

# Specialty Polyurethane Soft Segments. III. Synthesis and Characterization of *N*-Isopropyl Polyether Polyamine Oligomers Containing Backbone Urea or Amide Moieties

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## SYNOPSIS

Primary polyether polyamine oligomers containing preformed urea or amide moieties in their backbones were converted to the corresponding *N*-isopropyl polyether polyamine oligomers (secondary amines) by reaction with acetone and hydrogen in the presence of a catalyst. The best results were from reactions carried out at about 150°C using a supported platinum or palladium catalyst in a fixed bed. Reactants and products were monitored by quantitative carbon-13 NMR, size exclusion chromatography, and amine titration. Perchloric acid titration was used to quantify the number of urea moieties per molecule. Amide backbone materials gave very little backbone degradation. However, some backbone degradation was observed with urea backbone materials, leading to products with lower molecular weights. These polyether polyamine oligomers, containing urea or amide moieties in their backbones, are useful in urethane/urea polymer systems. The lower reactivity of these secondary amines (toward polyisocyanates) results in their utility in a broader range of polyurethane fabrication technologies. © 1992 John Wiley & Sons, Inc.

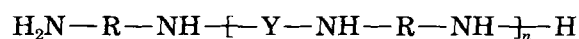
## INTRODUCTION

The (AB)<sub>*n*</sub> block copolymers are a major structural class of urethane/urea polymer systems, where A and B represent hard segment and soft segment blocks. Hydrogen bonding has a strong influence on the properties of these block copolymers, forming physical crosslinks between the hard segment molecules leading to microphase separation and further crosslinking of the hard segment blocks. If hydrogen bonding sites are also present in the backbone of the soft segment, then additional interactions are possible. These soft segment to soft segment and soft segment to hard segment interactions can lead to different polymer morphologies and properties.

There are a variety of moieties which can function as hydrogen bonding donor and/or acceptor sites if present in the backbone of a polyol or polyamine: Urethane, urea, thiourea, carbonate, amide, and

biuret are representatives of such moieties. Previous work from this laboratory has been concerned with effects of polyether polyols containing carbonate<sup>1-12</sup> moieties and polyether polyamines (primary amines) containing urea<sup>13,14</sup> moieties to control physical properties in polyurethane/urea systems. This paper deals with the synthesis and characterization of polyether diamines (secondary amines) containing urea or amide moieties in their backbones. Secondary amino end groups have significantly reduced reactivity toward polyisocyanates (relative to primary amines) and allow the incorporation of these materials into a wide variety of polyurethane/urea systems.

We are developing an approach to systems containing urea or amide moieties by studying the utility of polyether diamine oligomers containing preformed urea or amide moieties in their backbone. The general structure is depicted by



where R represents the polyether segments and Y

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is either —CO— (for urea) or —COR'CO— (for amide).

The primary, urea-containing aliphatic diamines are easily prepared from polyether diamines by their reaction with certain carbonates, phosgene, urea, or carbon dioxide. Several examples can be cited. For instance, Yamazaki<sup>15</sup> has reported the reactions of diamines with diphenyl carbonate to produce urea-modified diamines of the type shown above. The use of polyether polyamines is described by Waddill and Schulze<sup>16,17</sup> and alkylene carbonates are reported by Camerisi<sup>18</sup> to react with 1,6-diaminohexane. Polyether diamines also react with phosgene to produce materials containing urea moieties in their backbone<sup>16,17</sup> and Giori<sup>19</sup> has made related materials by the reaction of amino alcohols with phosgene. Yamazaki<sup>20-23</sup> has also made polyether polyamines containing urea moieties by the reaction of polyamines with carbon dioxide in the presence of diphenyl phosphite and pyridine.

Another very useful method for preparing polyether polyamines containing urea moieties in their backbone is by the reaction of urea with polyether polyamines. Some materials of this general type containing a low level of backbone urea moieties (mostly one per molecule) have been used as epoxy curing agents, sometimes in the presence of carboxylic anhydrides.<sup>16,17,24-26</sup> This is the general method used to prepare the urea backbone materials described in this paper. Prior to this work, the use of urea backbone modified polyether polyamines had not been reported in the synthesis of urethane/urea polymers.<sup>27,28</sup>

The primary, amide-containing aliphatic diamines are easily prepared from polyether diamines by their reaction with polycarboxylic acids, polycarboxylic acid esters, or polycarboxylic acid chlorides.<sup>27-32</sup> Polycarboxylic acids were used to prepare the primary, amide-containing aliphatic diamines described in this paper.

Subsequent papers in this series will detail the synthesis and characterization of other hydrogen bonding soft segment materials and will demonstrate the use of this hydrogen bonding to control and enhance polymer properties.<sup>33,34</sup>

## EXPERIMENTAL

### Materials

Jeffamine D-400 and D-2000, manufactured by Texaco, are aminated poly(propylene glycol)s having approximately 400 and 2000 g/mol molecular

weights, respectively. Urea, adipic acid, and acetone were purchased from the Aldrich Chemical Co. Palladium (0.3%) on carbon (4 × 8 mesh) catalyst was purchased from Girdler. Platinum (0.3%)-palladium (0.3%) on Al<sub>2</sub>O<sub>3</sub> pellets ( $\frac{1}{8}$  in.) catalyst and platinum (1.0%) on Al<sub>2</sub>O<sub>3</sub> pellets ( $\frac{1}{8}$  in.) catalyst were purchased from Engelhard. Platinum oxide powder catalyst and palladium oxide powder catalyst were purchased from Alfa. Perchloric acid (0.1*N* solution in acetic acid) and glacial acetic acid were purchased from the Fisher Scientific Co.

### Typical Synthesis of a Polyether Polyamine Oligomer (I) Containing Urea Backbone Moieties<sup>13,27</sup>

Jeffamine D-400 (3367.6 g, 7.514 mol) and urea (347.1 g, 5.780 mol) were mixed in a D-400 : urea molar ratio of 1.30 : 1 in a 5-L, three-necked flask equipped with an overhead stirrer, condenser, thermometer, nitrogen purge, and temperature controller. The exit from the condenser was attached to an aqueous scrubber to adsorb the byproduct ammonia. Nitrogen was slowly purged through the system, and the mixture was heated at 150°C for 24 h. The resultant viscous liquid was transferred to a rotary evaporator operating at 90°C under a 20 mm Hg vacuum to remove residual ammonia. The product weighed 3508.0 g, which corresponds to a weight loss of 206.7 g (based on reactants). The product was a clear, viscous liquid having the following properties: amine content, 1.019 meq/g (determined by titration of a methanolic solution with 0.1*N* aqueous HCl) which corresponds to a diamine molecular weight of 1964 g/mol; 3.19 urea moieties per average molecule (determined by titration of an acetic acid solution with 0.1*N* perchloric acid in acetic acid); Brookfield viscosity, 41,000 cps at 25°C.

A second sample (II) was prepared in a similar fashion. It had a diamine molecular weight of 2510 g/mol and 4.47 urea moieties per average molecule.

### Synthesis of a Polyether Diamine Oligomer (III) Containing Amide Backbone Moieties Based on Adipic Acid and Jeffamine D-400

Jeffamine D-400 (2981.7 g, 6.988 mol) and adipic acid (785.5 g, 5.375 mol) were mixed in a Jeffamine D-400 : adipic acid molar ratio of 1.30 : 1 in a 5-L, three-necked flask equipped with an overhead stirrer, condenser, thermometer, nitrogen purge, and temperature controller. A Dean Stark trap was located between the reactor and the condenser. The contents of the flask were heated at 130°C for 1 h

to form the corresponding amine salt. Toluene (250 mL) was added and the water formed during the reaction was removed in the trap. The bulk of the toluene was removed from the trap by continued heating until a pot temperature of 190°C was reached. The reactor was then cooled to ambient temperature and treated on a rotary evaporator at 90°C under a 10 mm Hg vacuum for 6 h. The product was a light yellow, viscous liquid with the following properties: basicity, 0.764 meq/g; molecular weight by end group titration, 2619; Brookfield viscosity, 63,500 cps at 25°C.

#### Synthesis of a Polyether Diamine Oligomer (IV) Containing Amide Backbone Moieties Based on Adipic Acid and Jeffamine D-2000

Jeffamine D-2000 (3175.5 g, 1.566 mol) and adipic acid (176.0 g, 1.205 mol) were mixed in a Jeffamine D-2000 : adipic acid molar ratio of 1.30 : 1 in a 5-L, three-necked flask equipped with an overhead stirrer, condenser, thermometer, nitrogen purge, and temperature controller. A Dean Stark trap was located between the reactor and the condenser. The contents of the flask were heated at 130°C for 1 h to form the corresponding amine salt. Toluene (250 mL) was added, and the water formed during the reaction was removed in the trap. The bulk of the toluene was removed from the trap by continued heating until a pot temperature of 190°C was reached. The reactor was then cooled to ambient temperature and treated on a rotary evaporator at 90°C under a 10 mm Hg vacuum for 5 h. The product was a light yellow, viscous liquid with the following properties: basicity, 0.232 meq/g; molecular weight by end group titration, 8624; Brookfield viscosity, 16,080 cps at 25°C.

#### Synthesis of *N*-Isopropyl Polyether Diamine Oligomers Containing Urea or Amide Moieties in Their Backbone

**Batch Reactions.** A portion of the polyether diamine starting material prepared above was dissolved in excess acetone to form an imine solution. The imine solution and catalyst(s) were weighed into a 300 mL stirred reactor (Autoclave Engineers) in a nitrogen atmosphere. The reactor was pressurized with hydrogen, agitated at 1600 rpm, and controlled at the desired temperature and time. Additional acetone and/or hydrogen were added in some experiments. Samples were taken periodically, stripped of acetone, and analyzed.

**Fixed Catalyst Bed Reactions.** Another portion of the polyether diamine starting material prepared above was dissolved in excess acetone to form an imine solution. The imine solution was pumped over a fixed catalyst bed (defined in text) at the desired flow rate, catalyst temperature, hydrogen flow rate, and reactor pressure. Samples were taken periodically, stripped of acetone, and analyzed.

#### Characterization Procedures

**Viscosity Measurements.** Ambient temperature Brookfield viscosities were measured using a Synchro-Lectric LTV Viscometer with an LV4 spindle at the appropriate spin rate under steady flow conditions.

**Molecular Weights and Distribution.** The molecular weights and distributions were determined by size exclusion chromatography (SEC) on Waters Ultrastaygel 1000, 10,000, and 100,000 Å columns in series. Tetrahydrofuran (THF) was the mobile phase. A refractive index detector was used to monitor the eluent stream. Narrow molecular weight distribution polystyrene standards were used for calibration.

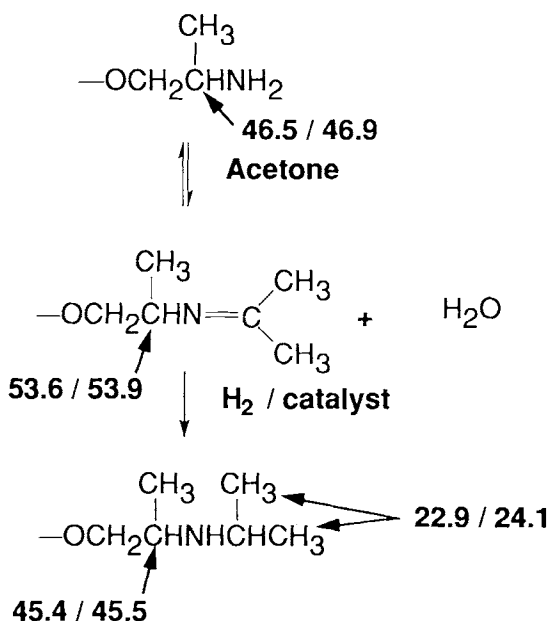
**Carbon-13 NMR.** Carbon-13 NMR spectra (in DCCl<sub>3</sub> or DMSO-d<sub>6</sub>) were obtained on a Varian Gemini-300 Spectrometer (75 MHz for carbon) using tetramethylsilane as an internal standard (0 ppm). Quantitative carbon-13 NMR measurements (in DCCl<sub>3</sub>) were obtained on an IBM NS/80 Spectrometer (20 MHz for carbon) using 90° pulses at 25-s intervals ( $T_1 < 1.5$  s), 1-s data acquisition time, and with proton decoupling turned on during acquisition.

**Perchloric Acid Titrations of Urea Moieties.**<sup>13</sup> An amount of sample necessary to give a total titration end point of about 15 mL was placed in a 250 mL beaker and weighed to four decimal places. Glacial acetic acid was added (200 mL) and the sample was stirred magnetically until dissolved (2–20 min). The sample was titrated with 0.1N perchloric acid in acetic acid on a Metrohm (Brinkmann) 636 Titroprocessor and an E-635 Dosimat. All results are reported as the average of three titrations.

## RESULTS AND DISCUSSION

### Reaction Progress

The polyether polyamines containing urea moieties in their backbones were first dissolved in excess ace-



**Figure 1** Reaction sequence for representative chain ends; carbon-13 NMR assignments ( $\text{DCCl}_3$ ).

tone to cut their viscosity and to convert some of the primary amine end groups into imine moieties. Excess acetone was used to favor imine formation. Hydrogenation of the imine moieties, in the presence of certain catalysts, resulted in the formation of *N*-isopropyl end groups (see Fig. 1). Quantitative carbon-13 NMR was used, in part, to follow the course of these reactions. The methine carbon atom adjacent to the terminal amine moiety shifts from 46.5/46.9 ppm (relative to tetramethylsilane) in the primary amine starting material to 53.6/53.9 ppm in the imine intermediate. This same methine carbon

atom shifts to 45.4/45.5 ppm in the secondary amine product. However, since these latter absorbance lines overlap another band, they are not suited for quantitative analysis. The terminal methyl groups in the secondary amine product at 22.9/24.1 ppm were used to quantify the product. An in-depth study of the carbon-13 NMR spectra of these materials will be presented later in this paper.

### Formation of Polyether Diamines Containing *N*-Isopropyl End Groups and Urea Moieties in Their Backbone

#### Initial Studies in a Batch Reactor

A portion of polyether polyamine I (100 g) dissolved in acetone (12 g) and  $\text{PtO}_2$  powder (1.0 g) were weighed into the batch reactor in a nitrogen atmosphere. The reactor was pressurized with 325 psi  $\text{H}_2$  and heated as shown in Table I with an agitator speed of 1600 rpm. After sample 3, additional acetone (14 g) was pumped in and the  $\text{H}_2$  pressure was increased to 400 psi. After sample 5, the  $\text{H}_2$  pressure was again increased to 425 psi. Additional acetone (15 g) and  $\text{H}_2$  (475 psi) were added after sample 6. More acetone (18 g) and  $\text{H}_2$  (600 psi) were added after sample 7. Some of the acetone was hydrogenated to propanol-2 during the process. Samples were taken periodically, stripped of acetone and analyzed (see Table I).

#### Reaction Progress by Carbon-13 NMR

The progress of the reactions from the primary amine starting material, through the imine intermediate, and to the secondary amine product can

**Table I** Preparation of an *N*-Isopropyl End Group Material Using a  $\text{PtO}_2$  Catalyst System: Temperature/Time Study

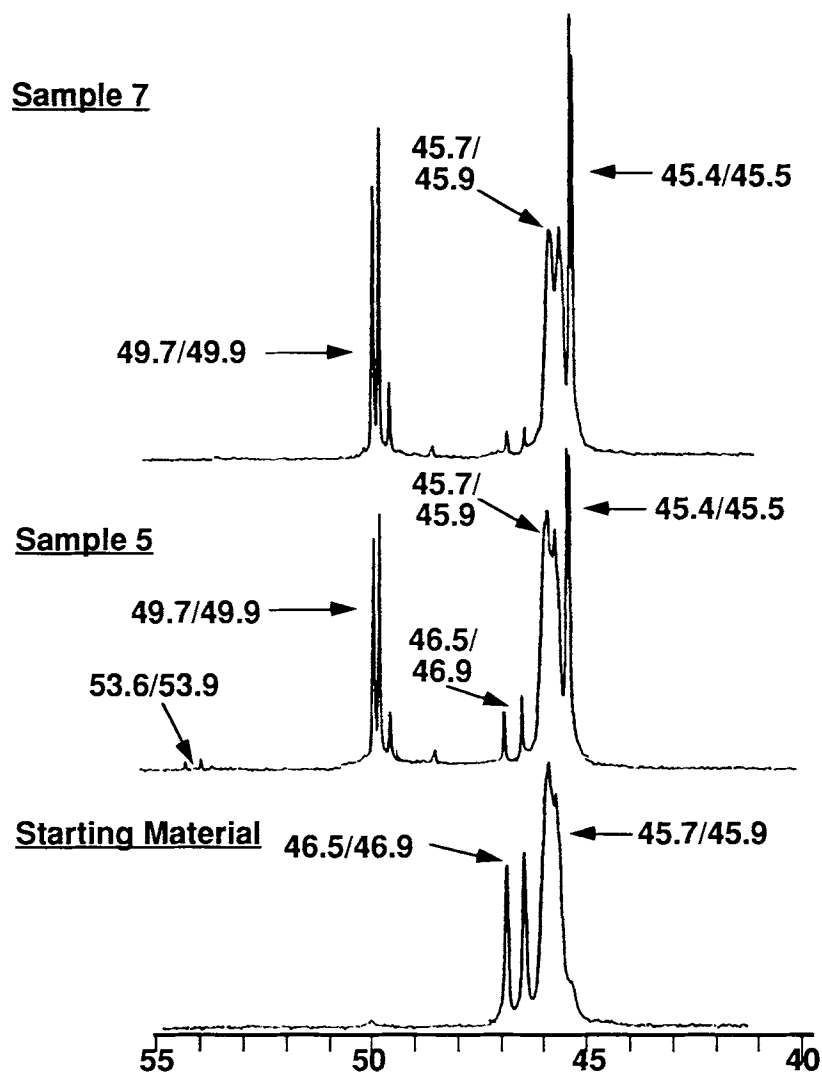
Sample	Conditions	Molecular Weight	Urea Moieties per Molecule	Carbon-13 NMR Assay (mol %) <sup>a</sup>		
				Primary Amine	Secondary Amine	Imine
1	Starting material	1964	3.19	—	—	—
2	4 h at 125°C	2014	3.22	100	0	0
3	+4 h at 140°C	2028	3.22	nd	nd	nd
4	+4 h at 140°C	2060	3.26	nd	nd	nd
5	+4 h at 140°C	2034	3.20	29	66	5
6	+4 h at 150°C	1999	3.10	27	73	0
7	+7 h at 150°C	1912	2.87	4	96	0
8	+7 h at 150°C	1798	2.58	2	98	0

<sup>a</sup> nd = not determined.

be followed readily by carbon-13 NMR. The changes occurring around the methine carbon atoms and the methyl carbon atoms are given in Figures 2 and 3, respectively. The primary amine starting material has methine carbon atoms at 46.5/46.9 and 45.7/45.9 ppm, which correspond to the methine carbon atoms adjacent to terminal amine and internal urea moieties, respectively. In addition, the primary amine starting material has three kinds of methyl groups at 19.8, 18.4, and 17.3 ppm which correspond to (1) the methyl carbon atoms attached to the methine carbon atoms adjacent to the terminal amine, (2) the methyl carbon atoms attached to the methine carbon atoms adjacent to the internal urea moieties, and (3) the methyl carbon atoms attached

to methine carbon atoms adjacent to the ether oxygen moieties, respectively.<sup>13</sup>

The imine structure is a transient intermediate whose presence can be followed by the shift of the methine carbon atoms attached to imine nitrogen to 53.6/53.9 ppm (Fig. 2). The secondary amine product has methine carbon atoms at 49.7/49.9, 45.7/45.9, and 45.4/45.5 ppm, which correspond to (1) the methine carbon atoms of the isopropyl end groups, (2) the methine carbon atoms of the internal urea moieties, and (3) the methine carbon atoms adjacent to terminal *N*-isopropylamine, respectively. In addition, the secondary amine product has five kinds of methyl groups at 24.1, 22.9, 18.4, 18.0, and 17.3 ppm, which correspond to (1 and 2) the methyl



**Figure 2** Carbon-13 NMR spectra of methine carbon atoms; product made using a  $\text{PtO}_2$  catalyst system ( $\text{DCCl}_3$ ).

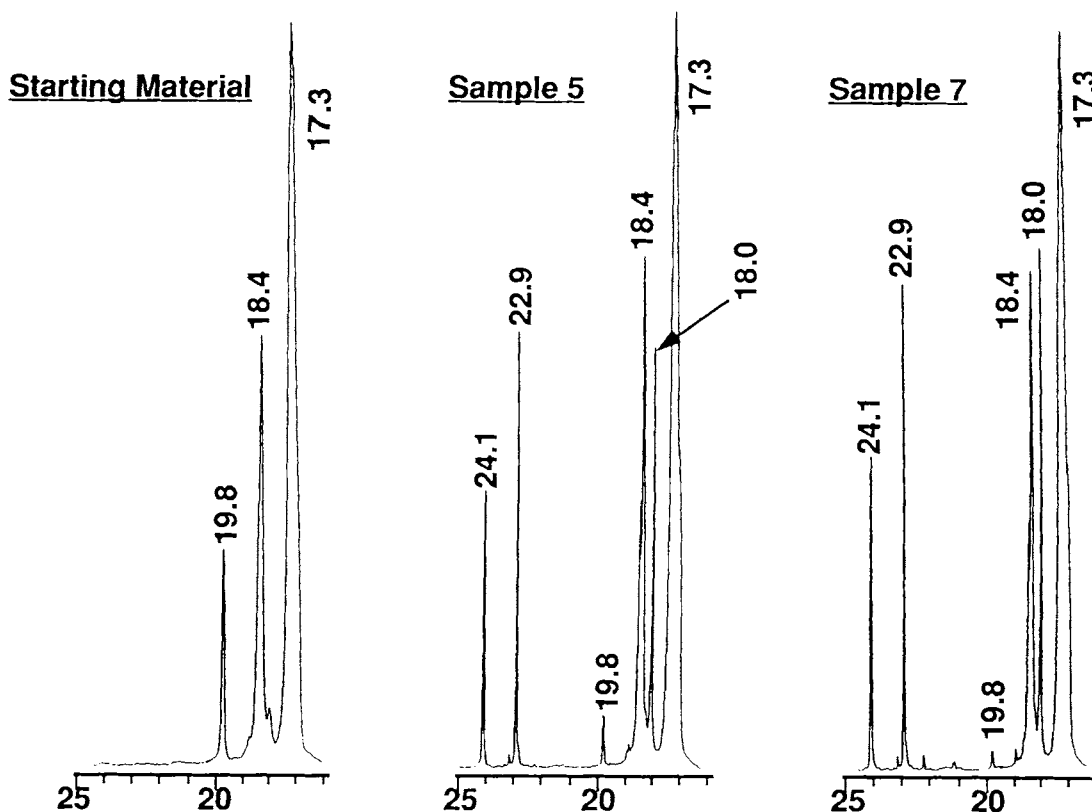


Figure 3 Carbon-13 NMR spectra of methyl carbon atoms; product made using a  $\text{PtO}_2$  catalyst system ( $\text{DCCl}_3$ ).

carbon atoms of the isopropyl end groups, (3) the methyl carbon atoms attached to the methine carbon atoms adjacent to the internal urea moieties, (4) the methyl carbon atoms attached to the methine carbon atoms adjacent to terminal *N*-isopropylamino moieties, and (5) the methyl carbon atoms attached to methine carbon atoms adjacent to the ether oxygen moieties, respectively.

#### Molecular Weight Effects

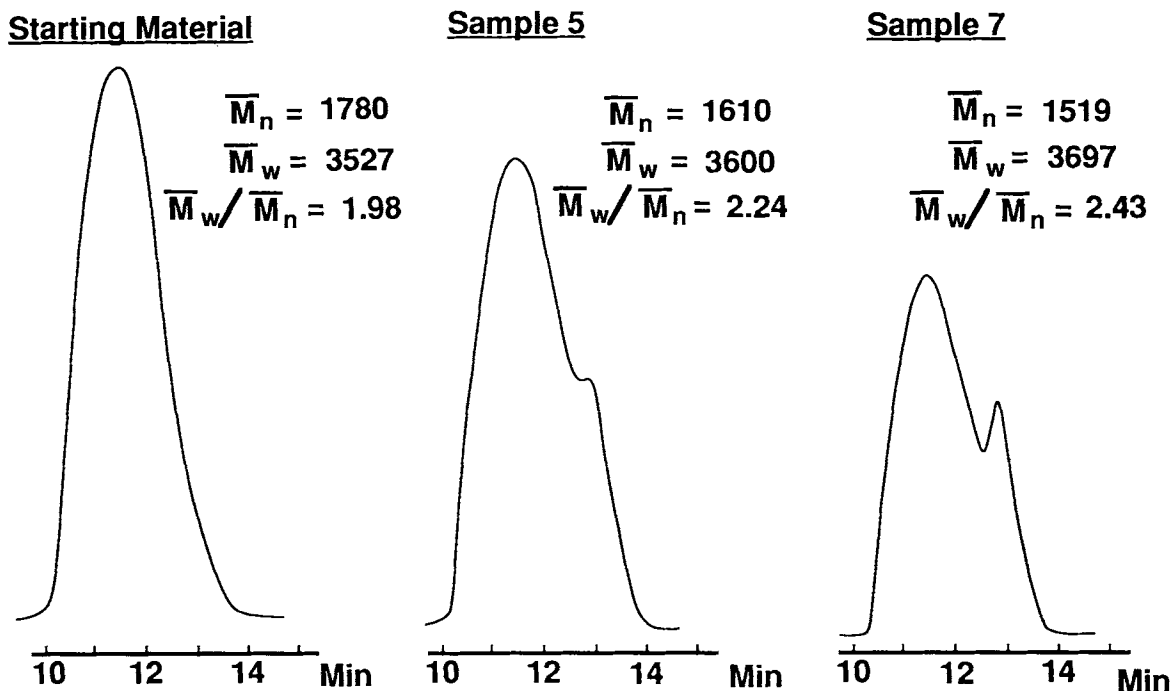
Table I shows that the primary amine starting material can be effectively converted to the secondary amine product under the reaction conditions applied. However, there appears to be some degradation of molecular weight during the process. The number average molecular weight (by HCl titration) dropped from 1964 to 1798 during the reaction. In addition, the average number of urea moieties per molecule (by  $\text{HClO}_4$  titration<sup>13</sup>) dropped from 3.19 to 2.58 during the reaction.

Size exclusion chromatography results are consistent with some backbone degradation (Fig. 4). Although the values determined for molecular

weight are somewhat different for this technique (hydrodynamic volume measurements relative to polystyrene standards), the curve shapes clearly indicate the formation of a lower molecular weight species during the reaction. In addition, as the molecular weight decreases, there is a systematic increase in polydispersity.

#### Product Structure by Carbon-13 NMR

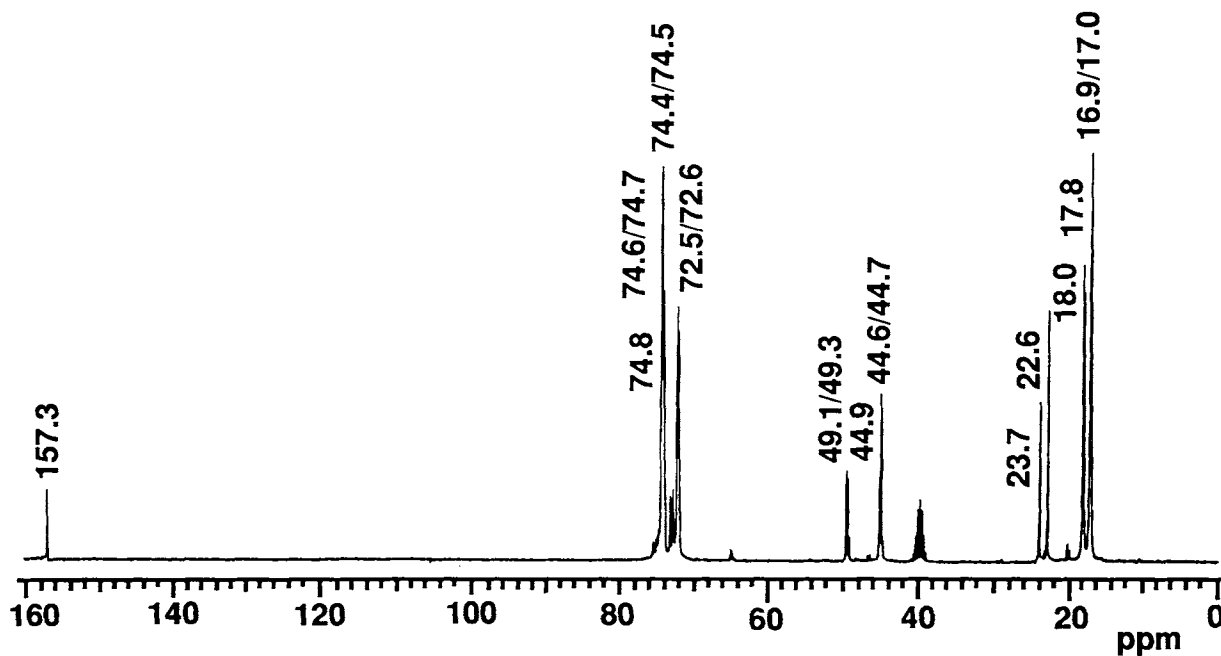
The carbon-13 NMR spectrum of the product is given in Figure 5; complete line assignments are given in Table II. This spectrum and the data presented above indicate that the desired product structure has been produced. It appears that the small amount of backbone degradation occurring during reaction results in the cleavage of a portion of the urea backbone moieties to the corresponding primary amines. No terminal urea moieties were detected by carbon-13 NMR.<sup>13</sup> These primary amine end groups under the reaction conditions are converted to the corresponding secondary amines. The net result is that the product formed has the required structure but with a somewhat reduced average mo-



**Figure 4** Size exclusion chromatography of urea backbone product made using a  $\text{PtO}_2$  catalyst system.

lecular weight. The overall reaction scheme is presented in Figure 6. The product and/or the imine intermediate can experience backbone degradation

at a urea moiety (Pathway b) to form lower molecular weight intermediates. Under the reaction conditions, these intermediates are converted to *N*-is-



**Figure 5** Carbon-13 NMR spectrum of an *N*-isopropyl polyether diamine containing urea and polypropyleneoxy moieties in its backbone ( $\text{DMSO-d}_6$ ).

**Table II Carbon-13 NMR Structural Assignments of a Representative Segment of an *N*-Isopropyl Polyether Diamine Containing Internal Urea Moieties and Polypropyleneoxy Moieties**

Assignment	Chemical Shift <sup>a</sup> (ppm)	
	In DCCl <sub>3</sub>	In DMSO-d <sub>6</sub>
1	157.7	157.3
2	75.3	74.8
3	75.2/75.4	74.6/74.7
4	75.0/75.2	74.4/74.5
5	72.9/73.3	72.5/72.6
6	49.7/49.9	49.1/49.3
7	45.7/45.9	44.9
8	45.4/45.5	44.6/44.7
9	22.9/24.1	22.6/23.7
10	18.4	18.0
11	18.0	17.8
12	17.3	16.9/17.0

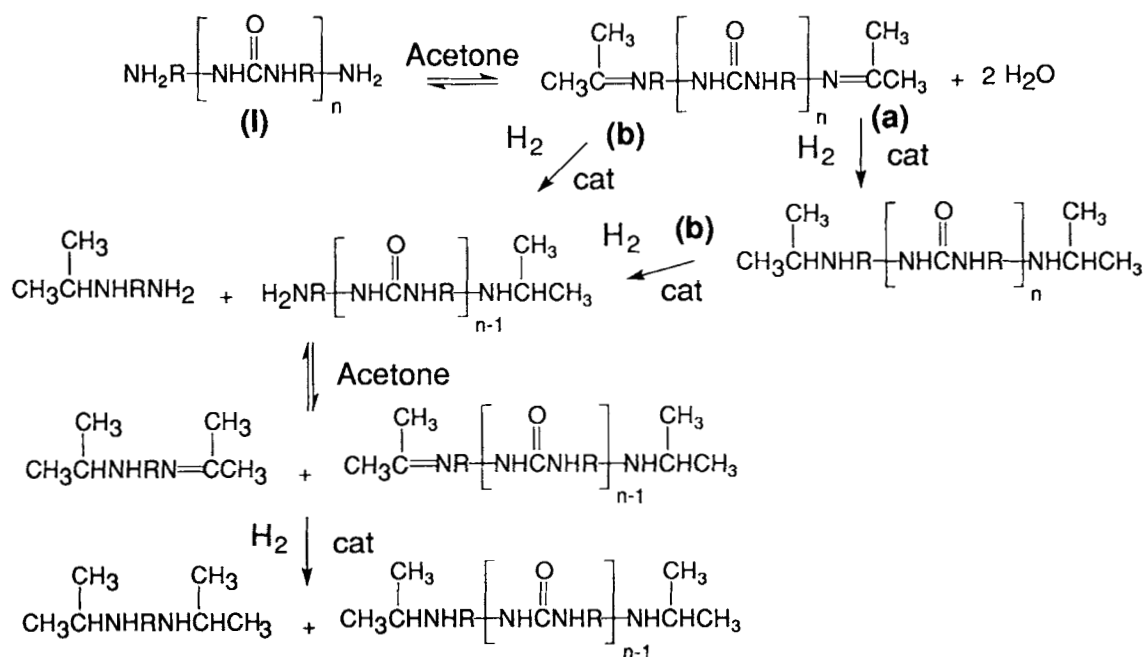
<sup>a</sup>Relative to tetramethylsilane (0 ppm).

opropylamine derivatives with reduced molecular weight. However, since these reduced molecular weight derivatives have the required end group functionality, they are suitable for further reactions with polyisocyanates to form polyureas. The majority of the reaction proceeds to the desired product (Pathway a).

#### Effects of Other Reaction Parameters in the Batch Reactor

A second portion of polyether polyamine I (80 g) dissolved in acetone (30 g) and PtO<sub>2</sub> powder (1.0 g) were weighed into the batch reactor in a nitrogen atmosphere. Reaction was carried out at 150°C and at 400 psig H<sub>2</sub> pressure for 25 h. The results are summarized in Table III and were comparable to the previous reaction. A high conversion of the primary amine starting material to the secondary amine product was obtained. However, some backbone degradation occurred, as indicated by the molecular weight reduction and the reduced number of urea moieties per molecule.

A third portion of polyether polyamine I (103.2 g) dissolved in acetone (30 g), PtO<sub>2</sub> powder (3.0 g), and Pd/C (3.0 g) were weighed into the batch re-



where R represents polyether segments

**Figure 6** Reaction scheme for the conversion of urea backbone modified polyether diamines to *N*-isopropyl polyether diamines.



**Table III Preparation of an *N*-Isopropyl End Group Material Using a PtO<sub>2</sub> Catalyst System**

Sample	Conditions	Molecular Weight	Urea Moieties per Molecule	Carbon-13 NMR Assay (mol %)		
				Primary Amine	Secondary Amine	Imine
1	Starting material	1964	3.19	—	—	—
2	7 h at 150°C	2092	3.31	30	48	22
3	13 h at 150°C	2090	3.23	13	70	17
4	19 h at 150°C	1989	3.04	9	76	15
5	25 h at 150°C	1730	2.51	5	95	0

actor in a nitrogen atmosphere. Reaction was carried out at 150°C and at 420 psig H<sub>2</sub> pressure for 7 h. Results are summarized in Table IV. Complete conversion to secondary amine product was obtained within 7 h. However, some backbone degradation still occurred with this catalyst system.

#### Study in a Fixed Bed Reactor

A portion of polyether polyamine **II** dissolved in acetone (11.5 wt %) was pumped over a fixed bed catalyst. The bed consisted of two tubes in series. Tube 1 was 36 × 0.87 in. ID and contained 0.3% Pd/C catalyst (218 g, 4 × 8 mesh). Tube 2 was 16 × 0.87 in. ID and contained 0.3% Pt–0.3% Pd on Al<sub>2</sub>O<sub>3</sub> (250 g,  $\frac{1}{8}$  in. pellets). The feed rate was 0.17 lb/h, the catalyst temperature was 100–130°C, and the reactor pressure was 940–1100 psig. Hydrogen was added at a 70–100 cc/min flow rate. The product was stripped of volatiles in a rotary evaporator (125°C) and analyzed (Table V). A high conversion of the primary amine starting material to the secondary amine product was obtained. However, backbone degradation occurred, as indicated by the molecular weight reduction and the reduced number of urea moieties per molecule.

A second portion of polyether polyamine **II** dissolved in acetone (11.5 wt %) was pumped over the same fixed bed catalyst. The feed rate was 0.14 lb/

h (increased contact time), the catalyst temperature was 100–130°C, and the reactor pressure was 750–1100 psig. Hydrogen was added at a 25–60 cc/min flow rate. The product was stripped of volatiles in a rotary evaporator (125°C) and analyzed (Table VI). A high conversion of the primary amine starting material to the secondary amine product was obtained. However, backbone degradation was even greater at this increased contact time, as indicated by the molecular weight reduction and the reduced number of urea moieties per molecule.

#### Formation of Polyether Diamines Containing *N*-Isopropyl End Groups and Amide Moieties in Their Backbone

##### Product Based on Jeffamine D-400 and Adipic Acid

A primary polyether diamine containing about six amide moieties per average backbone molecule **III** (molecular weight = 2619) was prepared based on Jeffamine D-400 and adipic acid.<sup>27</sup> A portion of polyether polyamine **III** dissolved in acetone (25 wt %) was pumped over a fixed bed catalyst. The bed consisted of a 15 ft × 0.87 in. ID tube filled with 1.0% Pt on Al<sub>2</sub>O<sub>3</sub> (1438 g,  $\frac{1}{8}$  in. pellets). The feed rate was 0.3 lb/h, the catalyst temperature was 150°C, and the reactor pressure was 450 psig. Hy-

**Table IV Preparation of an *N*-Isopropyl End Group Material Using a PtO<sub>2</sub> and Pd/C Mixed Catalyst System**

Sample	Conditions	Molecular Weight	Urea Moieties per Molecule	Carbon-13 NMR Assay (mol %)		
				Primary Amine	Secondary Amine	Imine
1	Starting material	1964	3.19	—	—	—
2	7 h at 150°C	1901	2.87	0	100	0

**Table V Preparation of an *N*-Isopropyl End Group Material Using a Fixed Bed Catalyst System; 0.17 lb/h Feed Rate**

Sample	Conditions	Molecular Weight	Urea Moieties per Molecule	Carbon-13 NMR Assay (mol %)		
				Primary Amine	Secondary Amine	Imine
1	Starting material	2510	4.47	—	—	—
2	4 h	1532	2.16	2	98	0

**Table VI Preparation of an *N*-Isopropyl End Group Material Using a Fixed Bed Catalyst System; 0.14 lb/h Feed Rate**

Sample	Conditions	Molecular Weight	Urea Moieties per Molecule	Carbon-13 NMR Assay (mol %)		
				Primary Amine	Secondary Amine	Imine
1	Starting material	2510	4.47	—	—	—
2	6 h	1296	1.71	2	97	1

drogen was added at a 750 cc/min flow rate. The product was stripped of volatiles in a falling film still (120°C) and analyzed: The product was characterized as 2886 molecular weight, no imine, and essentially all secondary amine by carbon-13 NMR (Table VII).

Molecular weight results indicate essentially no backbone degradation. Figure 7 gives the size exclusion chromatography traces of the starting material and product. Only a trace of backbone degradation is indicated by the small low molecular weight inflection.

The reaction was repeated at 130°C catalyst temperature with all other conditions identical to those defined above. No secondary amine was produced; only starting material was recovered (Table VII).

This result indicates the critical temperature dependence of this reaction sequence.

#### **Product Structure by Carbon-13 NMR**

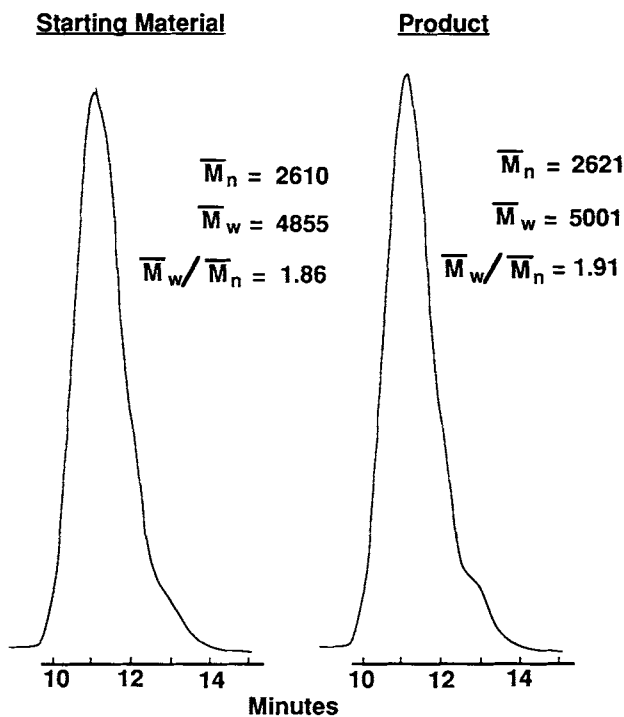
The carbon-13 NMR spectrum of the product is given in Figure 8; complete line assignments are given in Table VIII. This spectrum and the data presented above indicate that the desired product structure has been produced.

#### **Product Based on Jeffamine D-2000 and Adipic Acid**

A primary polyether diamine containing about six amide moieties per average backbone molecule **IV** (molecular weight = 8624) was prepared based on

**Table VII Preparation of *N*-Isopropyl Polyether Diamines Containing Amide Moieties**

Based on Jeffamine	Conditions	H <sub>2</sub> Flow Rate (psig)	Molecular Weight	Carbon-13 NMR Assay (mol %)		
				Primary Amine	Secondary Amine	Imine
D-400	Starting material	—	2619	—	—	—
D-400	130°C/450 psig	750	2620	100	0	0
D-400	150°C/450 psig	750	2886	0	100	0
D-2000	Starting material	—	8668	—	—	—
D-2000	152°C/450 psig	740	9060	0	100	0

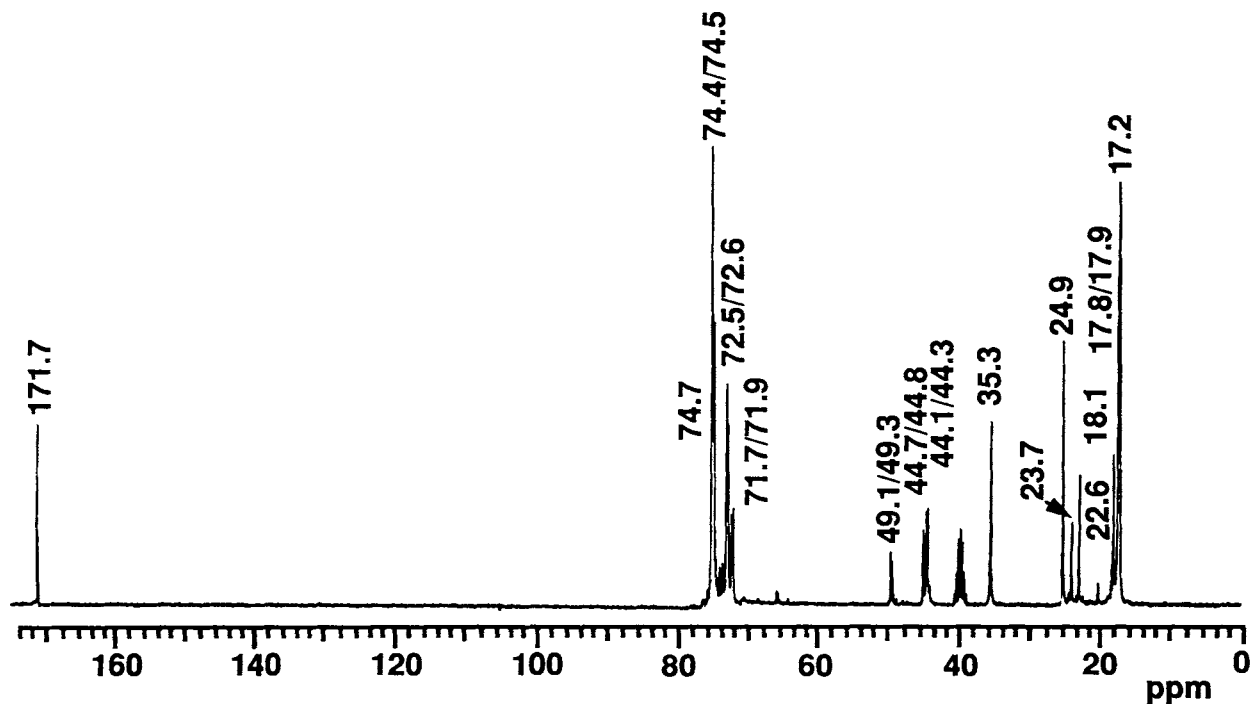


**Figure 7** Size exclusion chromatography of amide backbone product.

Jeffamine D-2000 and adipic acid.<sup>27</sup> A portion of polyether polyamine IV dissolved in acetone (25 wt %) was pumped over the same fixed bed catalyst used for the amide based on Jeffamine D-400. The feed rate was 0.28 lb/h, the catalyst temperature was 152°C, and the reactor pressure was 450 psig. Hydrogen was added at a 740 cc/min flow rate. The product was stripped of volatiles in a falling film still (120°C) and analyzed: 9060 molecular weight, no imine, and essentially all secondary amine by carbon-13 NMR (Table VII). There is no indication of backbone degradation by size exclusion chromatography.

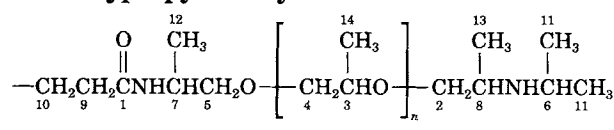
## CONCLUSIONS

Primary polyether polyamine oligomers containing preformed urea or amide moieties in their backbones can be conveniently converted to the corresponding *N*-isopropyl polyether polyamine oligomers (secondary amines) by reaction with acetone and hydrogen in the presence of certain catalysts. The best results were from reactions carried out at about 150°C using a supported platinum or palladium cat-



**Figure 8** Carbon-13 NMR spectrum of an *N*-isopropyl polyether diamine containing amide and polypropyleneoxy moieties in its backbone (DMSO- $d_6$ ).

**Table VIII Carbon-13 NMR Structural Assignments of a Representative Segment of an N-Isopropyl Polyether Diamine Containing Internal Amide Moieties Based on Adipic Acid and Polypropyleneoxy Moieties**



Assignment	Chemical Shift <sup>a</sup> (ppm)	
	In DCCl <sub>3</sub>	In DMSO-d <sub>6</sub>
1	172.2	171.7
2	75.2/75.4	74.7
3	75.0/75.1	74.4/74.5
4	73.0/73.4	72.5/72.6
5	72.0/72.2	71.7/71.9
6	49.9/50.0	49.1/49.3
7	45.5/45.6	44.7/44.8
8	45.2/45.4	44.1/44.3
9	36.4	35.3
10	25.2	24.9
11	22.9/24.1	22.6/23.7
12	18.1	18.1
13	17.8/17.9	17.8/17.9
14	17.2	17.2

<sup>a</sup> Relative to tetramethylsilane (0 ppm).

alyst in a fixed bed. When the polyether polyamine oligomer contained urea moieties, some backbone degradation was experienced under all of the reaction conditions studied. This degradation led to the formation of a product with the required end group reactivity but with a reduced molecular weight and fewer urea moieties per molecule. When the polyether polyamine oligomer contained amide moieties, very little backbone degradation was experienced.

These polyether polyamine oligomers, containing urea or amide moieties in their backbones, are useful in urethane/urea polymer systems. The lower reactivity of these secondary amines (toward polyisocyanates) result in their utility in a broader range of polyurethane fabrication technologies.

## REFERENCES

- R. F. Harris, *Polym. Prepr. Div. Polym. Chem. Am. Chem. Soc.*, **29**(2), 418 (1988).
- R. F. Harris, *J. Appl. Polym. Sci.*, **37**, 183 (1989).
- R. F. Harris and L. A. McDonald, *J. Appl. Polym. Sci.*, **37**, 1491 (1989).
- R. F. Harris, M. D. Joseph, C. Davidson, C. D. DePorter, and V. A. Dais, *Polym. Prepr. Div. Polym. Chem. Am. Chem. Soc.*, **30**(2), 235 (1989).
- R. F. Harris, *J. Appl. Polym. Sci.*, **38**, 463 (1989).
- R. F. Harris, *J. Appl. Polym. Sci.*, **40**, 1265 (1990).
- R. F. Harris, M. D. Joseph, C. Davidson, C. D. DePorter, and V. A. Dais, *J. Appl. Polym. Sci.*, **41**, 487 (1990).
- R. F. Harris, M. D. Joseph, C. Davidson, C. D. DePorter, and V. A. Dais, *J. Appl. Polym. Sci.*, **41**, 509 (1990).
- R. F. Harris, *J. Appl. Polym. Sci.*, **41**, 1937 (1990).
- R. F. Harris, M. D. Joseph, C. Davidson, and C. D. DePorter, *J. Appl. Polym. Sci.*, **42**, 3241 (1991).
- R. F. Harris, *J. Appl. Polym. Sci.*, **44**, 605 (1992).
- R. F. Harris and K. M. Lopez, *J. Appl. Polym. Sci.*, **44**, 1663 (1992).
- R. F. Harris, C. D. DePorter, and R. B. Potter, *Macromolecules*, **24**, 2973 (1991).
- R. F. Harris, R. M. Anderson, and D. M. Shannon, *J. Appl. Polym. Sci.*, **46**, 1547 (1992).
- N. Yamazaki and S. Nakahama, *Polym. Prepr. Div. Polym. Chem. Am. Chem. Soc.*, **20**, 146 (1979).
- H. G. Waddill and H. Schulze, U.S. Pat. 4,002,598 (1977).
- H. Schulze and H. G. Waddill, U.S. Pat. 4,115,360 (1978).
- G. Camerese, S. Fumasoni, M. Palazzo, and F. Pochetti, *Ann. Chim. (Rome)*, **57**, 927 (1967).
- C. Giori, *Polym. Prepr. Div. Polym. Chem. Am. Chem. Soc.*, **11**, 326 (1970).
- N. Yamazaki, T. Iguchi, and F. Higashi, *Tetrahedron Lett.*, **1979**, 1191.
- N. Yamazaki, T. Iguchi, and F. Higashi, *Tetrahedron*, **31**, 3031 (1975).
- N. Yamazaki, T. Iguchi, and F. Higashi, *J. Polym. Sci. Polym. Lett. Ed.*, **12**, 517 (1975).
- N. Yamazaki, T. Iguchi, and F. Higashi, *J. Polym. Sci. Polym. Chem. Ed.*, **13**, 785 (1975).
- H. Schulze, U.S. Pat. 4,154,724 (1979).
- H. G. Waddill and H. Schulze, U.S. Pat. 4,178,427 (1979).
- H. Schulze and H. G. Waddill, Ger. Pat. DE 2,748,705 (1984).
- R. F. Harris and C. D. DePorter, U.S. Pat. 4,916,201 (1990).
- R. F. Harris and M. D. Joseph, U.S. Pat. 5,055,544 (1991).
- J. M. Bentley, J. P. Brown, G. Frijns, and D. J. Sparrow, Eur. Pat. Appl. E.P. 240,196 (1987).
- J. M. Bentley, J. P. Brown, G. Frijns, and D. J. Sparrow, Eur. Pat. Appl. E.P. 242,974 (1987).
- J. M. Bentley, J. P. Brown, G. Frijns, and D. J. Sparrow, U.S. Pat. 4,751,255 (1988).
- J. M. Bentley, J. P. Brown, G. Frijns, and D. J. Sparrow, U.S. Pat. 4,849,460 (1989).
- R. F. Harris and M. D. Joseph, U.S. Pat. 5,068,306 (1991).
- R. F. Harris, C. E. Habermann, and M. D. Joseph, U.S. Pat. pending.

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