Macromolecules **1991,** *24,* 2973–2980

Speciality Polyurethane Soft Segments. 1. Synthesis and Characterization of Polyether Polyamine Oligomers Containing Backbone Urea Moieties

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Received September 28, 1990; Revised Manuscript Received December 5, 1990

ABSTRACT: A variety of polyether polyamine oligomers containing backbone urea moieties were prepared by the reactions of aminated polyglycols with urea. Reactions were carried out neat at 135–175 °C. The progress of the reactions was followed by the amine conversion and ammonia formation, which were monitored by titrimetry. Reactants and products were monitored by carbon-13 NMR. A perchloric acid titration method was also developed to rapidly quantify the number of urea moieties. Product molecular weight was primarily a function of the molar ratio of the reactants. The $\bar{M}_n$ range from 1800 to 3800 was studied by use of a 400 molecular weight aminated poly(propylene glycol) and urea. Analogous products were made from other aminated polyglycols. These polyether polyamines, containing preformed urea moieties in their backbone, are useful in urethane/urea polymer systems, particularly for reaction injection molding applications.

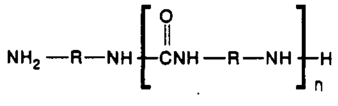
Introduction

The $(AB)_n$ 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 cross-links between 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 that 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 moieties to control physical properties in polyurethane systems.[1-10] This paper deals with the synthesis and characterization of polyether diamines containing urea moieties in their backbones.

A common way to form a urea moiety in urethane/urea systems is to react polyamines with polyisocyanates. It is done routinely in flexible foam systems using water, which reacts with a portion of the polyisocyanate, to form an amine and carbon dioxide. The carbon dioxide then functions as the primary blowing agent while the amine reacts further with polyisocyanate to form urea moieties.

However, we now are developing a different approach to systems containing urea moieties by studying the utility of polyether diamines containing preformed urea moieties in their backbone. The general structure is depicted by 1: where R represents the polyether segments.


$$NH_2-R-NH\left[\overset{O}{\overset{\|}{C}}NH-R-NH\right]_nH$$

1

These 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[11] 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[12,13] and alkylene carbonates are reported by Cameresi[14] to react with 1,6-diaminohexane. Polyether diamines also react with phosgene to produce materials containing urea moieties in their backbone,[12,13] and Giori[15] has made related materials by the reaction of amino alcohols with phosgene. Yamazaki[16-19] 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.[12,13,20-22] This is the general method used to prepare the 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.[23]

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.

Experimental Section

Materials. Jeffamine D-230, D-400, and D-2000, manufactured by Texaco, are aminated poly(propylene glycols) having molecular weights of approximately 230, 400, and 2000, respectively. Aminated poly(propylene glycol) of 1200 molecular weight and aminated poly(1,2-butylene glycol) of 2000 molecular weight were prepared by the reductive amination of the corresponding glycols. Perchloric acid (0.1 N solution in acetic acid) and glacial acetic acid were purchased from Fisher Scientific Co. Urea, thiourea, *n*-butylurea, 1,1-diethylurea, 1,3-diethylurea, 1,1,3,3-tetramethylurea, phenylurea, diphenylurea, (2-hydroxyethyl)-urea, ethyleneurea, and hydrantoin were purchased from Aldrich Chemical Co.

Typical Synthesis of a Polyether Polyamine Oligomer Containing Urea Backbone Moieties (Sample XVI). Jeffamine D-400 (3367.6 g, 7.514 mol) and urea (347.1 g, 5.780 mol)

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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 mmHg 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 an amine content of 1.427 mequiv/g (determined by titration of a methanolic solution with 0.1 N aqueous HCl), which corresponds to a diamine molecular weight of 1954. This product was further characterized by methods described later in this paper.

Procedures for Determination of Amine Conversion and Ammonia Formation. (1) Amine Conversion. Urea and a polyether polyamine were combined in a 500-mL, three-necked flask equipped as described above. After the reaction temperature was attained, samples were removed periodically, dissolved in methanol, and titrated with 0.1 N HCl, which reacted with the unreacted amine. The degree of amine conversion was calculated from the decrease in amine content.

(2) Ammonia Formation. Urea and a polyether polyamine were combined in a 500-mL, three-necked flask as described above. A gas sparger was connected to the exit tube from the condenser and was placed in a volumetric flask containing a known amount of 1.0 N sulfuric acid. The volumetric flask and reagents were replaced periodically. The solution and captured ammonia were diluted to known volume and an aliquot was titrated with 0.1 N NaOH to determine the amount of excess sulfuric acid. The amount of ammonia collected was calculated from the change in sulfuric acid concentration.

Characterization Procedures. (1) Viscosity Measurements. Ambient temperature Brookfield viscosities were measured by use of a Synchro-Lectric LTV viscometer with an LV4 spindle at the appropriate spin rate under steady flow conditions. Elevated temperature Brookfield viscosities were measured by use of a Synchro-Lectric digital viscometer with a Brookfield Thermosel heater and an HBTD No. 21 spindle. Temperature was controlled with a Model 84 Brookfield programmable temperature controller. Haake viscosity data were gathered on a RV3 Haake Rotoviscometer interfaced to an Apple II Plus computer. Temperature was controlled with a Haake L temperature controller. All measurements were made in either the MV or NV mode.

(2) Molecular Weights and Distribution. The molecular weights and distributions were determined by size exclusion chromatography (SEC) on Waters Ultrastyragel 500-, 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.

(3) Carbon-13 NMR. Carbon-13 NMR spectra (in $DCCl_3$ or $DMSO\text{-}d_6$) were obtained on a Varian Gemini-300 spectrometer (75 MHz for carbon) using tetramethylsilane as an internal standard (0 ppm).

(4) Perchloric Acid Titrations of Urea Moieties. An amount of sample necessary to give a total titration end point of ~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 0.1 N 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.

(5) Thermal Analyses. Glass transition temperatures were measured on a Du Pont instrument 910 differential scanning calorimeter (DSC) scanning from −100 to 240 °C at a rate of 10 °C/min under nitrogen. Samples of approximately 10 mg were encased in crimped aluminum pans. The chromel–alumel thermocouple was calibrated by using indium and lead standards. Elevated temperature weight loss data were measured on a Du Pont instrument 951 thermogravimetric analyzer (TGA) with an Omnitherm brand hot quartz beam and disposable aluminum pans from ambient temperature to 600 °C under nitrogen. The chromel–alumel thermocouple was calibrated by using indium and lead standards. The DSC and TGA modules were interfaced with a Du Pont 9900 thermal analyzer/computer for data reduction and analysis.

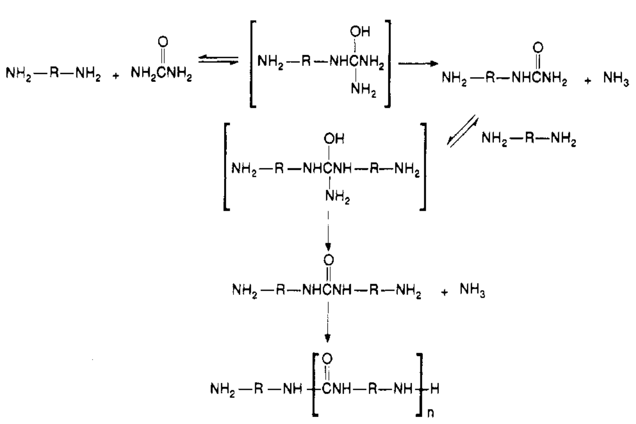


Figure 1. Proposed reaction sequence for the formation of polyether polyamine oligomers.

Table I
Carbon-13 NMR[a] of Reaction Center during Reaction of Jeffamine D-400 and Urea

material	structure of fragment	carbonyl carbon	methyl carbon	methine carbon
reactants	$OCH_2C(CH_3)HNH_2 + NH_2C(O)NH_2$	160.8	19.7	46.5/46.9
terminal urea	$OCH_2C(CH_3)HNHC(O)NH_2$	159.0	18.3	45.4/45.9
internal urea	$OCH_2C(CH_3)HNHC(O)NHC(CH_3)HCH_2O$	157.6	18.3	45.4/45.9

[a] ppm from tetramethylsilane (ppm TMS 0); $DCCl_3$ as solvent.

Results and Discussion

Stoichiometry of Reactants. The polyether polyamines containing urea moieties in their backbones were prepared from urea and polyether polyamines. Urea is a very inexpensive monomer, providing an economical route for the synthesis of these materials. Polyether polyamines are readily prepared by the reductive amination of the corresponding polyether polyols[24–30] or by the cyanoethylation of polyether polyols with acrylonitrile followed by hydrogenation.[31–34]

The stoichiometry of the products of the reactions of polyether diamines with urea was dependent on the molar ratio of the reactants. If excess amine was used, the product was amino-functional and contained internal urea moieties in its backbone.[12,13,20–22] By contrast, if excess urea was used, the product was urea-functional.[35–40] Both the product molecular weight and the average number of internal urea moieties per molecule were dependent on the molar ratio of the reactants.

The first step in the reaction sequence appeared to be a nucleophilic attack by the amino nitrogen on the carbonyl of urea followed by loss of ammonia, leading to the formation of an intermediate containing a terminal urea moiety. This terminal urea moiety could then react with additional amine by a similar reaction sequence leading to the formation of a product containing an internal urea moiety with the release of additional ammonia. Further reaction leads to the formation of oligomers (see Figure 1).

One way to follow the extent of these reactions is to measure the disappearance of amine as a function of time. In this way the processing parameters that lead to high amine conversion can be defined. However, this method does not distinguish between internal and terminal urea moieties.

The extent of reaction was also followed by measuring the amount of ammonia released from the reactor as a

Table II
Molecular Weight and Viscosity Data of Products Made by Using Jeffamine D-400/Urea Molar Ratios of 1.20:1 and 1.30:1

sample	amine/urea molar ratio	reactn temp, °C	% amine conversn	MW by HCl titratn	molecular weight by SEC peak	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	Brookfield viscos (25 °C), cps	density (25 °C), g/mL
I	1.20	135	93.0	2445	3272	1998	3088	1.55	66 600	1.02
II	1.20	135	94.6	2305	3238	2199	3518	1.60	71 900	1.03
III	1.20	150	102.8	3284	5618	3004	5162	1.72	336 000	1.03
IV	1.20	150	101.3	3657	8570	3493	7083	2.03	503 000	1.04
V	1.20	175	102.6	3458	5618	3034	5208	1.72	312 000	1.04
VI	1.20	175	99.2	2729	5932	2867	5631	1.96	145 000	1.03
VII	1.30	150	102.9	2387	4390	2200	3936	1.79	94 800	1.03
VIII	1.30	150	98.1	2106	4390	2239	4072	1.82	50 000	1.02
IX	1.30	175	99.0	2120	4390	2331	4388	1.88	46 400	1.02
X	1.30	175	100.5	2012	4046	2201	4042	1.84	35 000	1.03

Table III
Comparison of Amine Conversion and Ammonia Formation at Various Temperatures at a Jeffamine D-400/Urea Molar Ratio of 1.20:1[a]

time at temp, h	135 °C % amine conversn (I)	135 °C % ammonia formatn (II)	150 °C % amine conversn (III)	150 °C % amine conversn (XVIII)	150 °C % ammonia formatn (IV)	175 °C % amine conversn (V)	175 °C % ammonia formatn (VI)
0	9.1	8.1	30.1	26.9	23.7	70.1	67.3
1	45.8	46.3	74.4	72.4	67.7	96.7	95.1
2	58.0	58.8	83.6	83.4	79.7	99.2	97.9
3	64.5	66.7	88.4	88.1	87.1	100.6	98.6
4	68.8	72.2	92.1	90.6	91.1	101.3	98.8
5	71.9	76.7	94.9	92.6	92.8	101.5	98.9
6	75.4	nd	96.3	94.1	nd	102.4	nd
7	77.8	nd	nd	nd	nd	nd	nd
22	93.0	94.6	102.8	99.3	101.3	102.6	99.2

[a] nd, not determined.

function of time. This also did not distinguish between internal and terminal urea moieties. However, the disappearance of amine and appearance of ammonia corresponded temporally and quantitatively, which is consistent with the postulated reaction sequence.

Carbon-13 NMR was useful in monitoring the reaction progress and was substantially more specific. Both the terminal urea moieties and the internal urea moieties were clearly distinguishable (see Table I). There was a systematic change in the position of the carbonyl carbon chemical shifts in going from urea to monosubstituted urea to symmetrically disubstituted area. Both the methyl carbons and the methine carbons of the amine have chemical shifts appearing at lower values after reaction to form a substituted urea, clearly supporting the terminal and internal urea structures described above in 1. It was important to use reaction conditions that caused all terminal urea moieties to react, since terminal ureas are unreactive with isocyanates under normal conditions. The average number of urea moieties per molecule were quantified by the perchloric acid titration.

Process Variables. (1) Effects of Jeffamine D-400/Urea Molar Ratios. A series of reactions were carried out in a 500-mL reactor with Jeffamine D-400/urea molar ratios of 1.20:1 and 1.30:1 (see Table II). The highest molecular weight products were made at the lowest ratio. A molar ratio of 1.30:1 yielded a product with a number-average molecular weight of ~2100, while a molar ratio of 1.20:1 yielded a product with a number-average molecular weight of ~3500. Run-to-run variations in the molecular weight corresponded to variations in the percent of amine conversion. The lower molecular weight products produced at 135 °C reflected slow, incomplete reaction.

A second series of reactions were carried out in a 5-L reactor in order to make larger quantities of materials for evaluation. Jeffamine D-400/urea molar ratios of 1.15:1 to 1.35:1 were used. Molecular weight is plotted versus molar ratio of reactants in Figure 2. Variations in molecular weight with reactant molar ratio reflect variations in amine conversion. Data points falling below the line in Figure 2 (lower molecular weight than predicted) represent a lower amine conversion.

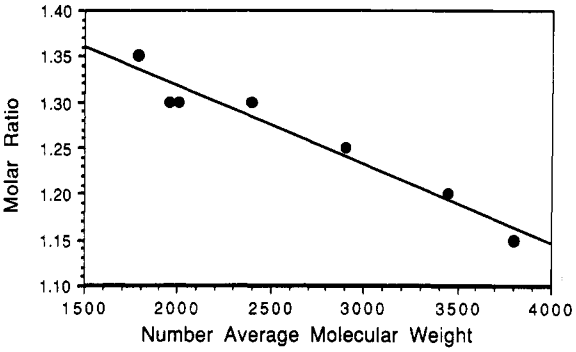


Figure 2. Correlation of Jeffamine D-400/urea molar ratio with molecular weight. Reaction temperature 150 °C.

(2) Correlations between Amine Conversion and Ammonia Formation. The progress of a reaction was followed by measuring both the percent amine conversion and the percent ammonia formation. Comparisons between these measurements have been made using a Jeffamine D-400/urea molar ratio of 1.20:1 (Table III). An excellent correlation exists in all cases. Similar results were obtained with a Jeffamine D-400/urea molar ratio of 1.30:1. This finding provides credibility to the postulated reaction stoichiometry presented above.

(3) Effect of Reaction Temperature. The effect of temperature on amine conversion and ammonia formation is demonstrated by the data in Table III. Note that the reaction was complete (to within 99% conversion) within 22 h at 150 °C and within 4–6 h at 175 °C. At 135 °C, the reaction was still incomplete (at ~94% conversion) after 22 h. This temperature effect is shown more clearly in Figure 3, where amine conversion vs time is plotted for samples made at 135, 150, and 175 °C using a Jeffamine D-400/urea molar ratio of 1.20:1.

(4) Scaleup of Jeffamine D-400/Urea Products. The products made by reacting Jeffamine D-400 with urea

Table IV
Scaleup Data Using Various Jeffamine D-400/Urea Molar Ratios (150 °C for 24 h)

sample	reactants D-400 mol	 urea, mol	 molar ratio	wt loss, g	ammonia formed, mol	amine after reactn, equiv	amine consumed, equiv	amine consumed/-urea charged	ammonia formed/-urea charged
XI	6.839	5.947	1.15	218.0	12.82	1.873	11.804	1.00	1.08
XII	8.180	6.816	1.20	257.0	15.11	1.914	16.359	1.06	1.11
XIII	8.156	6.525	1.25	242.0	14.23	2.498	16.312	1.06	1.09
XIV	7.840	6.031	1.30	209.5	12.32	2.973	15.680	1.05	1.02
XV	7.691	5.916	1.30	219.1	12.89	3.595	15.382	1.00	1.09
XVI	7.514	5.780	1.30	206.7	12.16	3.590	15.027	0.99	1.05
XVII	7.699	5.703	1.35	208.0	12.24	4.037	15.397	1.00	1.07

Table V
Products Made by Using Urea and Selected Aminated Polyglycols

sample	amine[a]	amine/urea molar ratio	temp, °C	time, h	% amine conversn	MW by HCl titratn	Brookfield viscos, cps
XIX	D-230	1.14	135	24	91.2	1466	>2000000
XX	A	2.00	135	22	95.7	2358	1200
XXI	A	2.00	150	18	nd[c]	2562	1138
XXII	A	2.00	150	8	96.0	2495	1090
XXIII	A	2.00	150	23	96.7	2500	nd
XXIV	D-2000	1.20	150	16	79.8	9866	17820
XXV	D-2000	2.00	150	16	95.4	4120	1840
XXVI	D-2000	1.20	135	24	89.0	8088	7960
XXVII	D-2000	1.20	150	46	81.6	11261	nd[c]
XXVIII	D-2000	1.20	150	39	80.7	11119	24050
XXIX	B	1.20	150	23	89.0	8203	11500

[a] A, an aminated poly(propylene glycol) of 1252 molecular weight; B, an aminated poly(1,2-butylene glycol) of 2070 molecular weight. [c] nd, not determined.

Table VI
Screen of Perchloric Acid Titrations of Selected Ureas

compound	structure	perchloric acid titratn, mequiv/g	mV at end point	form wt	MW by titratn
urea	$NH_2C(O)NH_2$	16.443	683	60.1	60.8
thiourea	$NH_2C(S)NH_2$	13.174	676	76.1	75.9
n-butylurea	$CH_3(CH_2)_3$-$NHC(O)NH_2$	8.500	685	116.2	117.6
1,1-diethylurea	$(C_2H_5)_2NC$-$(O)NH_2$	8.638	672	116.2	115.8
1,3-diethylurea	C_2H_5NHC-$(O)NHC_2H_5$	8.473	677	116.2	118.0
1,1,3,3-tetramethylurea	$(CH_3)_2NC$-$(O)N(CH_3)_2$	8.284	684	116.2	120.7

Table VII
Perchloric Acid Titration of Sample XXX, A 1.20:1 Jeffamine D-400/Urea Reaction Product (MW = 2303)

	first end point, mequiv/g	mV at end point	second end point, mequiv/g	mV at end point
	0.8799	455	2.7223	659
	0.8702	455	2.7257	666
	0.8780	460	2.7213	661
$\bar{X}$	0.8760		2.7231	
σ	0.0051		0.0023	

were scaled up top a 5-L reactor in order to make larger quantities of materials for evaluation and to further study reaction parameters. At this scale, accurate weight loss data could be obtained and used as a simpler measure of the moles of ammonia released. The equivalents of amine present after reaction were determined by acid titration. The equivalents of amine consumed were calculated by subtracting the equivalents of amine present after reaction from the equivalents of amine in the reactants. Table IV shows the results as a function of various Jeffamine D-400/urea molar ratios at 150 °C. The molar ratio of amine consumed to urea charged ranged from 0.99 to 1.06; the highest values correspond to the highest amine conversions. The ratios of ammonia formed (by weight loss) to urea charged ranged from 1.02:1 to 1.11:1.

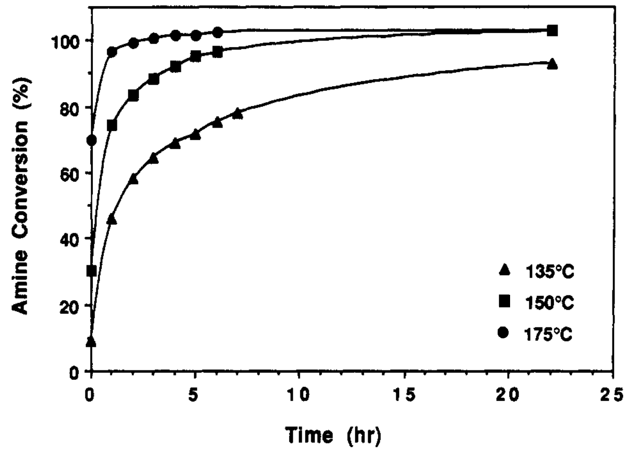


Figure 3. Effect of temperature on the extent of amine conversion using a Jeffamine D-400/urea molar ratio of 1.20:1.

(5) Effects of Using Other Diamines. Other diamines (as well as higher functional amines) could be reacted with urea to form the analogous products. Table V gives a partial tabulation of products made by replacing the Jeffamine D-400 with Jeffamine D-230, Jeffamine D-2000, an aminated poly(propylene glycol) of 1252 molecular weight, or an aminated poly(1,2-butylene glycol) of 2070 molecular weight. Reactions proceeded as expected.

Titration of Urea Moieties. For our application, a method was needed to quantify the number of urea moieties per product molecule.

Urea is known to act as a monobasic compound and form salts with strong acids. In 1913, urea was shown to react quantitatively with nitric acid to form urea nitrate, $CO(NH_2)_2 \cdot HNO_3$.[41] Several workers have also reported the quantitative formation of perchloric acid salts of urea, substituted ureas, and thiourea (see, for example, ref 42).

Titrations of urea are quantitative in certain nonaqueous media using perchloric acid as titrant. A variety of solvents have been employed such as acetone and methyl ethyl ketone,[43] 1,4-dioxane,[43] nitromethane,[44] and propylene carbonate.[45] However, glacial acetic acid was

Table VIII
Effect of Amine Conversion on Urea Balance, A 1.20:1 Jeffamine D-400/Urea Reaction Product at 150 °C (XXXI)

sample	time at 150 °C, h	amine (mequiv/g)	amine conversn, mol %	mequiv total urea moieties[a]/g		% total urea moieties found by titratn
				calcd[b]	found by $HClO_4$ titratn	
XXXI-1	0	2.3041	49.3	1.6887	1.6121	95.5
XXXI-2	1	1.4381	75.9	1.7202	1.6403	95.4
XXXI-3	4	0.9512	90.9	1.7385	1.6894	97.2
XXXI-4	20	0.8267	94.7	1.7433	1.6913	97.0

[a] Total of urea, terminal ureas, and internal ureas. [b] Corrected for ammonia lost during reaction.

Table IX
Perchloric Acid Titrations of Urea Backbone Polyether Diamines Made by Using Various Jeffamine D-400/Urea Molar Ratios

sample	amine/urea molar ratio	reactn temp, °C	% amine conversn	MW		urea moieties/molecular[a]	
				HCl titratn	$HClO_4$ titratn	calcd	titratn
XI	1.15	150	98.4	3796	3805	nd	nd
I	1.20	135	93.0	2445	2429	4.45	4.47
II	1.20	135	94.6	2305	2314	3.90	4.03
XXX	1.20	135	95.2	2303	2283	4.12	4.22
XXXI	1.20	150	94.7	2419	2419	4.08	4.09
XVIII	1.20	150	98.7	2823	2785	4.97	4.90
III	1.20	150	102.8	3284	3445	6.31	6.35
XII	1.20	150	104.9	3443	3487	6.32	6.36
IV	1.20	150	101.3	3657	3667	7.13	6.76
VI	1.20	175	99.2	2729	2697	4.70	4.67
XXXII	1.20	175	99.9	2995	3020	5.33	5.33
V	1.20	175	102.6	3458	3421	6.69	6.32
XIV	1.30	150	103.9	2389	2397	4.34	4.10
VII	1.30	150	102.9	2387	2386	4.33	4.10
VIII	1.30	150	98.1	2106	2086	3.50	3.43
XXXIII	1.30	150	97.4	1964	1965	3.19	3.19
IX	1.30	175	99.0	2120	2107	3.50	3.46
X	1.30	175	100.5	2012	1993	3.22	3.18
XXXIV	1.30	175	97.2	1993	1987	3.18	3.18
XVII	1.35	150	97.6	1785	1781	2.80	2.79

[a] nd, not determined.

Table X
Perchloric Acid Titrations of Urea Backbone Polyether Diamines Made by Using Urea and Selected Aminated Polyglycols

sample	amine[a]	amine/urea molar ratio	temp, °C	time, h	% amine conversn	MW		urea moieties/molecule	
						HCl titratn	$HClO_4$ titratn	calcd	titratn
XIX	D-230	1.14	135	24	91.2	1466	1459	4.57	4.73
XXI	A	2.00	150	18	nd[b]	2562	2537	1.02	0.99
XXII	A	2.00	150	8	96.0	2495	2542	0.97	0.99
XXV	D-2000	2.00	150	16	95.4	4120	4242	0.93	0.97
XXIV	D-2000	1.20	150	16	79.8	9866	10111	3.61	3.70
XXVIII	D-2000	1.20	150	39	80.7	11119	11331	4.44	4.40
XXXIV	D-2000	1.20	150	68	101.2	13361	13426	5.47	5.34
XXIX	B	1.20	150	23	89.0	8203	8084	2.93	2.92

[a] A, an aminated poly(propylene glycol) of 1252 molecular weight; B, an aminated poly(1,2-butylene glycol) of 2070 molecular weight. [b] nd, not determined.

recognized early as a preferred medium since it enhances the basicity of the urea.[46-49]

(1) Perchloric Acid Titration of Low Molecular Weight Ureas. A series of low molecular weight aliphatic ureas were titrated with 0.1 N perchloric acid in acetic acid (Table VI). Urea, thiourea, substituted terminal aliphatic ureas, and substituted internal ureas all could be titrated effectively and their molecular weight could be calculated from titration data. However, aromatic ureas and aromatic/aliphatic ureas were not titrated by this procedure. Diphenylurea, phenylurea, and (2-hydroxyethyl)phenylurea were not titrated. In addition, cyclic aliphatic ureas having five-membered rings such as ethyleneurea and hydantoin were not titrated under the same conditions.

(2) Perchloric Acid Titration of Polyether Polyamines Containing Urea Moieties in Their Backbones. The perchloric acid titration of polyether polyamines containing urea moieties in their backbones provides a rapid (10–30 min) method for obtaining the stoichiometric relationships between the amino end groups and the internal urea moieties. A diamine of 2303 molecular weight, synthesized by reacting Jeffamine D-400 with urea at a 1.20:1 Jeffamine D-400/urea molar ratio (sample XXX), was titrated with 0.1 N perchloric acid in acetic acid. An example of the titration curve is given in Figure 4 and the results of three titrations are given in Table VII.

Up to the first end point of the titration curve, the amino end groups were selectively titrated. From there to the second end point of the titration curve, the urea moieties were titrated. Reactions that are believed to have occurred are shown in Figure 4 with the measured solution potentials at the end points.

The number-average molecular weight, $\bar{M}_n$, of the diamine (XXX) and the average number of urea moieties per molecule, n, (Table VII) were computed as follows:

It was also possible to calculate n from the molecular

molecular weight, $\bar{M}_n$ =

$$\frac{(2 \text{ end groups/molecule})\,(1000 \text{ mg/g})}{(0.8760 \text{ mequiv/g})}$$

$$\bar{M}_n = 2283$$

urea moieties/molecule, n =

$$\frac{2(2.7231 \text{ mequiv/g} - 0.8760 \text{ mequiv/g})}{(0.8760 \text{ mequiv/g})}$$

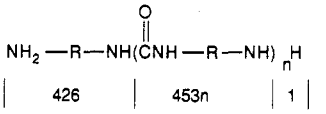
$$n = 4.22$$

weights of the reactants and products.

$$\bar{M}_n \text{ of Jeffamine D-400} = 427$$

$$\bar{M}_n \text{ of product} = 2303$$

Therefore:



$$\underbrace{NH_2-R-}_{426}\underbrace{NH(\overset{O}{\overset{\|}{C}}NH-R-NH)_n}_{453n}\underbrace{H}_{1}$$

$$453\,n + 427 = 2303$$

$$n = 4.14$$

This calculation is independent of the experimental results of the perchloric acid titration, but furnished the same value of n within experimental error.

(3) Effect of Amine Conversion on Urea Balance. Since urea (as reactant), aliphatic terminal ureas, and aliphatic internal ureas (as products) could all be titrated with perchloric acid, the total number of moles of urea should remain constant throughout the amine conversion. Therefore, while the first end point in a perchloric acid titration is a measure of amine conversion, the second end point is a measure of all the urea in the system.

An additional series of experiments were carried out using a 1.20:1 molar ratio of Jeffamine D-400 to urea at 150 °C (sample XXXI). Samples were removed at various times from 49 to 95% amine conversion (Table VIII). The total molar amount of urea moieties was calculated based on the moles of reactants charged and the moles of ammonia released at each stage of conversion. Each calculated value was then compared to the total amount of urea moieties found by the perchloric acid titration of the corresponding sample. In excess of 95% of the expected total urea was found in each case. Small amounts of urea were apparently lost from the system by entrainment during the early stages of the reaction when ammonia release was most rapid. The unrecovered urea was present at the bottom of the condenser.

This correlation gives additional support to the proposed reaction sequence for oligomer formation and it furnishes evidence that the perchloric acid titration is quantitative in these systems.

Titrations of Urea Backbone Diamines Made Using Jeffamine D-400 and Urea under Various Reaction Conditions. The molecular weights of diamines made from Jeffamine D-400 and urea were primarily controlled by the molar ratios of the reactants. The other reaction parameters (temperature and time) must be such that high amine conversion is obtained. For guidelines to these conditions, the results of the perchloric acid titration method on materials made from Jeffamine D-400 and urea under a variety of reaction conditions are given in Table IX.

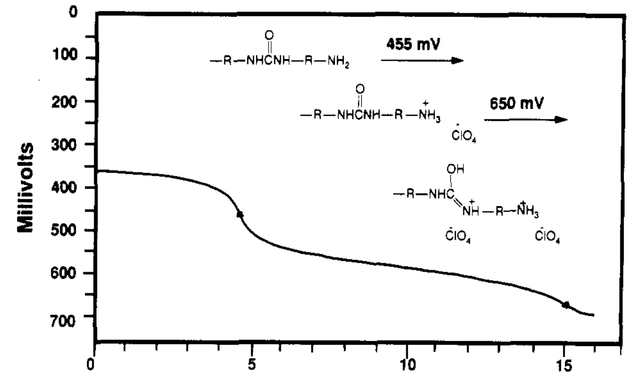


Figure 4. Perchloric acid titration of sample XXX, A 1.20:1 Jeffamine D-400/urea reaction product (MW = 2302).

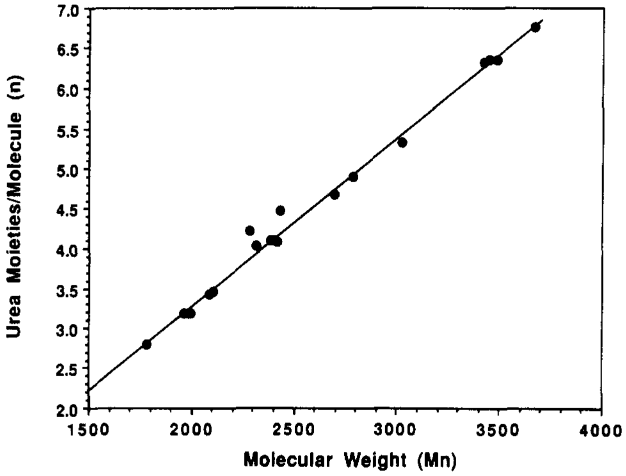


Figure 5. Correlation between the average number of urea moieties/molecule and number-average molecular weight for various materials based on Jeffamine D-400.

The number-average molecular weight of each material was determined by titration with both 0.1 N HCl and 0.1 N $HClO_4$. Excellent agreement was obtained. The average number of urea moieties per molecule, n, was also determined by two procedures: one utilized the perchloric acid titration results and the other utilized the molecular weights of the reactants and products. Agreement was very good. The average number of urea moieties per molecule, as determined by perchloric acid titration, is plotted vs the number average molecular weight in Figure 5, showing the expected linear correlation. This correlation indirectly verifies that the perchloric acid titration is quantitative.

Titrations of Urea Backbone Diamines Made Using Urea and Other Aminated Polyglycols. Aminated poly(propylene glycols) with molecular weights ranging from 230 to 2000 and poly(1,2-butylene glycol) of 2070 were reacted with urea to form the corresponding polyether diamines containing internal urea moieties. Table X presents a list of these materials. There was very good agreement between molecular weights as determined by HCl and $HClO_4$ titrations. Agreement between the calculated and titration determined values of n was also good.

Product Characterization. (1) Viscosity. The Brookfield viscosities (25 °C) of a range of selected polyether diamines containing internal urea moieties within their backbones are given in Tables II and V. Diamines containing urea moieties and poly(propyleneoxy) spacers in their backbones have relatively high viscosities at ambient temperature due to intermolecular hydrogen

Table XI
Effect of Temperature on Viscosity of a Polyether Polyamine Having Four Urea Moieties per Average Molecule

temp, °C	viscosity, cps	temp, °C	viscosity, cps
30	72800	80	1080
40	25600	90	660
50	7600	100	420
60	3640	110	280
70	1960		

Table XII
Effect of Number of Urea Moieties, Product Molecular Weight, and Size of Poly(propyleneoxy) Blocks on Glass Transition Temperature

sample	MW of starting mater	molar ratio	MW of product	urea moieties/ av molecule	T_g, °C
D-2000	2000		2000	0	−70
XXV	2000	2.00	4120	2.0	−66
XXIV	2000	1.20	9866	3.9	−64
XXI	1200	2.00	2562	2.1	−63
IX	400	1.30	2120	3.5	−44

bonding. Viscosity is readily reduced by heating (Table XI).

The effects of shear rate on the viscosity of selected materials were measured on a Haake viscometer at 25, 50, and 90 °C. Only limited shear rate ranges were possible with the equipment available. The shear rate dependence of viscosity for a polyether diamine containing about four urea moieties per molecule (based on Jeffamine D-400) is nearly Newtonian throughout the shear rate ranges employed (0.4–442 cm^{-1}). There could be the beginnings of some shear thinning at the highest temperature and shear rate. The shear rate dependence of viscosity for a polyether diamine containing about one urea moiety per molecule (based on aminated poly(propylene glycol) of 1200 molecular weight) was Newtonian throughout the shear rate range employed (10–2350 cm^{-1}).

(2) Molecular Weight and Distribution. Molecular weight data on various materials included in this paper can be found in Tables II and V and in Figure 2. Molecular weights were controlled primarily by the molar ratios of the reactants.

Molecular weight was determined both by titration of the amino end groups of urea backbone polyether diamines and by SEC. End group titration had the advantage of providing a number-average molecular weight and quantifying the number of end groups available for reactions with other materials. SEC had the advantage of providing information on the molecular weight distribution. However, SEC had the disadvantage of providing uncertain information since polystyrene standards were used for reference. Therefore, there were differences in the number-average molecular weights obtained by these two methods.

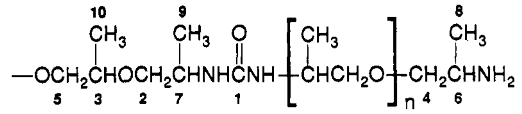
(3) Density. The densities of a range of selected polyether diamines containing internal urea moieties, synthesized from Jeffamine D-400, are given in Table II. Densities vary from 1.02 to 1.04 g/mL and appeared to have a weak molecular weight dependence. Polyether diamines based on Jeffamine D-2000 and containing an average of about four internal moieties per molecule (XXIV and XXVIII) had a density of 1.00.

(4) Glass Transition Temperature. The glass transition temperature, T_g, of selected polyether diamines containing internal urea moieties and poly(propyleneoxy) moieties were determined by DSC and compared to Jeffamine D-2000 (see Table XII). The most important product characteristics affecting T_g were (1) the average number of urea moieties per molecule, (2) the molecular weight of the poly(propyleneoxy) spacers between adjacent internal urea moieties, and (3) the molecular weight of the product. The lowest molecular weight poly(propyleneoxy) spacer and the highest number of urea moieties per average molecule produced the largest increase in T_g. The effect of poly(propyleneoxy) spacer molecular weight can be seen by comparing samples XXIV and IX (T_g = −64 and −44 °C). The effect of the average number of urea moieties per molecule can be seen by comparing Jeffamine D-2000 and sample IX (T_g = −70 vs −44 °C; $\bar{M}_n \sim 2000$).

Table XIII
Weight Loss Data by TGA on Selected Polyether Diamines Containing Internal Urea Moieties

				temperature, °C	
sample	amine	molar ratio	MW of product	2% wt loss	5% wt loss
D-2000	D-2000		2036	211	236
XIX	D-230	1.14	1466	158	206
XVII	D-400	1.35	1785	215	239
XXXII	D-400	1.30	1964	216	238
XXX	D-400	1.20	2303	218	242
XXVIII	D-2000	1.20	11119	201	214

Table XIV
Carbon-13 NMR Structural Assignments of a Representative Segment of a Polyether Polyamine Containing Internal Urea Moieties and Poly(propyleneoxy) Moieties



$$-OCH_2\overset{CH_3}{\overset{|}{C}}HOCH_2\overset{CH_3}{\overset{|}{C}}HNH\overset{O}{\overset{\|}{C}}NH-\left[\overset{CH_3}{\overset{|}{C}}HCH_2O\right]_n-CH_2\overset{CH_3}{\overset{|}{C}}HNH_2$$

	chemical shift,[a] ppm	
assgnmt	in $DCCl_3$	in DMSO-d_6
1	157.6	157.4
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	46.5/46.9	46.2/46.4
7	45.4/45.9	44.7/44.9
8	19.7	19.7
9	18.3	18.0
10	17.1/17.3	16.9/17.0

[a] Relative to tetramethylsilane (0 ppm).

(5) Thermal Stability. The thermal stability of selected polyether diamines containing internal urea moieties was studied by thermal gravimetric analysis (TGA) in a nitrogen purge using a heating rate of 10 °C/min. Results are given in Table XIII and are compared to those for Jeffamine D-2000. The temperatures at which a 2 and 5% weight loss occur are reported. The weight loss data for all Jeffamine D-400 based materials were essentially the same as Jeffamine D-2000. The material based on Jeffamine D-230 had a lower molecular weight and a greater volatility, resulting in a greater weight loss. The values for the Jeffamine D-2000 based material was also low.

Carbon-13 NMR Spectroscopy. The carbon-13 NMR chemical shift assignments for a representative segment of a polyether polyamine containing internal urea and poly(propyleneoxy) moieties are given in Table XIV. Assignments were made by a detailed examination of the resonance lines and by comparisons with spectra of related structures. Attached proton spectra were also run to ascertain which carbon atoms have an even number of attached hydrogens (produces a positive response) and which carbons have an odd number of attached hydrogens (produces a negative response). This technique easily distinguishes methylene carbons from methyl and methine carbons. A representative carbon-13 NMR spectrum

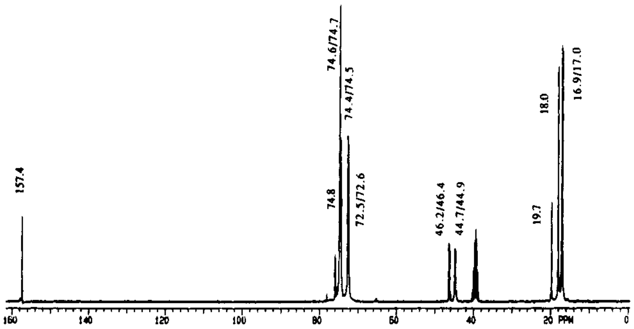
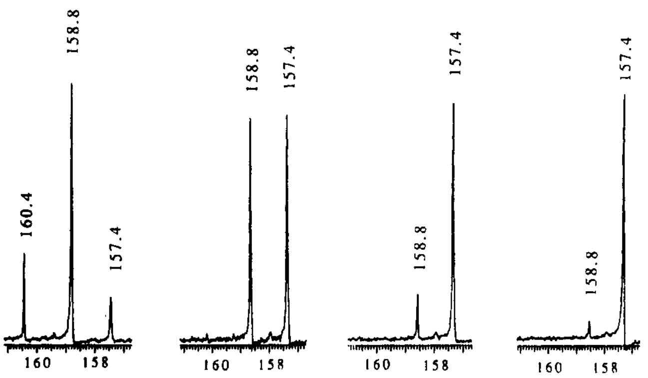


Figure 6. Carbon-13 NMR spectrum of sample XVII.



49.3% Amine Conversion

75.9% Amine Conversion

90.9% Amine Conversion

94.7% Amine Conversion

Figure 7. Carbon-13 NMR spectra of carbonyl carbon atoms vs amine conversion.

is given in Figure 6.

The disappearance of urea, the formation and subsequent disappearance of terminal ureas, and the formation of internal ureas can easily be followed by carbon-13 NMR. An experiment was conducted in which a 1.20:1 molar ratio of Jeffamine D-400/urea was heated at 150 °C. Samples were removed at various amine conversions. Figure 7 shows the carbon-13 NMR spectra. At 49.3% amine conversion, the urea (160.4 ppm) was markedly depleted and the terminal urea (158.8 ppm) was clearly the dominant species present. Some internal urea (157.4 ppm) had been formed. At 75.9% amine conversion, the urea was gone and roughly equal amounts of terminal and internal urea were present. At 94.7% amine conversion, internal urea was the dominant species present, while terminal urea was only present at low levels.

Chemical shifts in the carbon-13 NMR line patterns of the methine carbon adjacent to the amino end group as well as the methyl and methylene carbon atoms attached to this methine carbon were also useful in following the progress of the reaction sequence.

Conclusions

A variety of polyether polyamine oligomers containing backbone urea moieties were prepared by the reactions of aminated polyglycols with urea. Reactions were carried out neat at 135–175 °C. The progress of the reactions was followed by amine conversion, ammonia formation, and carbon-13 NMR. A terminal urea was formed as a reaction intermediate. Further reaction of this terminal urea with amine produced the desired internal urea. A reaction sequence was proposed, consistent with all of the measurements made.

A perchloric acid titration method was also developed to rapidly quantify the number of urea moieties. Amino end groups were titrated at the first break and urea moieties were titrated at the second break. Thus a quantitative relationship was established from which the average number of urea moieties per molecule *n*, could be calculated. This titrated value of *n* agreed very well with the predicted value based on the amount of reactants charged.

Product molecular weight was primarily a function of the reactant molar ratio. The $\bar{M}_n$ range from 1800 to 3800 was studied by using a 400 molecular weight aminated poly(propylene glycol). The products were scaled up to a 5-L reactor to make 3.5-kg quantities for evaluation and to study reaction parameters. The corresponding products were made from other aminated polyglycols. These polyether polyamines containing preformed urea moieties in their backbone are useful in urethane/urea polymer systems, particularly reaction injection molding.

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