polymers were found to be soluble in a wide variety of organic solvents but were insoluble in water. The highest molecular weight poly(oxyvinylene)caprolactam polymer (0.07 dL/g) was found to be insoluble in chloroform and only soluble in methanol and tetrahydrofuran on heating. Further work on preparing high molecular weight polymers by reaction of acyl lactams with different substituents is under way.

Acknowledgment. We gratefully acknowledge financial support from the 3M Corp. for this research and helpful discussions with Dr. Steve Heilmann of 3M.

Registry No. **4a**, 43170-60-1; **4b**, 98303-90-3; **4b** (homopolymer), 98303-91-4; **4c**, 98303-85-6; **4c** (homopolymer), 98303-89-0; **4d**, 98303-92-5; **4d** (homopolymer), 98303-93-6; **4e**, 101697-80-7; **4e** (homopolymer), 101697-81-8; **4f**, 1888-91-1; **5a**, 101712-14-5; **5b**, 101712-15-6; **5c**, 101712-16-7; **5d**, 101712-17-8; **6a**, 101697-82-9; **6a** (homopolymer), 101697-83-0; **6b**, 101697-84-1; **6b** (homopolymer), 101697-85-2; $ClCH_2COCl$, 79-04-9; 2-pyrrolidone, 616-45-5.

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Synthesis and Characterization of Poly(methyl 2-decanamidopropenoate) [Poly(*N*-decanoyldehydroalanine methyl ester)]: A Novel Comb Polymer Derived from a Difunctional Monomer

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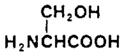
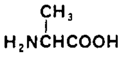
ABSTRACT: The synthesis of the difunctional vinyl monomer methyl 2-decanamidopropenoate [*N*-decanoyldehydroalanine methyl ester] was accomplished by using two general routes starting with D,L-serine (2-amino-3-hydroxypropanoic acid). The amino acid was methyl esterified, N-acylated, and dehydrated with a mild carbodiimide procedure. Alternatively, the hydroxy ester was converted to the chloride, N-acylated, and dehydrochlorinated with base to form the monomer. Characterization of the monomer included ^{13}C FT-NMR, FT-IR, and GC/MS. Radical polymerization [AIBN] in isomeric hexanes resulted in clear, high molecular weight polymers. Solution properties were studied in THF at 25 °C and included dilute solution viscometry, low-angle laser light scattering and size-exclusion chromatography. Intrinsic viscosities ranged from 0.36 to 8.79 dL/g, with $\bar{M}_w$ between 1×10^5 and 15.2×10^6. The Mark–Houwink constants K and a were calculated to be 2.63×10^{-4} and 0.63, respectively ([η] in dL/g, 0.1–2.63 million $\bar{M}_w$). Polymer configuration was examined by ^{13}C NMR and appeared to be essentially atactic. Wide-angle X-ray spectroscopy of a thin film indicated side-chain order typical of comblike polymers.

Introduction

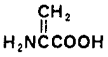
Dehydroalanine (Dha), the vinyl analogue of alanine (Ala), is a substituent of many naturally occurring peptides which exhibit antibiotic properties. These antibacterial polypeptides have been isolated from numerous sources and contain as many as eight dehydroalanine residues. This fact, coupled with the search for new synthetic antibiotics, generated much interest in the preparation of peptides containing biologically active dehydroalanine residues. A review of dehydroamino acids, including dehydroalanine-containing peptides, appeared in 1979.[1]


$\mathrm{H_2N\overset{\overset{CH_2OH}{|}}{C}HCOOH}$

Ser


$\mathrm{H_2N\overset{\overset{CH_3}{|}}{C}HCOOH}$

Ala


$\mathrm{H_2N\overset{\overset{CH_2}{\|}}{C}COOH}$

Dha

Many synthetic methods have been established for the introduction of the dehydroalanine residue into peptides. Indirect routes include base-catalyzed elimination reactions on substituted residues of *N*-hydroxy-,[2] *N*-chloro-,[3] and 3-chloroalanine,[4,5,6] ester elimination from 2-acetoxyamino acids,[7] and tosyl esters of serine (Ser)[8] and threonine,[9] and Hofmann elimination from 2,3-diamino acids.[10] Other methods have recently been reported and include direct elimination from cysteine using silver carbonate[11] and the dehydration of serine residues using isoureas,[12] carbodiimides,[13] and a triphenylphosphine–azidodicarboxylate complex.[14] Simpler analogues have been prepared by the direct condensation of pyruvic acid with various amides to produce N-substituted derivatives of dehydroalanine.[15,16] In fact, *N*-acetyldehydroalanine [2-acetamidoacrylic acid] is currently available commercially.[17]

Synthetic polymers have been prepared from various N-substituted derivatives of dehydroalanine and are the subject of numerous patents and publications. British (1946)[18] and US (1949)[19] patents describe the bulk and solution polymerization of *N*-acetyldehydroalanine methyl ester [methyl 2-acetamidoacrylate] to produce a clear, water-soluble homopolymer. Copolymers with acrylonitrile, methyl methacrylate, and styrene were also described.

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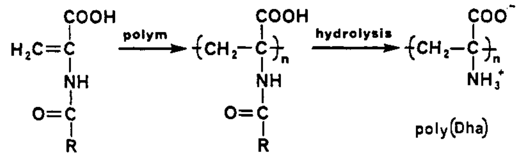
In 1952, polymers derived from 2-formamido-, 2-(carbobenzoxyamino)- and 2-(carbethoxyamino)acrylic acids were reported.[20] Intrinsic viscosities from 0.13 ($\bar{M}_w$ = 30 000 by light scattering] to 0.58 dL/g were obtained. Attempts to hydrolyze these polymers to poly(2-aminoacrylic acid), the simplest amphoteric polymer, were unsuccessful. This polyelectrolyte was eventually prepared in 1961 via radical polymerization of either the *N*-carboxyanhydride of dehydroalanine or *N*-phthaloyldehydroalanine followed by hydrolysis and hydrazinolysis, respectively.[21] Characterization was limited to pH titration for the determination of the COOH:NH_2 ratio. This polymer was also obtained by hydrolysis of a high molecular weight sample of poly(*N*-acetyldehydroalanine).[22]



The apparent molecular weight of the unhydrolyzed polymer (light scattering in aqueous NaCl) was 7 × 10^6 and corresponded to an intrinsic viscosity of 2.0 dL/g at pH 4.4. At higher pH, the dilute solutions of the hydrolyzed polymer displayed typical polyelectrolyte behavior.

A variety of functionalized derivatives of dehydroalanine have been synthesized and polymerized. A five-membered ring cyclopolymer was proposed for the *N*-methacryloyl methyl ester although characterization was limited to spectroscopic evidence of the polymer structure.[23] Optically active polynucleotide analogues based on purine- and pyrimidine-substituted dehydroalanine polymers were obtained with inherent viscosities from 0.35 to 0.78 dL/g (0.5 g/dL in DMF).[24] Cross-linked derivatives of these polymers were also prepared with bis- and tris(dehydroalanine) agents derived from phthaloyl and trimesoyl chlorides.[25] These hydrophilic polymers were used for affinity chromatographic separation of adenosine and uridine. A final example of the broad applicability of poly(*N*-substituted-dehydroalanines) involves photoactive polymers.[26] The 9-carboxymethylcarbazole derivatives of both dehydroalanine and its methyl ester were converted to polymers with intrinsic viscosities (THF, 28 °C) of 0.36 and 1.05 dL/g, respectively.

The versatility of the dehydroalanine moiety as a polymerizable group derives from the dual reactivity of the ampholyte which allows incorporation of substituents at *both* the amino and carboxyl groups. The range of substituents incorporated, despite the potential for steric and electronic inhibition of polymer formation, confirms the high reactivity of this vinylene group in polymerization.

Comb (or comblike) polymers have received considerable attention and were reviewed in 1974.[27] More recently, a review appeared on crystalline atactic polymers, with a section devoted to polymers containing long linear side chains.[28] Comblike polypeptides have also been reported. The base-catalyzed polymerization of alkyl derivatives of amino acid *N*-carboxyanhydrides resulted in polymers with conformational order.[29,30,31] The molecular weights so obtained ranged from 5 × 10^3 to 1.9 × 10^5.

One of our current areas of research involves synthesis of a variety of new polymers by taking advantage of dehydroalanine's bifunctionality and high reactivity in free radical polymerization. This paper deals with one member of a new family of alkanoic amides based on the dehydroalanine methyl ester. In fact, we were surprised at the ease of synthesis and polymerizability of the decanamide compound 4 and report here the synthesis and characterization of this new comb polymer.

Experimental Section

Reagents. All solvents used were reagent grade unless otherwise indicated. Methanol (Fisher), chloroform (VWR), methylene chloride (Baker), triethylamine (Aldrich), *N,N'*-diisopropylcarbodiimide (DIPC, Aldrich), and isomeric hexanes (Baker Spectrograde) were dried over Linde 4-A molecular sieves (Fisher) for at least 24 h prior to use. D,L-serine (Vega Biochemicals), hydrogen chloride gas (Matheson), *n*-decanoyl chloride, cuprous chloride, phosphorous pentachloride, 2-nitropropane (Aldrich), and benzene and acetone (Baker) were used as received. AIBN (Pfaltz & Bauer) was recrystallized from absolute ethanol and vacuum dried at room temperature. Tetrahydrofuran (HPLC, Baker) was used for viscosity and low-angle laser light scattering (LALLS) determinations. Methanol (HPLC, Baker) was used for the reprecipitation of polymers. Deionized water (Barnsted Type I, >15 MΩ/cm) was used where required.

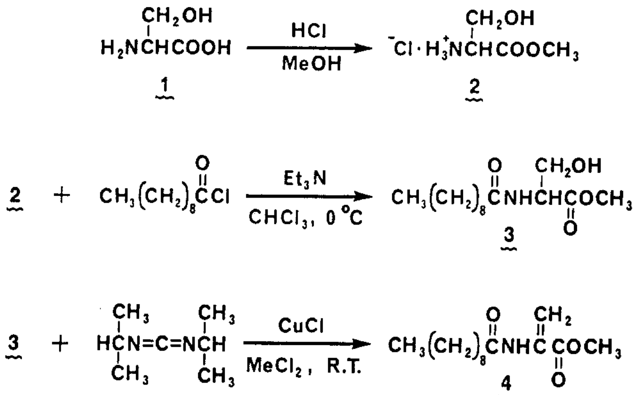
Analytical Equipment. ^{13}C NMR spectra were obtained with a JEOL FX90Q FT-NMR spectrometer. Infrared spectra were recorded on a Nicolet 5DX FT-IR spectrometer with KBr dispersions or thin films. Gas chromatography was performed with a Hewlett-Packard 5880A GC equipped with a 25 M fused-silica capillary column (SE-54, Quadrex, Inc.) using purified nitrogen carrier gas and flame-ionization detection. Mass spectra (EI, 70 ev) were obtained with a Hewlett-Packard 5985 GC/MS operated with helium carrier gas. Cross-polarized light microscopy was performed with a Leitz Orthoplan-POL microscope and melting points were determined with a Mettler FP5/52 thermal accessory at a heating rate of 2 °C/min. Light scattering data was obtained with a Chromatix KMX-16 laser differential refractometer and KMX-6 low-angle laser light scattering (LALLS) spectrophotometer with output recorded on a strip-chart recorder. Dilute solution viscosity measurements of polymer solutions (THF, 25.0 ± 0.1 °C) were performed with a Cannon–Ubbelohde No. 50 viscometer with solvent efflux time greater than 150 s to minimize kinematic effects. Sample **6f** was tested for shear effects with a Cannon–Ubbelohde No. 50 four-bulb shear dilution viscometer. Size exclusion chromatography (SEC) data was obtained with a system designed and built at the USM Department of Polymer Science.[32]

D,L-Serine Methyl Ester Hydrochloride (2). To a 1-L reaction kettle equipped with a magnetic stirring bar and containing 600 mL of dry methanol was added D,L-serine (210.2 g, 2.0 mol) at room temperature. Hydrogen chloride gas was introduced through a fritted glass inlet tube until the suspension cleared. The vessel was maintained in a hot water bath at reflux for 4–6 h. Solvent was then removed with a rotary evaporator. The procedure was repeated to ensure pure product (by ^{13}C NMR), which was then dried under vacuum. The white crystalline material was used without further purification but could be recrystallized from a minimum amount of methanol at −15 °C; mp 134.5–135.7 °C (lit.[33] mp 134–136 °C).

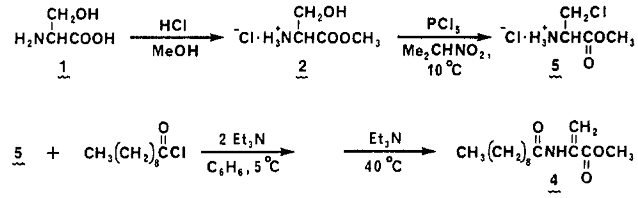
Methyl 2-Decanamido-3-hydroxypropanoate or *N*-Decanoylserine Methyl Ester (3). A 1-L reaction kettle with a magnetic stirring bar was cooled in an ice bath. To this was added D,L-serine methyl ester hydrochloride (31.12 g, 200 mmol) and 300 mL of dry chloroform. A mixture of triethylamine (61.5 mL, 440 mmol) and 38.5 mL of chloroform was slowly added until the suspension cleared. A solution of *n*-decanoyl chloride (41.5 mL, 200 mmol) in 58.5 mL of chloroform was added dropwise over a period of 4 h while maintaining the temperature below 5 °C. The reaction was refrigerated overnight and subsequently extracted with 2 × 50 mL of ice-cold 0.1 N HCl and 2 × 50 mL type I water. The organic solvent was removed by rotary evaporation under reduced pressure leaving a light yellow oil; crude yield, 106%. The oil crystallized within 15 min at room temperature. Bulk recrystallization was accomplished by melting in the presence of an aqueous layer to remove excess amine and cooling to room temperature, yield 74% based on original reagents; mp 63–63.5 °C.

Methyl 2-Decanamidopropenoate or *N*-Decanoyldehydroalanine Methyl Ester (4) (Scheme I). To an oven-dried 125-mL 24/40 Erlenmeyer flask was added *N*-decanoyl serine methyl ester (10.94 g, 40 mmol), 80 mL of methylene chloride, DIPC (5.55 g, 42 mmol), CuCl (0.197 g, 2 mmol), and

Scheme I



Scheme II



a magnetic stirring bar. The mixture was stirred at 30–40 °C in the dark for 4 days or until the reaction was found to be complete by GLC analysis. The green solution containing white crystals of *N*,*N'*-diisopropylurea was refrigerated and filtered through a fritted glass filter. Major impurities in the filtrate were removed by silica gel column chromatography with methylene chloride solvent. Solvent removal under reduced pressure gave a clear oil, yield approximately 90%. Crystalline product was obtained by refrigeration at −10 °C; mp 10.3–11.5 °C.

Methyl 2-Amino-3-chloropropanoate Hydrochloride or 3-Chloroalanine Methyl Ester Hydrochloride (5). To a 1-L reaction kettle equipped with a mechanical glass stirring rod and chilled in ice was added 300 mL of 2-nitropropane and PCl_5 (230 g, 1.1 mol). The suspension was stirred while adding D,L-serine methyl ester hydrochloride (155.6 g, 1.0 mol) in small portions over a period of 2 h and left at ice temperature overnight. The semisolid mass was filtered through a fritted glass filter under nitrogen purge to remove most of the solvent and byproducts. The white residue was recrystallized from a minimum volume of hot methanol, filtered, and rinsed with methylene chloride followed by acetone. The fine white crystalline product was vacuum dried at room temperature and stored in a refrigerated dessicator; yield, 76%, mp 137.9–138.3 °C (lit.[34] mp 134–136 °C).

Methyl 2-Decanamidopropenoate or *N*-Decanoyldehydroalanine Methyl Ester (4) (Scheme II). To a 500-mL round-bottom flask containing 3-chloroalanine methyl ester hydrochloride (8.70 g, 50 mmol) was added 200 mL of benzene and a magnetic stirring bar. The suspension was stirred in an ice bath while triethylamine (7.0 mL, 50 mmol) was added in one portion. Small portions of triethylamine (7.0 mL total) and *n*-decanoyl chloride (10.5 mL, 50 mmol total) were added alternately over a period of 1 h. The reaction temperature was kept below 10 °C for an additional hour before adding another portion of triethylamine (7.0 mL) to effect the dehydrohalogenation step. The suspension was brought to 40 °C in a water bath for 2 h and placed in a refrigerator overnight. GLC analysis confirmed complete reaction. The cold suspension was filtered and the precipitate rinsed with benzene. The filtrate was washed with 2 × 50 mL of 0.1 N HCl and 2 × 50 mL of water to obtain a light yellow organic layer. Solvent removal left a yellow oil; crude yield, 97%. Crystalline product was obtained from isomeric hexanes at −15 °C, mp 10.3–11.5 °C.

Poly(methyl 2-decanamidopropenoate) or Poly(*N*-decanoyldehydroalanine methyl ester) (6a–g). An oven-dried 10-mL test tube was charged with monomer (approximately 1 g, 4 mmol), 6 mL of hexanes, and AIBN initiator (5–50 mg, 0.03–0.3 mmol). The AIBN was found to be sparingly soluble even at this low concentration but was used for all polymerizations for consistency. The tube was closed with a septum and degassed with dry nitrogen for 5 min before suspending in a 60 °C oil bath. Typically, gelation occurred within 4 h, but the reaction was continued for up to 20 h before solvent removal by slow evacuation. The clear polymer was dissolved in THF and transfered to a polypropylene syringe (Aldrich) for reprecipitation in stirred, ice-cold methanol. The polymer mass was removed with forceps and vacuum oven dried at 70 °C overnight, typical yield, >65%.

Low-Angle Laser Light Scattering (LALLS). With a precalibrated Mettler H54AR five-place balance, approximately 0.1 g of polymer was added directly to a 25-mL volumetric flask. Static electricity neutralization was accomplished with a Zerostat (Discwasher, Inc., from Aldrich). Tetrahydrofuran was added to within 5 mL of the calibration line and the solution left overnight. In all cases, the polymer solutions were made the night prior to analysis and diluted to the calibration line 1 h before making 1/10, 2/10, 3/10, and 5/10 dilutions for analysis. For consistency, the same cleaned pipets were used for each polymer sample analyzed. The refractive index increment for each dilution was determined after equilibration at 25 °C for at least 1 h and represents an average of five or more values. Concurrently, light scattering was performed on a 4–5-mL sample filtered through a 0.2-μm PTFE filter and pumped at a flow of 1 mL/h using a Sage No. 352 syringe pump equipped with a 5-mL polypropylene syringe. Scattering was detected at 6–7° aperture with output continuously recorded on a strip-chart recorder.

Dilute Solution Viscosity. Viscosities were determined at 25 ± 0.1 °C with the solutions obtained directly from the photocell of the differential refractometer. However, the highest concentration was taken from the stock solution to check for systematic errors. Efflux times were averaged for four runs which were typically within 0.2 s of each other. The zero-shear intrinsic viscosity of sample **6f** was determined from a solution prepared separately from that used for light scattering. The constant dilution technique was employed. In addition, dilutions of this sample were prepared as before and checked for accuracy against the viscosity data obtained previously.

Size Exclusion Chromatography (SEC). A 2-mL aliquot of the stock solution was evaporated to about half the original volume under a stream of nitrogen. A 0.2-mL sample was injected on the SEC apparatus using a column set packed with 75, 500, and 750 Å controlled-porosity glass (Electonucleonics, Inc.). A calibration method proposed by Hester and Mitchell[35] was used with polystyrene standards (Waters) in THF at room temperature.

Wide-Angle X-ray Spectrometry (WAXS). A film of sample **6f** was cast from chloroform and oven dried at 70 °C for 4 h. A highly birefringent area of the sample (as observed by cross-polarized light microscopy) was placed in a nickel-filtered Cu Kα collimated beam and exposed for 11.5 h at a sample-to-film distance of 5.00 cm.

Results and Discussion

Monomer Preparation. Two general synthetic routes were developed from published literature methods. For both procedures, readily available racemic serine (2-amino-3-hydroxypropanoic acid) was used as the starting material. The final elimination step to generate the vinylene group converted the original asymmetric center into an sp^2 carbon and obviated any need for optical purity in the starting material. The first method involved initial methyl ester formation, N-acylation, and final dehydration to give the desired monomer (Scheme I).[12–14] After column chromatography to remove the residual diisopropylurea and copper salts, the monomer was generally pure enough for polymerization.

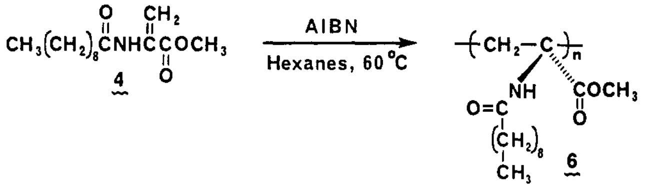
The second route (Scheme II) was developed to increase synthetic generality and reduce overall synthesis time.[4–6] The serine methyl ester hydrochloride was converted to the β-chloro derivative, N-acylated, and dehydrochlorinated. The final crude material usually required no purification or a single recrystallization to obtain monomer purity. Advantages for the latter method include a one-pot conversion for the last two steps, faster reactions, especially for the alkene-forming step, elimination of expensive

Table I
^{13}C NMR Chemical Shifts (ppm from Me_4Si) of Compounds 1–5 and Polymer 6[a,b]

	chemical shifts[c]											
sample	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_{9-11}	C_{12}	C_{13}	C_{14}
1	177.0	57.8	63.2									
	178.0	57.9	66.6									
2	169.7	55.7	60.2	54.5								
	178.0	56.6	60.7	54.7								
5	168.4	55.0	42.9	54.9								
	178.0	56.5	42.7	54.2								
3	175.2	55.2	61.9	51.7	171.2	35.8	25.7	29.2	29.2	31.9	22.6	13.5
	178.0	51.0	63.6	54.7	176.5	33.2	25.4	29.0	29.7	32.2	22.8	13.7
4	164.6	130.8	108.4	52.8	171.9	37.6	25.3	29.2	29.2	31.8	22.6	14.0
	166.0	131.2	102.3	54.2	176.5	33.6	25.4	29.0	29.7	32.2	22.8	13.7
6	173.0	42.8	59.9	52.1	171.6	36.7	24.2	29.5	29.5	31.9	22.6	14.0
	181.0	*d*	*d*	54.7	174.7	33.2	25.4	29.0	29.7	32.2	22.8	13.7

[a] Solvents: 0.1 N NaOH (1 and 2); $CHCl_3$ for all others. Dioxane was used as a reference (67.2 ppm). [b] Upper entries are experimental values; lower entries are values calculated as in ref 36. [c] Refer to Figure 1 for carbon positions. [d] Not calculable from tables used.

Scheme III



reagents (diisopropylcarbodiimide) and metal catalysts (CuCl), and comparable yields with better monomer purity. With these two approaches, a range of *N*-amide substituents have been incorporated into the basic methyl ester monomer. Additional work is under way on the corresponding free acid derivatives and various other ester and carboxamide moieties at the 1-position.

Polymerization. Homogeneous polymerization of 10% solutions of the decanamide monomer in mixed hexanes was carried out at 60 °C (Scheme III). AIBN was used as the initiator despite its poor solubility in hexanes. Reactions were carried out overnight although solution gelation had usually occurred within 4 h. The resulting tough gels were readily soluble in a variety of solvents. Polymer purification involved dissolving the vacuum-dried gel in THF and precipitating in ice-cold methanol.

The range of polymer molecular weights desired for viscosity and light scattering characterization was obtained by varying the initiator concentration. Even under conditions designed to obtain very low molecular weight samples (high initiator concentrations), polymers with molecular weights of several hundred thousand were obtained. This fact attests to the high reactivity of the monomer and low degrees of chain transfer and spontaneous termination. In fact, this monomer (and dehydroalanine monomers in general) are difficult to *keep* from going to high polymer. The highest molecular weight sample described here was the product of spontaneous reaction in which initiation occurred at 0–5 °C. Polymer formation took place over 20–30 h at room temperature, and the final sample was found to display a very high viscosity. The polymer molecules were apparently so large that filtration for light scattering evaluation was not possible and only viscosity data was obtained for this sample.

Spectroscopic Characterization. The proton-noise-decoupled ^{13}C NMR chemical shifts for all compounds studied are given in Table I. Peak assignments were based on calculated chemical shifts and comparison to model compound spectra found in the Sadtler Spectral Collection. In some cases, peak identifications were assisted by off-resonance proton-decoupled experiments. The ^{13}C NMR spectra of the monomer and polymer are shown in Figure 1. As expected, the vinyl carbons with peaks at 130.5 and 109.1 have clearly been converted to backbone carbons observed at 43.0 and 62.0 ppm, respectively. The molecular mobilities of the carbons labeled 1, 4, 5, 6, and 14 have decreased in the polymer to such an extent that the peaks are broadened significantly even at a solution temperature of 80 °C. Tacticity information obtained on these polymer samples indicates that stereoregular polymer is not being formed under these conditions.

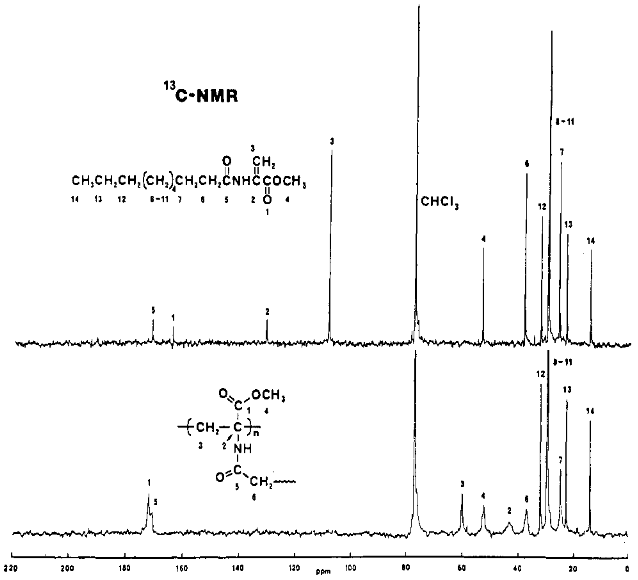


Figure 1. Proton-noise-decoupled ^{13}C NMR spectra of methyl 2-*N*-decanamidopropenoate (4) and polymer 6 in chloroform.

The FT-IR absorbance spectra of monomer and polymer are compared in Figure 2. The monomer vinyl absorptions due to C–H stretch (3100 cm^{-1}), C=C stretch (1634 cm^{-1}), and out-of-plane C–H bend (900 and 800 cm^{-1}) are completely absent in the spectrum of the polymer. Characteristic bands are observed in the polymer spectrum for both the methyl ester group and the long alkyl amide functionality.

Further confirmation of the monomer composition was obtained by mass spectral analysis. The mass spectrum of *N*-decanoylserine methyl ester, the precursor to the monomer (3 in Scheme I) had a molecular ion peak at m/e 273. The spectrum of *N*-decanoyldehydroalanine methyl ester (4) had a molecular ion peak at m/e 255, showing the loss of H_2O in the dehydration step. Both values are identical with the calculated molecular weights for the respective compounds.

Table II
Dilute Solution Viscosity of Poly(*N*-decanoyldehydroalanine methyl ester) in THF at 25 °C

sample	$[\eta]^a$	k'	corr coeff	$[\eta]^b$	k''	corr coeff	$k' - k''$	C^{*c}
6a	0.36	0.372	0.879	0.36	−0.146	0.578	0.518	0.12
6b	1.41	0.298	0.996	1.40	−0.170	0.995	0.468	0.78
6c	1.70	0.332	0.999	1.70	−0.155	0.997	0.488	0.78
6d	2.29	0.296	0.998	2.27	−0.168	0.991	0.464	1.00
6e	2.62	0.341	0.997	2.62	−0.150	0.990	0.491	1.06
6f	3.11	0.325	0.999	3.09	−0.148	0.993	0.473	1.35
6g	3.53	0.453	0.999	3.56	−0.111	0.992	0.564	1.45
6h	8.76	0.428	0.999	8.83	−0.121	0.995	0.549	1.16

[a] Huggins equation: $\eta_{sp}/c = [\eta] + k'[\eta]^2c$. [b] Kraemer equation: $\ln \eta_r/c = [\eta] + k''[\eta]^2c$. [c] Overlap parameter: $[\eta]$ times the highest concentration.

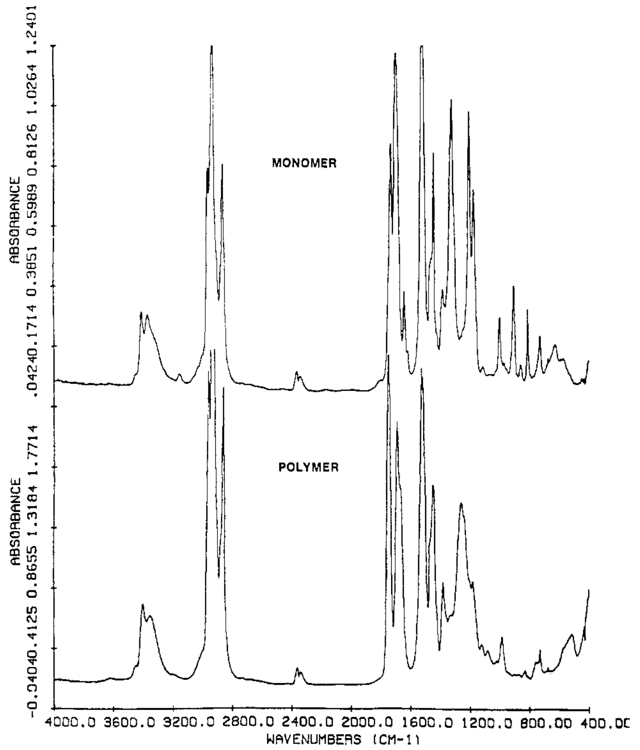


Figure 2. Infrared spectra of monomer 4 and polymer 6.

Final indication of monomer purity was obtained by GLC analysis. While good conversion of this reactive monomer to polymer was observed initially with impure material (<95% purity), better results were obtained with monomer of >99% purity available with the second synthetic method and using careful recrystallization.

Dilute Solution Viscosity. The dilute solution viscosity data of eight samples obtained from separate polymerization experiments is summarized in Table II. The data include the Huggins (k') and Kraemer (k'') constants obtained from the slopes of the reduced and inherent viscosity curves. A composite plot of the reduced viscosity/concentration data (for all but the two highest molecular weights) is shown in Figure 3. Excellent linearity was observed for all intrinsic viscosity plots. The lowest molecular weight sample had a low correlation coefficient because of the near zero slope. Observed values of the Huggins constants for these samples are close to the 0.35 value normally seen for flexible polymers in good solvents. This typical value is usually independent of molecular weight, although we see some deviation at the high and low ends of our sample range. The values of $k' - k''$, however, are close to the ideal difference of 0.5 even for those samples which have Huggins constants somewhat removed from 0.35. In addition, the overlap parameter (defined as the intrinsic viscosity multiplied by the concentration of the solution) is normally less than 1.0 for dilute solutions and between 1.0 and 10.0 for semidilute solutions. For the samples described here, only the higher concentrations of each approach semidilute conditions, which might result in shear-dependent behavior. Finally, the two highest molecular weight samples have somewhat larger Huggins values, which may mean that THF is becoming a somewhat poorer solvent at these molecular weights or that shear effects are coming into play. The zero-shear intrinsic viscosity for sample **6f** was found to be 3.28 dL/g, or 5.5% higher than the value obtained by the regular method (3.11 dL/g). Since this sample was the largest molecular weight used for the determination of the Mark–Houwink constants, the shear dependence was considered negligible. Furthermore, the latter value is only 0.3% higher than the average intrinsic viscosity shown in Table III. This is an indication of the excellent analytical accuracy of the method.

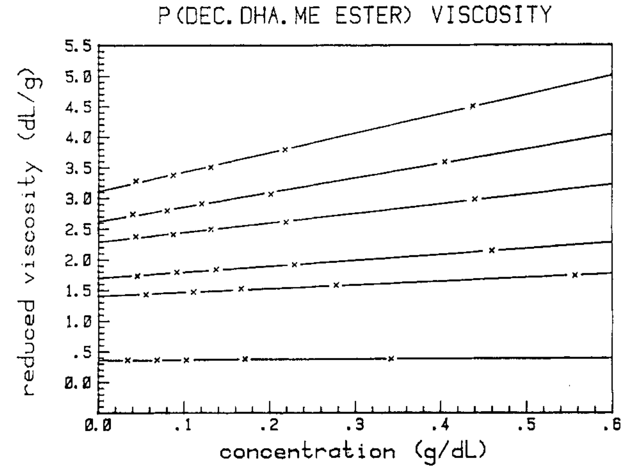


Figure 3. Reduced viscosity plots for polymer samples **6a** (bottom plot)–**6f** (top plot) used in the Mark–Houwink relationship.

Low-Angle Laser Light Scattering. The light scattering data is summarized in Table III. Attempts to analyze samples **6g** and **6h** by LALLS were unsuccessful. Extreme back-pressure on final filtering was encountered even when filters of large pore size were used (1 μm). This may indicate the presence of microgels, although the dilute solution viscosity data indicated otherwise. For comparison purposes only, the molecular weights of these two samples were calculated according to the Mark–Houwink relationship derived from the other data. The extremely high molecular weight of sample **6h** suggests that chain termination by transfer to monomer is very low.

Table III also contains dn/dc values and second virial coefficients for samples **6a**–**f**. Each dn/dc value was determined from the five different concentrations for that individual sample. Some variation is evident despite the excellent correlation coefficients observed. The *combined*

Table III
Low-Angle Laser Light Scattering of Poly(*N*-decanoyldehydroalanine methyl ester) in THF at 25 °C

sample	$[\eta]$[a]	d*n*/d*c*	corr coeff	$M_w \times 10^{-6}$[b]	$A_2 \times 10^4$	corr coeff	$M_w \times 10^{-6}$[c]	$A_2 \times 10^4$	corr coeff
6a	0.36	0.0824	0.999	0.10	0.82	0.999	0.10	0.84	0.999
6b	1.41	0.0816	0.999	0.69	2.29	0.998	0.66	2.39	0.998
6c	1.70	0.0851	0.999	1.22	1.80	0.997	1.27	1.73	0.997
6d	2.28	0.0846	0.999	1.90	2.53	0.996	1.95	2.47	0.996
6e	2.62	0.0839	0.999	2.25	2.79	0.996	2.28	2.76	0.995
6f	3.10	0.0850	0.995	2.54	2.84	0.995	2.63	2.76	0.995
6g	3.54	0.0861	0.999				3.58[d]		
6h	8.79	0.1517	0.999				15.2[d]		

[a] Average of values in Table II. [b] Uses d*n*/d*c* value shown. [c] Uses d*n*/d*c* value of 0.0835 from combined data **6b**–**f**. [d] Molecular weight estimates from Mark–Houwink equation. LALLS data unavailable.

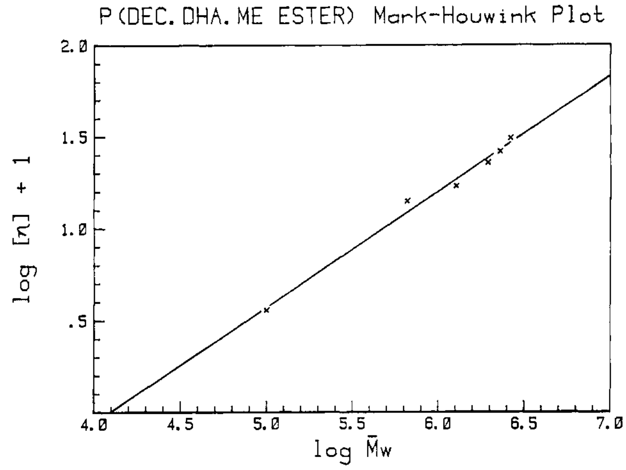


Figure 4. Mark–Houwink plot for samples **6a**–**f** (M_w = 0.1–2.63 million).

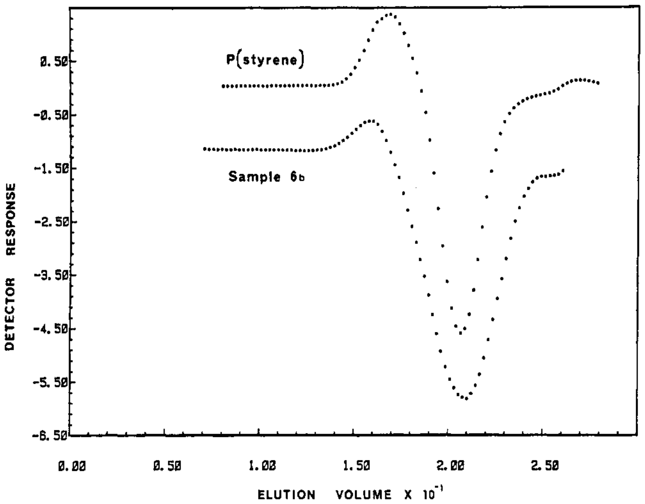


Figure 5. Size-exclusion chromatogram of sample **6b** (M_w = 660 000) and polystyrene standard (M_n = 35 000, MWD = 1.02).

Table IV
Solubility Data for Sample 6c ($M_w = 1.27 \times 10^6$) of Poly(*N*-decanoyldehydroalanine methyl ester)

solvent	δ[a]	15 min	24 h
petroleum ether	7.0	3×[b]	3×
diethyl ether	7.4	+	+
carbon tetrachloride	8.6	1×	+
toluene	8.9	1×	+
ethyl acetate	9.0	+	+
tetrahydrofuran	9.1	1×	+
benzene	9.2	+	+
chloroform	9.3	+	+
methylene chloride	9.7	1×	+
acetone	9.9	+	+
dioxane	10.0	2×	+
acetic acid	10.1	1×	5×
dimethylacetamide	10.8	–	2×
2-propanol	11.5	–	+
acetonitrile	11.9	–	–
dimethyl sulfoxide	12.0	–	–
dimethylformamide	12.1	2×	2×
ethanol	12.7	–	–
methanol	14.5	–	1×
water	23.4	–	–

[a] Solubility parameter. [b] Approximate swollen volume.

d*n*/d*c* data for samples **6b**–**f**, that is, the 25 individual measurements of refractive index difference for these five samples, were analyzed by linear least squares to give an overall d*n*/d*c* value of 0.0835.

Typical plots of Kc/R_θ vs. concentration were observed for these polymers. From such data, two values of the weight-average molecular weight were calculated for each sample and are given in Table III. The first used the individually determined d*n*/d*c* value while the second employed the combined value. Molecular weights calculated are in excellent agreement with each other.

Mark–Houwink Relationship. The viscosity and molecular weight data for samples **6a**–**f** are plotted in Figure 4 in the traditional log–log manner. The value of the preexponential K was found to be 2.63×10^{-4} while the exponent a was determined to be 0.63 to give the Mark–Houwink relationship as follows:

$$[\eta]^{25^\circ\mathrm{C}}{}_{\mathrm{THF}}\ (\mathrm{dL/g}) = 2.63 \times 10^{-4}\bar{M}_w{}^{0.63}$$

The correlation coefficient for this plot was 0.985, indicating reasonable linearity despite cumulative errors resulting from the use of two determinations involving extrapolation to zero concentration. As mentioned above, these values were used to estimate the molecular weights of samples **6g** and **6h** (Table III).

Size-Exclusion Chromatography. Discussion of the solution properties and molecular weights of this series of polymers requires a brief description of initial results from size-exclusion chromatography (SEC) investigations. Figure 5 gives a typical SEC plot for these samples compared to a polystyrene standard. This data is consistent with the elimination of any low molecular weight fractions and residual monomer from the samples. The shape of the chromatogram confirms a near monomodal distribution of molecular weights. This indicates that the polymerization proceeds with essentially a single mode of termination. Other evidence (not discussed here) indicates that termination proceeds almost completely by coupling.

The last sample **6h** is especially interesting since it has an apparent molecular weight of approximately 15 million. These dehydroalanine monomers may well be useful in the synthesis of very soluble and readily characterized ultrahigh molecular weight polymers. Such materials should be valuable as models for investigating the upper range

Table V
Wide-Angle X-ray Spectrometery Data for a Film of Poly(*N*-decanoyldehydroalanine methyl ester), Cu Kα, Nickel Filter (1.54 Å)

dist, cm	rel intensity	angle θ	d spacing, Å
0.50	strong	2.86	15.50
0.95	medium	5.38	8.21
1.80	strong	9.90	4.48
3.50	v. weak	17.50	2.56

behavior of comb polymers and may also have important commercial application as viscosifiers.

Solubility. Table IV gives the solubility behavior of a representative sample of the decanamide polymer **6c** with a weight-average molecular weight of 1.27 million. With a repeat unit molecular weight of 255, this sample has a degree of polymerization of approximately 5000. It also possesses an interesting combination of oleophilic backbone and long alkyl pendent groups, attached polar, hydrogen-bonding amide moieties, and pendent methyl ester units. Despite polymerization in mixed hexanes, the polymer is not soluble in saturated hydrocarbons, although it swells to approximately 3 times its initial volume. It dissolves readily in benzene and chloroform but not in toluene and carbon tetrachloride. While it is rapidly taken up in diethyl ether, complete dissolution in THF and dioxane requires longer times.

Overall, the polymer is soluble mainly in solvents with solubility parameters between 7.4 and 10.0, although longer alkyl alcohols (e.g., 2-propanol with a solubility parameter of 11.5) dissolve it gradually. Highly polar aprotic solvents like DMF and Me_2SO, and protic solvents like the lower alcohols, water, and acetic acid are apparently not able to solubilize the long alkyl units despite strong interaction with the ester and amide linkages. The molecular behavior of the monomers and polymers that are involved in these effects are being explored further in terms of polymerization systems and the eventual application of the polymers obtained.

Wide-Angle X-ray Data. Table V gives the WAXS results for a birefringent film of sample **6f** that was prepared by casting from chloroform with subsequent heating at 70 °C. Side-chain crystallinity of similar long-alkyl-substituted polymers (e.g., poly(vinyl stearate)) results in strong scattering bands near 4.2 Å. The analogous strong band for the decanamide polymer is centered at 4.48 Å, giving support to the possibility of such side-chain crystallinity in the dehydroalanine polymers. Investigation of this behavior is currently in progress with longer alkyl chain analogues of the polymer reported here.

Conclusion

A new class of polymers has been prepared from a monomer derived from racemic serine. The alkanamido-substituted monomer displays efficient free radical polymerization to very high molecular weights. Dilute solution properties of the polymer indicate near ideal behavior, even for the autopolymerized sample having a calculated molecular weight approaching 15 million.

Thermal properties have yet to be thoroughly examined, but preliminary results indicate a melting endotherm at about 190 °C with decomposition above 220 °C. A slight endotherm at about 80 °C is also evident. Cross-polarized microscopic examination of a film at this temperature also displays a loss of birefringence. The overall thermal behavior indicates the polymer may be melt processed to produce clear, impact-resistant materials.

Anionic polymerization of the monomer has produced a polymer with different characteristics, probably due to a hydrogen-transfer type mechanism which includes the amide nitrogen in the backbone. Further work on this polymer is in progress.

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