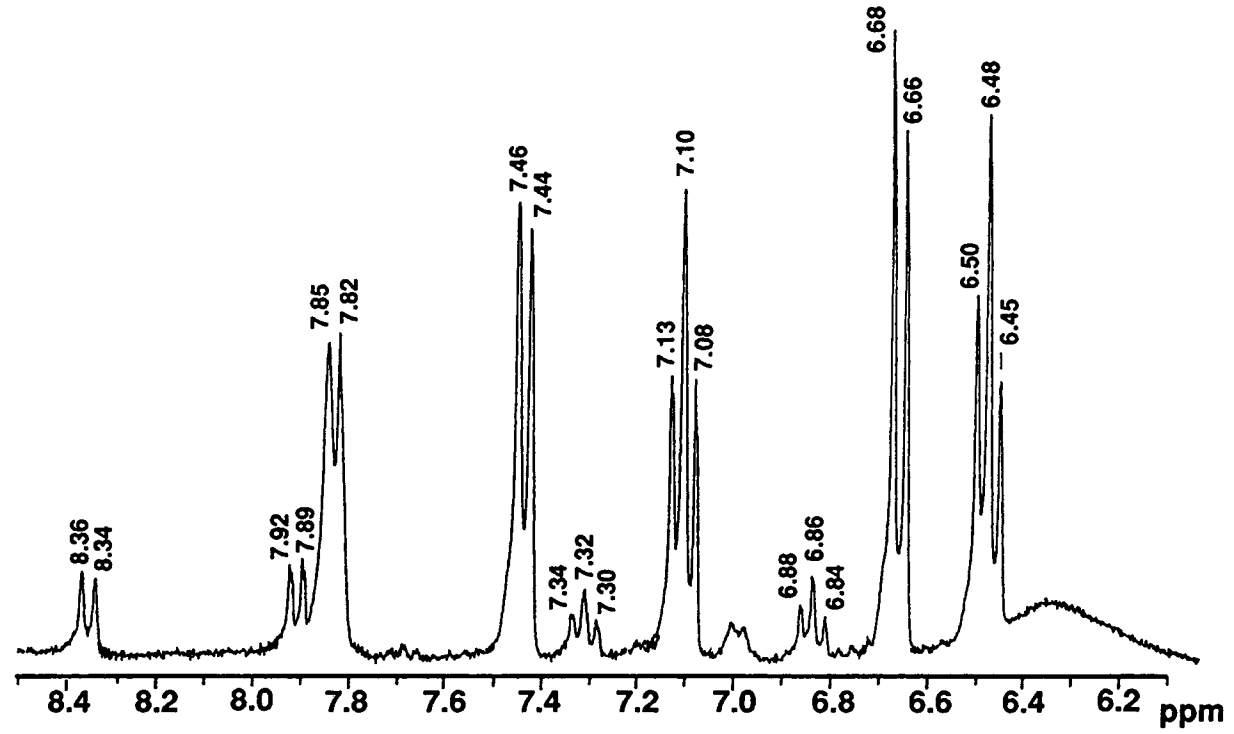


Figure 10 Proton NMR spectrum of Jeffamine M-600 and isatoic anhydride adduct using 1 : 1 molar ratio.

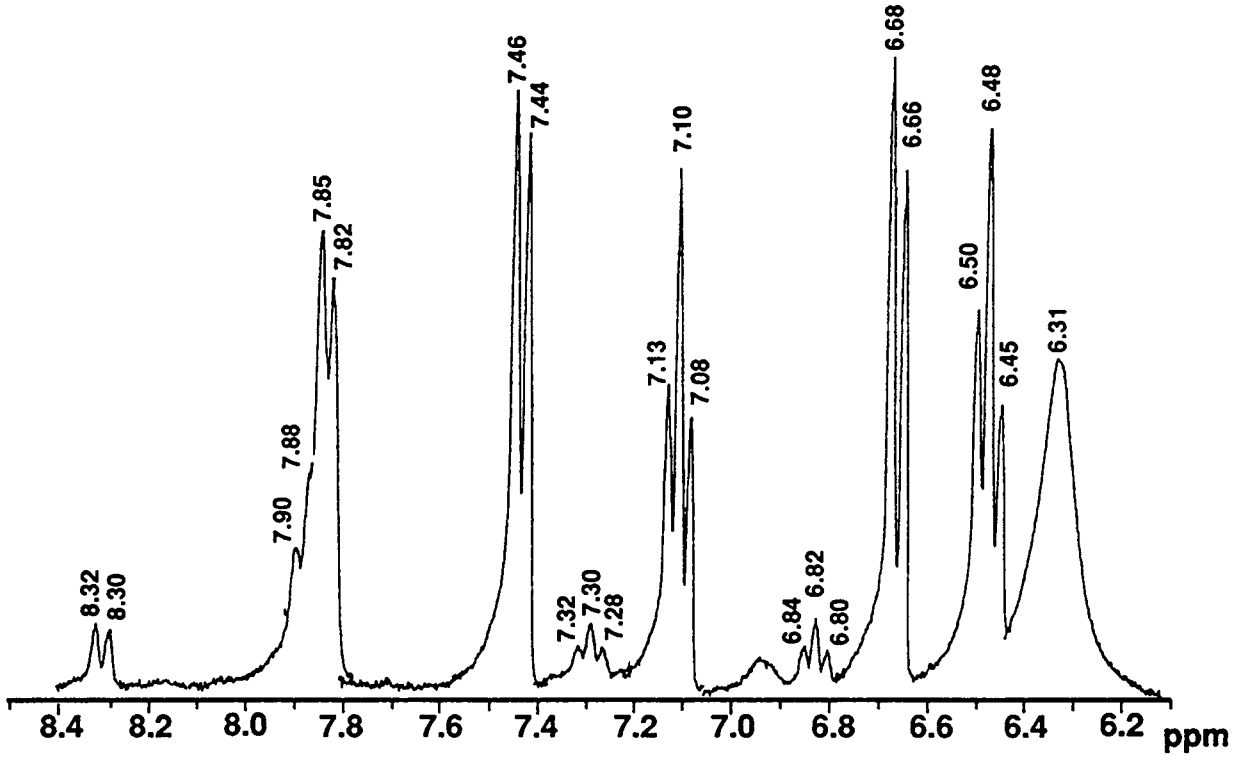


Figure 11 Proton NMR spectrum of Jeffamine D-2000 and isatoic anhydride adduct using conditions of Marquis and Yeakey patent (**X**).

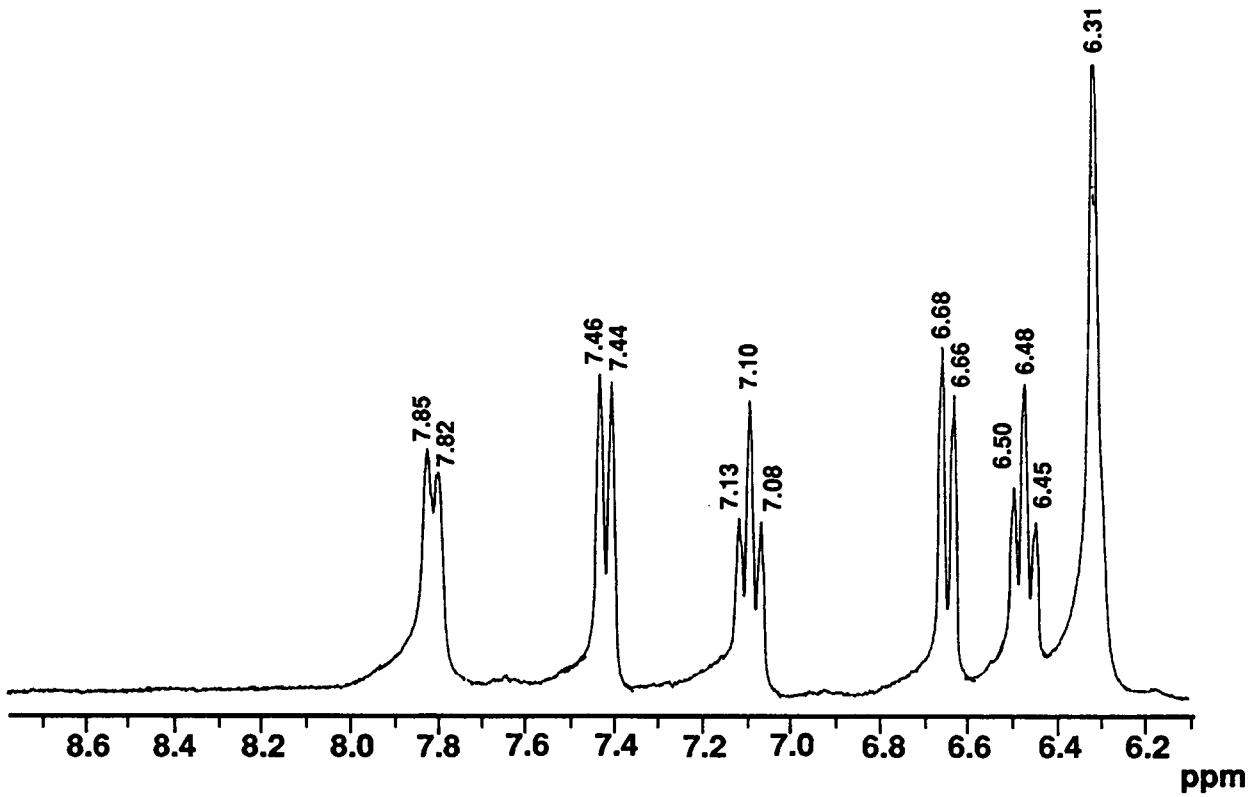
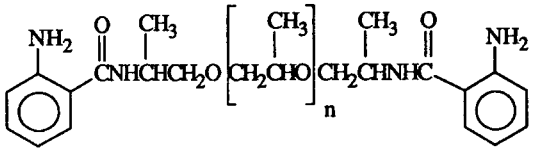


Figure 12 Proton NMR spectrum of *o*-aminophenyl amide based on Jeffamine D-2000 (**XII**).

A variety of materials should be useful as inert fluids. Aromatic hydrocarbons, such as toluene, should be good dispersing liquids and easily stripped from the product after reaction. The more volatile ketones should also be useful.

Results of using the dispersing fluid concept are summarized in Table VII. Sample **X** represents the conditions of the Texaco process; 13.2 mol % of the aromatic region of the proton NMR spectrum is represented by urea carboxylic acid. In sample **XI,** isatoic anhydride was placed in the reactor and D-2000 was added quickly (5 min). The urea carboxylate content was nearly unchanged at 12.2 mol %. However, in sample **XII,** the isatoic anhydride was slurried in toluene at 60°C and D-2000 was added dropwise over 90 min period. After additional heating and toluene removal, there was no detectable urea carboxylic acid and/or its salt present.[13] The product was 94.9 wt % of the corresponding *o*-aminophenyl amide and 3.8 wt % unreacted amino end groups (calculated as D-2000):



These compositional changes are clearly evident in the proton NMR spectra of these materials. In sam-

Table VII Summary of Experimental Results

Sample	Mol Reactant D-2000	Mol Reactant IA	Dispersing Solvent	D-2000 Addition Time (min)	Reaction Temp during Addition (°C)	Additional Heating Schedule	% Amine Conversion	Mol % *o*-Amino Amide	*o*-Amino Amide : Urea Carboxylic Acid Molar Ratio
X	0.100	0.200	None	IA added to amine	30–40	40°C/2 h 50°C/16 h 100°C/5 h 150°C/3 h	95.9	81.0	87.8/12.2
XI	0.100	0.200	None	5	40	40°C/1 h 50°C/1 h 90°C/5 h 150°C/3 h	95.4	86.3	88.8/11.2
XII	0.100	0.200	Toluene	90	60	60°C/1 h 125°C/2 h/1 mm 150°C/3 h	95.7	95.1	100/0
XIII	0.100	0.200	Toluene	110	100	100°C/1 h 100°C/2 h/1 mm 150°C/3 h	93.6	90.8	100/0
XIV	0.100	0.200	Acetone	75	50	50°C/20 h 90°C/1 h/1 mm 150°C/3 h	94.9	93.8	100/0
XV	0.100	0.200	MEK	73	75	75°C/18 h 110°C/2 h/1 mm 150°C/3 h	95.2	93.6	100/0
XVI	0.100	0.210	Toluene	92	40	100°C/3 h 110°C/3 h/1 mm 150°C/3 h	96.5	93.4	98.2/1.8
XVII	0.100	0.210	Toluene	120	60	60°C/5 h 125°C/1 h/1 mm 150°C/3 h	97.3	96.3	99.0/1.0
XVIII	0.100	0.210	Toluene	95	80	80°C/3 h 110°C/2 h/1 mm 150°C/3 h	96.8	94.4	100/0
XIX	0.100	0.210	Toluene	82	100	100°C/3 h 120°C/3 h/1 mm 150°C/3 h	96.7	96.0	99.5/0.5

Table VIII Results Using Previous Product to Disperse Isatoic Anhydride; D-2000 Added Dropwise to Isatoic Anhydride at 60°C

Sample	o-Amino Amide : Urea Carboxylic Acid Molar Ratio	o-Amino Amide (Wt %)	Urea Carboxylic Acid and/or Salt (Wt %)	D-2000 (Wt %)	Total (Wt %)
XII	100 : 0	94.9	0	3.8	98.7
XX	100 : 0	95.7	0	4.2	99.9
XXI	100 : 0	94.9	0	3.5	98.4

ple **X** (Fig. 11; 6.0–8.8 ppm), urea carboxylic acid (ring protons) is indicated by lines centered at 8.34 (doublet), 7.88 (doublet), 7.34 (triplet), and 6.86 (triplet) ppm. Sample **XI** has a similar spectrum. However, no urea carboxylic acid or its salt is detected in the proton NMR spectrum of sample **XII** (Fig. 12).

Additional experiments (Table VII) indicate that reaction temperatures from 60 to 100°C are useful for making high-quality material. It appears that 40°C (sample **XVI**) is not quite hot enough. Ketones such as acetone and methyl ethyl ketone are very effective dispersing fluids. Small excesses of isatoic anhydride can also be used.

Methanol is not a good dispersing fluid since it is not inert to the reaction conditions. The polyamine catalyzes the reaction of methanol with isatoic anhydride to yield the methyl ester of anthranilic acid. Presumably, other alcohols will react in a similar manner.

A preferred inert dispersing fluid is a portion of a product made in a previous run. The *o*-aminophenyl amide product from D-2000 and isatoic anhydride was used for this purpose and performed very well.[13] Table VIII compares a product made at 60°C using toluene as the dispersing fluid (**XII**) to two products made using a previous product as dispersing fluid (**XX** and **XXI**). After the addition of D-2000 is complete (at 60°C), the reaction temperature is increased to 150°C for 3 h to complete the reaction. The product can be used as is, since there is no dispersing fluid to remove.

Use of Other Aminated Polyols

Several other aminated polyols were converted to the corresponding *o*-aminophenyl amide derivatives by this improved process (Table IX).[13] Urea carboxylic acid was only detected in the product derived from Jeffamine T-403. The products can be very viscous. Viscosity appears to be a consequence of functionality (number of amide moieties/molecule) and block size (molecular weight between amide moieties). Lower block size and/or higher functionality lead to higher viscosity.

Product Characterization by NMR

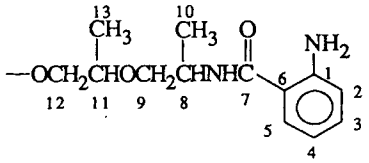
During the course of this study, a variety of materials were made in which the end groups were very similar. Carbon-13-NMR and proton NMR line assignments of these *o*-aminophenyl amide end groups based on *sec*-butylamine, Jeffamine M-600, Jeffamine D-2000, and Jeffamine D-400 are compared in Tables X and XI, respectively. Agreement is excellent. It was also

Table IX Summary of Results Using Various Aminated Poly(Propylene Glycols)[a]

Sample No.	Amine	% Amine Conversion	o-Amino Amide (mol %)	o-Amino Amide : Urea Carboxylic Acid Molar Ratio	o-Amino Amide (Wt %)	Urea Carboxylic Acid (Wt %)	Starting Amine (Wt %)	Brookfield Viscosity (cps; 22°C)
XII	D-2000	95.7	95.1	100 : 0	94.9	0.0	3.8	2,860
XXII	T-5000	95.9	93.0	100 : 0	93.3	0.0	3.9	3,710
XXIII	D-400	93.2	92.4	100 : 0	92.3	0.0	4.5	670,500
XXIV	T-403	89.5	85.5	95.8 : 4.2	85.8	4.4	5.9	> 2,000,000
XXV	M-600	97.0	91.3	100 : 0	91.4	0.0	2.5	910

[a] All reactions were carried out by the dropwise addition of the amine to a slurry of isatoic anhydride in toluene at 60°C using equivalent quantities of amine and isatoic anhydride.

Table X Carbon-13 NMR Line Assignments for *o*-Aminophenyl Amides from Different Secondary Amines:



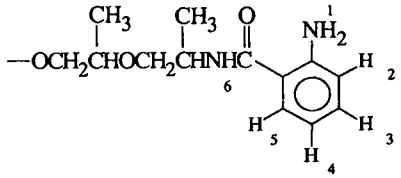
Carbon Atom	Line Assignments[a] of Corresponding *o*-Aminophenyl Amides Made from Different Secondary Amines (ppm)			
	sec-Butylamine (IV)	M-600 (XXV)	D-2000 (XII)	D-400 (XXIII)
1	149.4	149.9	149.9	149.9
2	115.1	114.7	114.7	114.7
3	131.7	131.8	131.8	131.8
4	116.5	116.5	116.5	116.5
5	128.3	128.5	128.5	128.5
6	115.9	115.4	115.4	115.4
7	168.7	168.8	168.8	168.8
8	46.2	44.4/44.6	44.4/44.6	44.4/44.6
9	29.1	71.6/71.8	71.6/71.8	71.6/71.8
10	20.4	18.2	18.2	18.2
11	—	74.6/74.8	74.6/74.8	74.6/74.8
12	—	72.4/72.6	72.4/72.6	72.4/72.6
13	—	17.2	17.2	17.2

[a] ppm from tetramethylsilane (TMS = 0); DMSO-d_6 as solvent.

possible to confirm line assignments by line intensity changes. For example, there is a fivefold increase in the number of methylene groups associated with an end group (carbon 9, Table X) relative to methylene groups associated with the backbone repeat unit (carbon 12, Table X) in going from a D-2000-based product to a D-400-based product.

The proton NMR and carbon-13-NMR spectra

Table XI Proton NMR Line Assignments for *o*-Aminophenyl Amides from Different Secondary Amines:



Hydrogen Atom	Multiplicity	Line Assignments[a] of Corresponding *o*-Aminophenyl Amides Made from Different Secondary Amines (ppm)			
		sec-Butylamine (IV)	M-600 (XXV)	D-2000 (XII)	D-400 (XXIII)
1	Singlet	6.25	6.31	6.31	6.32
2	Doublet	7.46	7.45	7.45	7.44
3	Triplet	7.10	7.10	7.10	7.11
4	Triplet	6.49	6.48	6.48	6.48
5	Doublet	6.67	6.67	6.67	6.68
6	Doublet	7.87	7.84	7.84	7.85

[a] ppm from tetramethylsilane (TMS = 0); DMSO-d_6 as solvent.

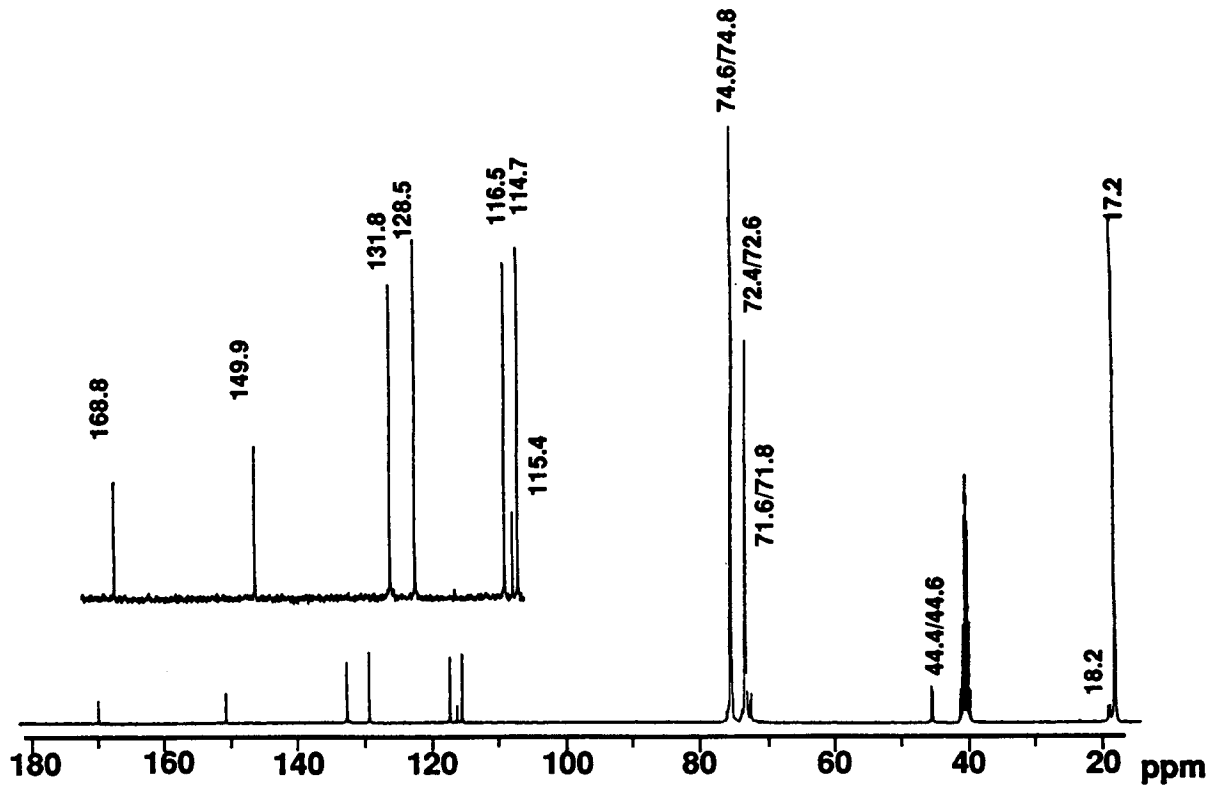


Figure 13 Carbon-13-NMR spectrum of *o*-aminophenyl amide based on Jeffamine D-2000.

of the *o*-aminophenyl amide of D-2000 are given in Figures 12 and 13, respectively, since this material has not been previously reported in this state of high purity.

CONCLUSIONS

Although Marquis and Yeakey[14] reported that aminated poly(propylene glycols) react with isatoic anhydride to yield cleanly the corresponding *o*-aminophenyl amide (**II**), this paper shows that a competing reaction leads to the formation of about 10% of the corresponding urea carboxylic acid (**III**) under their conditions. Reaction with isatoic anhydride would provide a way to reduce the reactivity of these polyamines toward polyisocyanates and, thereby, increase their utility. However, the presence of 10% of an impurity (unreactive toward polyisocyanates) limits the usefulness of (**II**) in urethane/urea polymers.

Model compounds have been used to define the course of these reactions. Structural assignments have been established by proton and carbon-13-NMR. A procedure has been developed to quantify (**II**) and (**III**). Based on the insight gained with these model compounds, a process has been developed to produce the corresponding *o*-aminophenyl amide derivatives of aminated poly(propylene glycols) in a state of high purity ($\sim$ 100%). A given aminated poly(propylene glycol) is added dropwise to a slurry of isatoic anhydride in an inert fluid (such as toluene or a previously prepared product) at a temperature (60–100°C) at which reaction is rapid. Local excesses of unreacted amine are minimized to prevent formation of urea carboxylic acid impurities.

Using this new process,[13] the corresponding *o*-aminophenyl amide (**II**) has been prepared in a state of high purity, suitable for polymer preparations by reactions with polyisocyanates. This new process has general application and has been applied to the preparation of the corresponding derivatives of a variety of aminated poly(propylene glycols). Products have been characterized by potentiometric titration and by proton and carbon-13-NMR spectroscopy. Polymers based on the reaction products of these polyamines and polyisocyanates, which have potential utility in high modulus automotive body panel applications, will be the subject of a subsequent publication.

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