Macromolecules **1991,** *24,* 35-41

Multifunctional Captodative Monomers: Urea-Containing Dehydroalanines and Their Polymers

David W. Kurz and Lon J. Mathias*

Department of Polymer Science, University of Southern Mississippi, Hattiesburg, Mississippi 39406-0076

Received January 23, 1990; Revised Manuscript Received May 16, 1990

ABSTRACT: The synthesis and characterization of a new family of urea derivatives of dehydroalanines are described. Ten alkyl and seven aryl monomer and polymer urea derivatives of dehydroalanine methyl ester were synthesized. The radical chain end formed from these monomers during polymerization is assumed to be especially stabilized by the synergistic captodative effect involving electron-donating and -withdrawing substituents on the radical carbon. This is consistent with rapid formation of high molecular weight polymers as indicated by intrinsic viscosity values up to 1.7 dL/g. Viscosity values for THF-soluble polymers were consistent with SEC estimates for random coil polymers of several million molecular weight. FT-IR and ^{13}C NMR spectra confirmed compound structures. X-ray diffractograms showed side-chain crystallinity in the longer alkyl urea derivatives as exemplified by the *n*-octadecyl polymer. The availability of a wide range of isocyanate precursors to the monomers makes possible a variety of derivatives possessing intra- and intermolecular hydrogen-bonding units in the polymers.

Introduction

Derivatives of dehydroalanine (DHA) are known to readily undergo radical polymerization. Figure 1 shows the general synthesis and basic structures of a dehydroalanine monomer and the subsequent polymer. The first reports of these monomers appeared in the patent literature in 1946[1] and 1949[2], describing the solution and bulk polymerization of *N*-acetyldehydroalanine methyl ester. A water-soluble homopolymer was reported as were copolymers with monomers such as acrylonitrile and styrene. Polymers synthesized from 2-formamido-, 2-(benzyloxycarbamido)-, and 2-(ethoxycarbamido)acrylic acids were reported in 1952.[3] The intrinsic viscosities in water ranged from 0.13 to 0.58 dL/g, with a molecular weight of 30 000 for the latter measured by light scattering. Attempts to hydrolyze the polymers to the amphoteric poly(α-aminoacrylic acid) were reported to be unsuccessful.

A different approach to synthesizing this polymer was described in 1961.[4] α-(*N*-Phthalimido)acrylic acid and the *N*-carboxyanhydride of dehydroalanine were each polymerized radically followed by hydrazinolysis and hydrolysis, respectively. A 1:1 ratio of COOH and NH_2 groups was confirmed by titration. Another successful synthesis of this polymer was accomplished by hydrolyzing a high molecular weight sample of poly(*N*-acetyldehydroalanine).[5] At higher pH, the dilute-solution characteristics of the polymer were consistent with typical polyelectrolyte behavior.

Several other derivatives of dehydroalanine have been synthesized and polymerized. A divinyl compound, the *N*-methacryloyl methyl ester of DHA, was synthesized and cyclopolymerized to soluble product.[6] The structure was postulated to be a five-membered-ring cyclopolymer. Other workers have reported chiral purine- and pyrimidine-substituted dehydroalanine polymers (polynucleotide analogues) with intrinsic viscosities ranging from 0.35 to 0.78 dL/g.[7] Bis- and tris(dehydroalanine) agents synthesized from phthaloyl and trimesoyl chlorides were prepared and used to form cross-linked systems.[8] The polymer gels thus obtained were utilized in affinity column chromatography to separate adenosine and uridine. Photoactive poly(N-substituted dehydroalanines) have also been prepared.[9] For example, the 9-(carboxymethyl)carbazole derivatives of dehydroalanine and its methyl ester were prepared and polymerized to give products with intrinsic viscosities ranging from 0.36 to 1.05 dL/g. These many examples illustrate the great variety of monomers and polymers that can be prepared based on the dehydroalanine functionality and polymerizability.

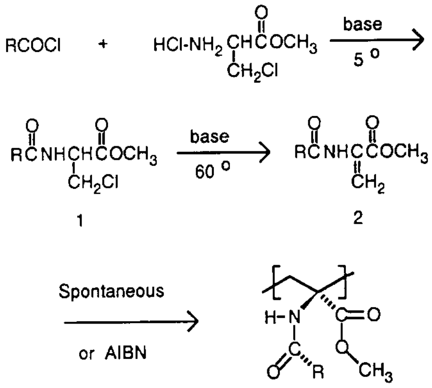

Figure 1. Synthesis of amide-containing dehydroalanines.

We have been involved recently with the synthesis and polymerization of a variety of amide derivatives to extend the utility of dehydroalanines as monomers. The general synthetic pathway for the amide monomers (as shown in Figure 1) involves loss of HCl from β-chloroalanine derivatives such as 1. Synthesis of 2 (as the methyl ester) takes place in high yield to give easily purified monomers. Polymer formation from the alkyl amide derivatives was surprisingly facile. For example, spontaneous polymerization at room temperature was observed for a number of monomers, leading to molecular weights in the millions to tens of millions when held above the melting point for several minutes with no initiator present,[10] or by monolayer and vesicle polymerization.[11,12] The series of 2-alkanamide derivatives of methyl propenoate were characterized by viscosity and X-ray diffraction. A long *d* spacing was observed and shown to vary consistently with side-chain length corresponding to interchain distances with nonintercalated packing.

The results obtained with the amide derivatives suggested that urea analogues might have unique and useful properties based on the bifurcated hydrogen bonding possible with urea groups. A preliminary study showed that the methyl-, ethyl-, *n*-propyl-, and *n*-butylurea

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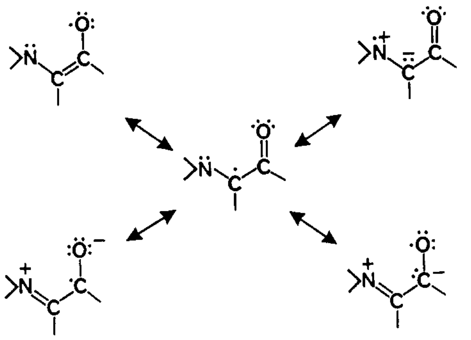

Figure 2. Resonance stabilization due to the captodative effect.

derivatives of dehydroalanine could be readily prepared by reaction of the appropriate isocyanate with dehydroalanine. These monomers readily formed polymer spontaneously or with added initiator.[13]

We believe the facile polymerizability of these DHA derivatives is attributable to enhanced stability of the intermediate radicals due to the captodative effect. Captodative radical stabilization involves synergistic interaction of the electron-withdrawing (capto) substituent and the electron-donating (dative) substituent as illustrated in Figure 2.[14] In monomers based on structure **2**, these are ester and amide groups, respectively. The great variety of inexpensive, readily available isocyanates makes a large number of urea derivatives of DHA possible. The presence of a urea group pendant to the polymer chain would be expected to result in properties strongly affected by the urea substituent with its capability to form strong inter- and intramolecular hydrogen bonds. It was thought that the increased stability of hydrogen bonds (compared to the amide derivatives) might also result in monomers with increased amphophilic character, thus allowing more ready formation of ordered structures such as monolayers or vesicles. On the basis of the preliminary synthetic results showing that urea substituents in place of the amide groups allow high-polymer formation,[13] we carried out a general study of this new family of multifunctional monomers (analogous to **2**) and describe here in detail synthesis and characterization of the monomers and their polymers.

Experimental Section

Reagent grade solvents and reagents were used as received. All ^{13}C NMR spectra were obtained on a Bruker MSL-200 or Bruker AC-300. FT-IR spectra were recorded on a Nicolet 5DX as KBr disks or thin films cast from solvent. Dilute-solution viscosity measurements were made at 30 ± 0.1 °C with Cannon-Ubbelohde semimicroviscometers (no. 75 for water and no. 50 for THF and $CHCl_3$). Thermal analyses were performed on a Du Pont 9900 analyzer equipped with 910 DSC and 952 TGA cells using heating rates of 10 °C/min with nitrogen purge. X-ray diffractograms were obtained on a Philips APD 3520 all-purpose diffractometer using packed-powder samples or solvent-cast films. Optical activity was measured in chloroform with a PolyScience Corp. SR-6 polarimeter. The methyl ester hydrochloride salt of D,L-serine and the corresponding β-chloroalanine salt were prepared as described previously.[10]

Monomer Synthesis. The urea derivatives were synthesized by different methods depending on the isocyanate substituent. The general approach involved reacting freshly liberated β-chloroalanine with the isocyanate to form the urea followed by heating with addition of more base to form the unsaturated monomer. Alternatively, the β-chloroalanine ureas were isolated and purified prior to conversion to monomer. Representative examples of dehydrohalogenation follow.

Methylurea Derivative. To a 10-mm NMR sample tube containing the methylurea β-chloroalanine methyl ester (0.70 g, 4.02 mmol) was added 3 mL of CH_3OD with 3 drops of DMSO. Triethylamine (0.85 g, 8.40 mmol) was added, and the tube was shaken and immediately placed in the NMR for continuous monitoring. After the NMR spectrum indicated complete formation of the dehydroalanine derivative, the sample was stored overnight in a refrigerator and then filtered through a fritted glass filter to remove triethylamine hydrochloride salt. The solvent was removed by rotary evaporation, and the yellow product was recrystallized from methanol (0.48 g, 3.48 mmol, 87% yield). This derivative was further purified by column chromatography (ethyl acetate solvent, with 60/200-mesh silica gel) but spontaneously polymerized and precipitated upon exiting the column. We have been unable to isolate this material, or the corresponding ethylurea derivative, following chromatography due to high reactivity.

Isopropylurea Derivative. To a 250-mL round-bottom flask containing isopropylurea β-chloroalanine methyl ester (1.02 g, 4.58 mmol) was added 150 mL of chloroform with stirring at 5 °C under a nitrogen blanket. Triethylamine (0.50 g, 4.94 mmol) was added and the mixture heated at 60 °C for 6 h when the reaction was complete as indicated by thin-layer chromatography. The reaction mixture was stored overnight in a refrigerator and filtered. Solvent was removed by rotary evaporation, and the yellow product was recrystallized from methanol (0.77 g, 4.13 mmol, 90% yield, mp 88–90 °C). This derivative was further purified by column chromatography (ethyl acetate with 60/200-mesh silica gel).

***n*-Butylurea Derivative.** To a 250-mL round-bottom flask containing *n*-butylurea β-chloroalanine methyl ester (2.21 g, 9.34 mmol) was added 150 mL of chloroform with stirring at 5 °C under a nitrogen blanket. Triethylamine (0.95 g, 9.34 mmol) was added and the mixture heated at 60 °C for 1 h when the reaction was complete as indicated by thin-layer chromatography. The reaction mixture was washed twice with 0.1 N HCl and twice with deionized water, filtered through phase separation filter paper, and stored overnight in a refrigerator. The triethylamine hydrochloride salt was removed by filtration, and the solvent was removed by rotary evaporation. The yellow product (1.72 g, 8.59 mmol, 92% yield, mp 68–70 °C) was purified further by recrystallization from methanol and by column chromatography (chloroform with 60/200-mesh silica gel). Repeated recrystallization from methanol resulted in fine, white needles, mp 69 °C.

Phenylurea Derivative. To a 10-mm NMR sample tube containing phenylurea β-chloroalanine methyl ester (0.50 g, 1.95 mmol) was added 3 mL of $CDCl_3$ and 3 drops of DMSO. Triethylamine (0.20 g, 2.0 mmol) was added, and the tube was shaken and immediately placed in the NMR. The reaction was followed by NMR, which indicated that during formation of the dehydroalanine derivative, a byproduct formed that gradually increased to approximately a 50:50 ratio with the desired product after the starting material had completely reacted. The solution was washed twice with 0.1 N HCl and twice with deionized water, filtered through phase separation filter paper, and stored overnight in a refrigerator. Filtration through a fritted glass filter removed triethylamine hydrochloride salt, and the solvent was removed by rotary evaporation to give a yellow solid (0.29 g, 1.91 mmol, ca. 80–90% crude yield).

Polymer Synthesis. The urea dehydroalanine monomers that were soluble were polymerized by methods involving thermal or photoinitiation. Several typical polymerization schemes follow.

Ethylurea Derivative Polymer. A sample of ethylurea dehydoalanine methyl ester (1.30 g) was purified by column chromatography (60/200-mesh silica gel, ethyl acetate solvent). Polymer formation and precipitation occurred spontaneously as the compound was exiting the column. The polymer was dissolved in methanol, filtered through a 5.0-μm filter, and precipitated into 50:50 diethyl ether/petroleum ether. The white powder was dried under high vacuum (0.78 g, 60% yield), giving polymer with an intrinsic viscosity of 1.68 dL/g in methanol and 1.69 dL/g in water.

***n*-Butylurea Derivative Polymer.** A sample of *n*-butylurea dehydroalanine methyl ester (1.50 g) was purified by column chromatography (60/200-mesh silica gel, chloroform solvent) but polymerized upon rotary evaporation of the solvent. The polymer was dissolved in tetrahydrofuran (THF), filtered through a 5.0-μm filter, and precipitated into 50:50 diethyl ether/petroleum ether. The white powder was dried under high vacuum (0.77 g, 51% yield); intrinsic viscosity 0.65 dL/g in THF and 0.71 dL/g in methanol.

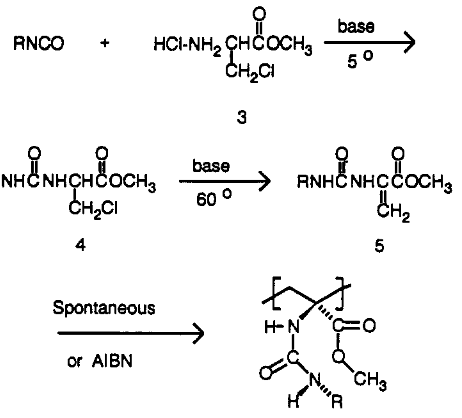

Figure 3. Synthesis of urea-containing dehydroalanine monomers and polymers.

***n*-Butylurea Derivative Polymer.** A sample of *n*-butylurea dehydroalanine methyl ester (1.0 g) was purified by column chromatography (60/200-mesh silica gel, chloroform solvent), dissolved in 6 mL of benzene, and purged with nitrogen. Vazo 67 azo initiator (5.0 mg) was added, and the mixture was held at 60 °C for 24 h. The resulting gel was dissolved in THF, filtered through a 5.0-μm filter, and precipitated into 50:50 diethyl ether/petroleum ether. The white powder was dried under high vacuum (0.41 g, 41% yield). The polymer possessed an intrinsic viscosity of 0.11 dL/g in THF.

***n*-Butylurea Derivative Polymer (Bulk Polymerization).** A sample of *n*-butylurea dehydroalanine methyl ester (0.50 g) was purified by column chromatography (60/200-mesh silica gel, chloroform solvent). Solvent was removed, and the viscous sample was purged with nitrogen and held at 90 °C for 24 h. The resulting gel was dissolved in THF, filtered through a 5.0-μm filter, and precipitated into 50:50 diethyl ether/petroleum ether, and the white powder was dried under vacuum (0.18 g, 36% yield). The polymer had an intrinsic viscosity of 0.93 dL/g in methanol.

***n*-Octadecylurea Derivative Polymer.** A sample of *n*-octadecylurea dehydroalanine methyl ester (0.51 g) was purified by column chromatography (60/200-mesh silica gel, chloroform solvent), dissolved in 6 mL of benzene, and purged with nitrogen. Vazo 67 azo initiator (4.0 mg) was added, and the mixture was held at 60 °C for 24 h. The resulting viscious solution was dissolved in THF, filtered through a 5.0-μm filter, and precipitated into 50:50 diethyl ether/petroleum ether. The white powder was dried under high vacuum (0.29 g, 51% yield), giving a polymer with an intrinsic viscosity of 0.26 dL/g in THF.

Results and Discussion

General monomer synthesis (as shown in Figure 3) involved either a two-step, one-pot process or a sequential two-step process with intermediate isolation that is easy and straightforward. Intermediates 4 were synthesized by reaction of various alkyl and aryl isocyanates with β-chloroalanine ester after triethylamine neutralization of the HCl salt 3. A second equivalent of triethylamine resulted in dehydrochlorination to give the urea monomers 5 in 40–90% yield. Tables I and II list the derivatives synthesized along with recrystallization solvent and monomer yields or yields of spontaneously formed polymer.

Table I
Alkylurea DHA Monomers and Polymers Synthesized

R group	isol monomer yield, g	spontaneous polymer yield, g	reacn solvent	recryst solvent
methyl		0.48 (87%)	ethyl acetate	
ethyl		0.29 (91%)	ethyl acetate	
n-propyl	1.48 (98%)		ethyl acetate	methanol
isopropyl	0.77 (90%)		chloroform	chloroform
n-butyl	1.72 (92%)		chloroform	methanol
tert-butyl	0.30 (86%)		chloroform	chloroform
cyclohexyl	0.82 (95%)		benzene	cyclohexane
bis(1,6-hexyl)		0.33 (79%)	benzene	
n-octyl	7.72 (94%)		chloroform	chloroform
n-octadecyl	2.02 (92%)		chloroform	
p-toluenesulfonyl		0.55 (89%)	benzene	
(*R*)-(+)-α-methylbenzyl		1.22 (82%)	benzene	
(*S*)-(−)-α-methylbenzyl		0.79 (88%)	benzene	

Table II
Arylurea DHA Derivatives Synthesized

R group	yield, g		reactn solvent	recryst solvent
	monomer	cyclic compd		
phenyl		0.29 (91%)[a]	benzene	chloroform
o-tolyl	0.20 (46%)[a]	0.20 (46%)[a]	benzene	chloroform
m-tolyl	0.08 (16%)[a]	0.40 (80%)[a]	benzene	chloroform
p-tolyl	0.02 (5%)[a]	0.39 (90%)[a]	benzene	chloroform

[a] Estimated from ^{13}C NMR spectra.

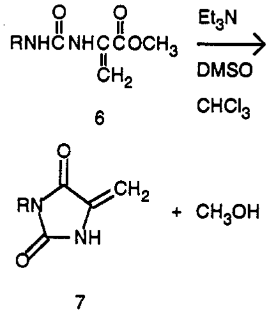

Figure 4. Synthesis of phenylurea cyclic dehydroalanine.

Monomer purification involved chromatography (methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, and *tert*-butyl compounds) or aqueous extraction followed by recrystallization in solvents such as methanol. While the one-pot procedure usually gave good yields of acceptably pure products, some of the products were difficult to purify, formed byproducts, or polymerized upon purification. Alternatively, formation of the urea β-chloroalanine methyl ester occurred in high yields, and these materials could be recrystallized from methanol to give pure precursors for the second step. These β-chloro derivatives were much easier to recrystallize than the monomers and were stable under nitrogen at room temperature. They could be stored and converted to monomers by dehydrochlorination shortly before polymerization.

The *n*-propyl-, isopropyl-, *n*-butyl-, *tert*-butyl-, cyclohexyl-, and *n*-octadecylurea dehydroalanine monomers were relatively stable upon isolation, although the methyl, ethyl, tosyl, (*R*)-(+)-α-methylbenzyl, and (*S*)-(−)-α-methylbenzyl compounds almost always underwent spontaneous polymerization during purification. For example, the methyl and ethyl derivatives spontaneously polymerized and precipitated as they exited the chromatography column. As a consequence, we have been able to obtain IR and NMR spectra of these materials only as slightly impure reaction products.

To complicate matters even more, the pheny, *o*-tolyl, *m*-tolyl, *p*-tolyl, and 4-nitrophenyl compounds formed cyclic byproducts under typical synthesis conditions. Formation of these compounds (as determined by ^{13}C and ^{1}H NMR) involved intramolecular nitrogen displacement of the ester methoxy group of 6 as shown in Figure 4. This led to a method of clean and high-yield formation of the cyclic phenyl compound 7 as one example of the synthesis of this new family of heterocyclic compounds. It was found, however, that in the presence of excess triethylamine,

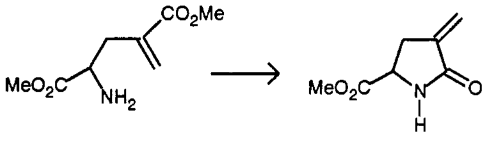

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Figure 5. Non-Michael-addition ring-closure example.

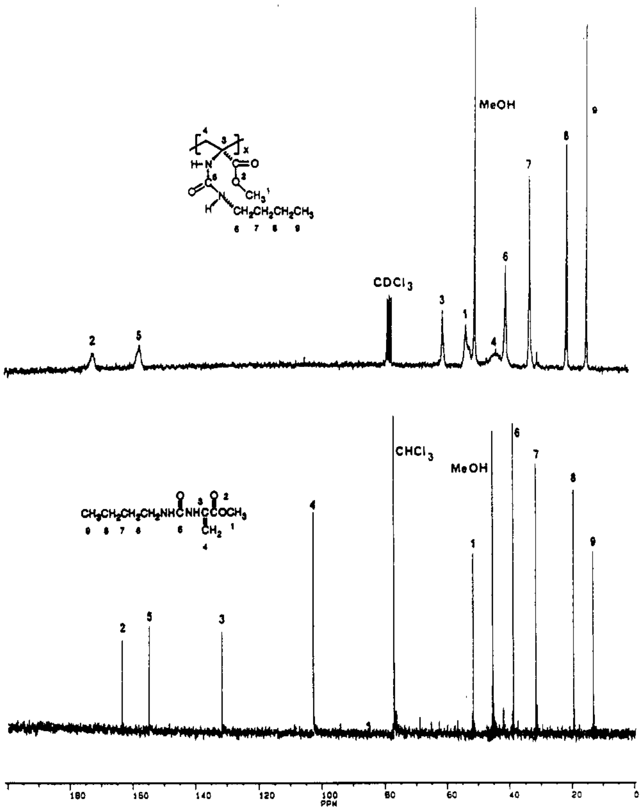

Figure 6. ^{13}C NMR of *n*-butylurea dehydroalanine monomer (lower trace) and polymer (upper trace).

additional peaks gradually appeared in the ^{13}C NMR spectrum suggesting that further base-catalyzed reaction was occurring. Formation of these compounds involves preferential attack at the ester group rather than at the β-position to the carbonyl which would lead to an intramolecular Michael addition product. This preference is consistent with the reaction of a similar compound 8 (Figure 5) in which the orientation of the attacking nucleophile with respect to the sp^2-hybridized electrophiles determines the site of reaction to give 9.[15]

Monomer polymerization used typical radical initiators in organic and (for the methyl- and ethylurea derivatives) aqueous solutions. Polymerizations were also accomplished neat by heating the compounds above the melting points. Some of the monomers spontaneously polymerized upon solvent evaporation during purification. Polymer isolation involved dissolution, precipitation into a nonsolvent, and vacuum-drying.

Structure determination of the monomers and polymers was accomplished with FT-IR and ^{13}C NMR. Figures 6 and 7 show typical ^{13}C NMR spectra obtained for the *n*-butyl and *n*-octadecyl derivatives, respectively. All monomers and polymers gave nearly identical spectra, differing only in areas associated with increasing alkyl chain length or aryl content. Table III lists the ^{13}C NMR peak assignments for the dehydroalanine derivatives, and Table IV lists the assignments for the polymers. All of the monomer spectra showed characteristic vinyl peaks at 104.5 and 132.1 ppm.

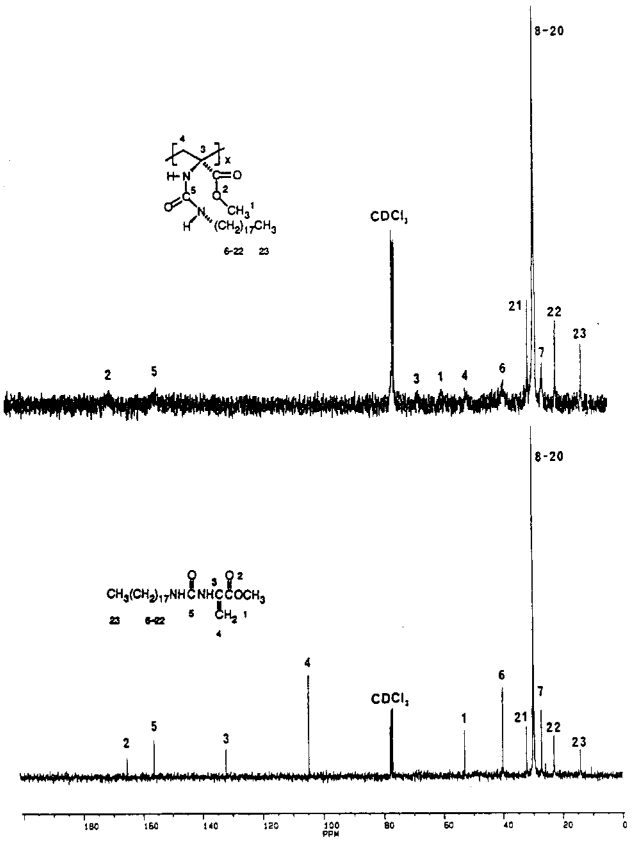

Figure 7. ^{13}C NMR of *n*-octadecylurea dehydroalanine monomer (lower trace) and polymer (upper trace).

These alkene peaks disappeared on polymer formation, and new peaks appeared upfield with chemical shifts (at ca. 40–52 and 55–62 ppm) and line widths characteristic of polymer backbone carbons. Some evidence is apparent for tacticity information (as seen, for example, in peak 1 for the methyl ester carbon in Figure 6 for the *n*-butyl polymer) although stereochemical assignments have not yet been made.

The final loss of HCl from the urea β-chloroalanine methyl esters to form the methy-, ethyl-, phenyl-, *o*-tolyl-, *m*-tolyl-, and *p*-tolylurea and bis(1,6-hexyldiurea) dehydroalanine derivatives was followed by ^{13}C NMR. The urea-containing β-chloroalanine derivative was added to the NMR sample tube along with triethylamine. Spectra were obtained every 5 min until no further change was detected. The alkyl urea derivatives showed clean conversion to the monomer with little byproduct formation. The aryl derivatives, however, showed initial conversion to the desired products followed by gradual formation of a subsequent product involving intramolecular displacement of the ester methoxy group as described above. While not all of these acrylic and cyclic aryl urea DHA compounds have been isolated yet, the phenyl compound has been fully characterized. Polymerization of these compounds awaits further study, and Table III contains data for nonisolated aryl intermediates.

FT-IR spectra for the *n*-butylurea dehydroalanine monomer and polymer are shown in Figure 8. All of the monomers and polymers gave nearly identical spectra, differing only in areas associated with increasing alkyl chain length and conversion of the alkene groups to polymer backbone units. The characteristic vinylidene peaks at 890 and 790 cm^{-1} were not present in the polymer spectra.

Polymer viscosities ranged from 0.07 to 1.68 dL/g but were generally in the range of values expected for reasonable polymer molecular weight (>0.2 dL/g). Table

Table III
^{13}C NMR of the Urea-Containing Dehydroalanine Derivatives

urea	carbon peak assignment 1	2	3	4	5	6	7	8	9	10	11	12
methyl	51.4	164.0	131.6	102.2	155.6	25.0						
ethyl	52.3	164.9	132.1	103.8	155.6	34.4	22.9	11.0				
n-propyl	52.2	164.8	132.1	104.5	155.9	41.5	32.0	19.9	13.6			
isopropyl	52.4	165.1	131.6	104.6	155.0	41.4	22.7					
n-butyl	52.5	165.1	132.1	104.8	155.9	39.8	32.0	19.9	13.6			
tert-butyl	51.6	164.4	131.6	103.4	154.4	45.4	28.5					
cyclohexyl	52.5	165.3	132.0	104.6	154.9	48.7	33.4	25.0	25.5			
bis(1,6-hexyl)	50.3	162.5	130.7	100.4	153.4	36.9	27.6	24.2				
n-octadecyl	51.3	163.8	131.6	101.8	154.7	44.9	38.4	30.6				
(*R*)-(+)-α-methylbenzyl	51.3	163.6	131.3	101.8	153.7	144.0	127.6	124.7	125.5	48.0	22.0	
(*S*)-(−)-α-methylbenzyl	51.2	163.4	131.2	101.7	153.6	143.8	127.1	124.6	125.4	47.7	21.9	
phenyl	50.9	162.9	130.7	102.3	151.2	138.1	127.0	116.6	120.3			
o-tolyl	51.6	163.3	131.1	102.9	152.1	135.7	127.3	120.8	121.8	124.7	128.8	16.9
m-tolyl	51.1	163.7	130.9	102.6	151.6	138.1	121.4	114.1	117.5	136.7	127.0	20.0
p-tolyl	51.5	163.7	128.4	103.1	152.2	136.0	128.1	117.6	18.1			
4-nitrophenyl	51.9	169.5	131.3	105.0	152.8	138.0	122.4	119.5	164.1			

Table IV
^{13}C NMR of the Urea-Containing Dehydroalanine Derivative Polymers

urea	carbon peak assignment 1	2	3	4	5	6	7	8	9	10	11	12
methyl	52.4	173.8	55.0	47.4	159.2	26.2						
ethyl	51.1	170.9	51.1	40.4	155.2	32.3	11.8					
n-propyl	61.0	173.1	51.6	44.0	158.5	42.4	23.9	11.5				
isopropyl	52.1	161.0	50.1	41.3	155.8							
n-butyl	61.0	173.6	53.0	43.6	158.5	40.6	32.9	20.9	13.8			
tert-butyl	50.7	173.0	62.3	52.0	158.0	34.3	28.8					
cyclohexyl	60.3	172.5	52.5	49.1	156.7	46.1	32.9	31.5	25.6			
n-octadecyl	53.4	171.5	58.0	52.0	159.7	39.2	30.7	30.7	28.6	28.2	24.5	24.4
(*R*)-(+)-α-methylbenzyl	51.3	169.3	52.6	45.3	155.7	144.0	127.6	124.7	125.5	48.0	19.8	
(*S*)-(−)-α-methylbenzyl	51.2	169.2	52.5	45.2	155.6	143.8	127.1	124.6	125.4	47.7	21.9	
tosyl	51.0	173.0	50.0	40.0	163.0	128.0	129.0					

V lists the intrinsic viscosity values obtained. Those values calculated with the Huggins equation closely matched the values obtained with the Kraemer equation, giving correlation coefficients ranging from 0.9 to 0.99 (most were 0.99). The intrinsic viscosities reported in Table V are the averages of the Huggins and Kraemer values. The Huggins (k') an Kraemer (k'') constants obtained were generally within the expected values, with $k' - k''$ ranging from 0.3 to 0.7 and with most of the values close to the expected value of 0.5.[16] Anomalous results for a few of the samples could be due to shear-induced stress since the viscosities were obtained in the laminar-flow regime rather than under zero-shear conditions. Strong intermolecular hydrogen bonding between the urea groups could increase such behavior.

The highest intrinsic viscosities were obtained from the spontaneous and thermally initiated bulk polymerizations of the isopropyl-, *n*-butyl-, and *n*-octadecylurea derivatives. Only the cyclohexyl- and *tert*-butylurea derivatives gave low-viscosity products, possibly due to steric hindrance between bulky side groups in the propagation step. The monomers that spontaneously polymerized during isolation at or below ambient temperatures resulted in both high [methyl, ethyl, *n*-propyl, and (*R*)-(+)-α-methylbenzyl] and low [(*S*)-(−)-α-methylbenzyl] intrinsic viscosities, suggesting that unpredictable concentrations of radicals or reactive impurities were formed (probably from atmospheric oxygen) even when the overall reaction conditions were similar.

The fact that many of the monomers spontaneously polymerized at ambient temperature or upon heating without added initiator suggests that the monomers form radicals readily. This is consistent with the captodative stabilization observed for analogous materials where radical

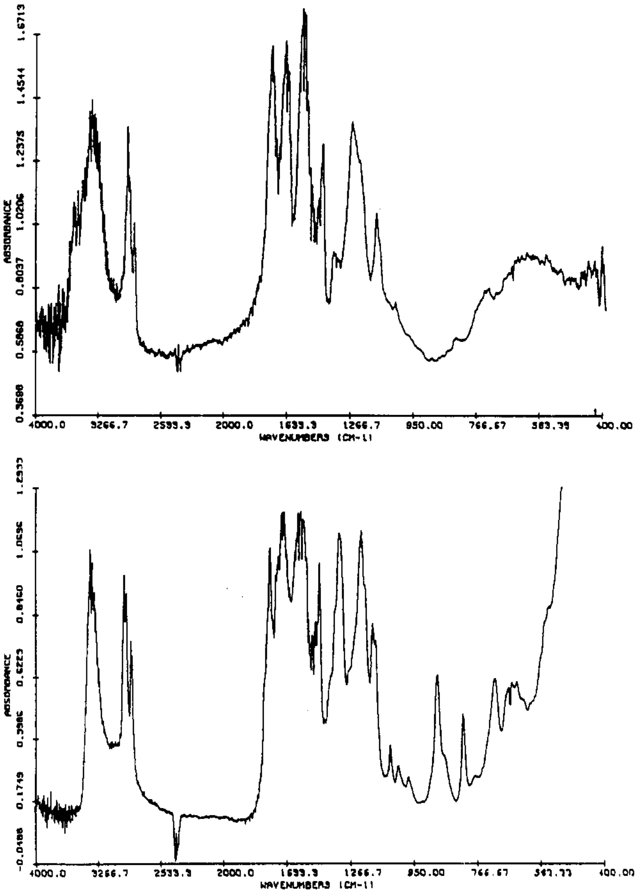

Figure 8. FT-IR spectra of *n*-butylurea dehydroalanine monomer (lower trace) and polymer (upper trace).

Table V
Viscosity Data

R group	[η], dL/g	solvent	yield, %	reacn conditions
methyl	0.40	water	43	spontaneous
ethyl	1.35	water	53	spontaneous
ethyl	1.69	methanol	55	spontaneous
n-propyl	0.48	methanol	61	spontaneous
n-propyl	0.24	methanol	44	solution
n-propyl	0.43	methanol	61	spontaneous
isopropyl	0.44	methanol	46	solution
isopropyl	1.04	methanol	43	bulk
n-butyl	0.43	THF	76	solution
n-butyl	0.65	THF	51	bulk
n-butyl	0.71	methanol	51	bulk
tert-butyl	0.19	THF	47	bulk
cyclohexyl	0.17	THF	28	solution
cyclohexyl	0.10	methanol	44	bulk
n-octadecyl	0.62	THF	42	bulk
n-octadecyl	0.26	THF	57	solution
(*S*)-(−)-α-methylbenzyl	0.07	chloroform	45	spontaneous
(*R*)-(+)-α-methylbenzyl	0.90	chloroform	46	spontaneous

generation involves addition of other radicals to activated alkenes or cleavage of substituted C–C dimers.[14]

Among the polymerizations initiated by the azo initiator (Vazo 67), midrange intrinsic viscosities resulted when the initiator concentration was <0.5% (*n*-propyl, isopropyl, *n*-butyl, cyclohexyl, and *n*-octadecyl derivatives), and low intrinsic viscosities were obtained when the initiator concentration was 5% or greater (*n*-propyl, *n*-butyl, an cyclohexyl derivatives and some of the low-viscosity samples not included in Table V). The initiator concentration/molecular weight trend is consistent with typical radical polymerizations where molecular weights decrease as the concentration of initiator increases.

DSC analysis of these polymers gave little evidence for glass transitions or melting points except for a sharp exothermic decomposition peak at 180–200 °C. TGA of several polymers showed catastrophic weight loss at 170–200 °C with depolymerization as the major decomposition pathway (product trapping and GC/MS identification of monomer). All of the derivatives appeared to be glassy to crystalline on microscopic inspection. DSC thermograms of the *n*-butyl and the *n*-octadecyl polymers are shown in Figure 9. The endotherm at 47 °C corresponds to side-chain melting for the latter material.

In agreement with the DSC results, the X-ray diffractogram of the *n*-octadecyl polymer showed a high degree of side-chain crystallinity. Amide dehydroalanine polymers with long-alkyl pendent groups such as the *n*-octadecyl derivative also showed side-chain crystallinity.[10,12] A sharp, intense peak for the *n*-octadecylurea polymer at 30 Å corresponds to end-to-end side-chain crystallinity without intercalation. The crystal sizes corresponding to these side chains were calculated from peak line widths at half-height using the Debye–Scherrer equation and were found to be 80–140 Å.

The (*R*)-(+)-α-methylbenzyl and (*S*)-(−)-α-methylbenzyl derivative monomers and polymers contain a side-chain chiral carbon and were expected to exhibit optical activity. The specific optical activities of the (*R*)-(+)-α-methylbenzyl isocyanate precursor, monomer, and precipitated polymer were measured to be −12, +45, and −40 deg mL dm^{-1} g^{-1}, respectively.

Conclusions

A series of urea-containing dehydroalanine monomers and polymers were synthesized and characterized. High molecular weight polymers were obtained for most monomers. Methyl- and ethyl-substituted polymers were water soluble and soluble in methanol, while higher linear and branched alkyl derivatives were only soluble in organic solvents such as CHCl$_3$ and THF. Aryl-substituted monomers could not be obtained cleanly due to formation of cyclic byproducts. An optically active monomer gave polymer with enhanced light rotation in the same direction as the isocyanate precursor but in the opposite direction to the dehydroalanine monomer. Similar to the amide polymers, the *n*-octadecylurea polymer displayed side-chain crystallinity by DSC and X-ray.

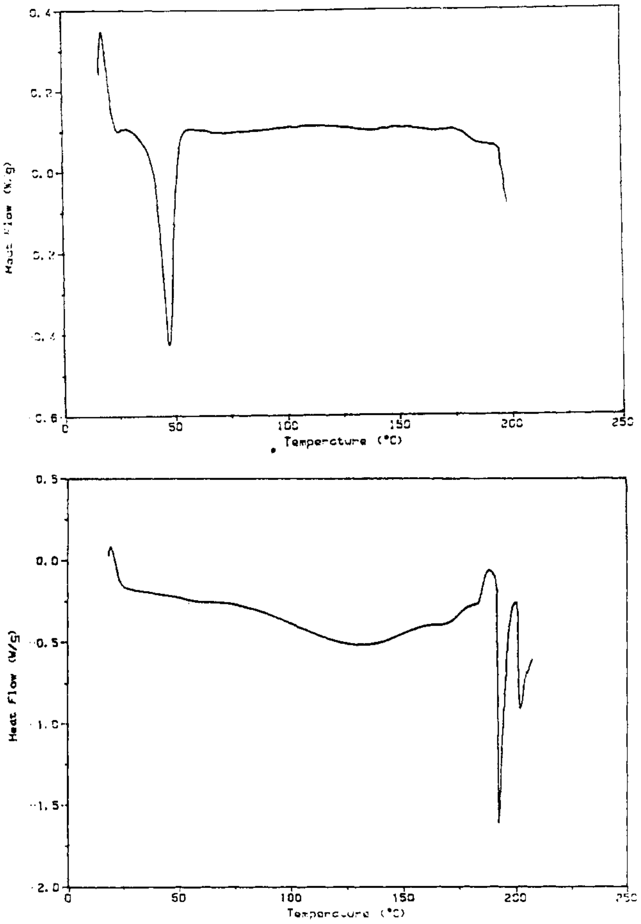

Figure 9. DSC scans of *n*-butylurea (lower trace) and *n*-octadecylurea dehydroalanine polymers (upper trace) with endothermic peaks down.

Acknowledgment. Grateful acknowledgment is made to the Division of Materials Research of National Science Foundation (Grant DMR-8620138) and to the donors to the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

References and Notes

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Registry No. **1** (R = methyl), 40026-27-5; **1** (R = *iso*-propyl), 130495-54-4; **1** (R = *n*-butyl), 130495-55-5; **1** (R = phenyl), 52778-74-2; **2** (R = methyl), 35356-70-8; **2** (R = methyl) (homopolymer), 111209-75-7; **2** (R = ethyl), 130468-67-6; **2** (R = ethyl)(homopolymer), 130468-79-0; **2** (R = *n*-propyl), 108414-60-4; **2** (R = *n*-propyl) (homopolymer), 108414-61-5; **2** (R = *iso*-propyl), 130468-68-7; **2** (R = *iso*-propyl) (homopolymer), 130468-80-3; **2** (R = *n*-butyl), 130468-69-8; **2** (R = *n*-butyl) (homopolymer), 130468-81-4; **2** (R = *tert*-butyl), 130468-70-1; **2** (R = *tert*-butyl) (homopolymer), 130468-82-5; **2** (R = cyclohexyl), 38524-21-9; **2** (R = cyclohexyl) (homopolymer), 130468-83-6; **2** (R = *n*-octadecyl), 115299-24-6; **2** (R = *n*-octadecyl) (homopolymer), 115299-25-7; **2** (R = (*R*)-(+)-α-methylbenzyl), 130468-73-4; **2** (R = (*R*)-(+)-α-methylbenzyl) (homopolymer), 130468-84-7; **2** (R = (*S*)-(−)-α-methylbenzyl), 130468-74-5; **2** (R = (*S*)-(−)-α-methylbenzyl) (homopolymer), 130268-85-8; **2** (R = 1,6-bis(hexyl)), 130468-71-2; **2** (R = octyl), 111209-73-5; **2** (R = tosyl), 130468-72-3; **2** (R = tosyl) (homopolymer), 130468-86-9; **2** (R = 4-nitrophenyl), 130468-78-9; **2** (R = phenyl), 24153-31-9; **2** (R = *o*-tolyl), 38524-25-3; **2** (R = *m*-tolyl), 38524-39-9; **2** (R = *p*-tolyl), 38527-21-8; **7** (R = Ph), 10582-78-2; **7** (R = *o*-tolyl), 130468-75-6; **7** (R = *m*-tolyl), 130468-76-7; **7** (R = *p*-tolyl), 130468-77-8.