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Polymers from Captodative Dehydroalanine Monomers: 2-Alkanamide Derivatives of Methyl Propenoate

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ABSTRACT: A series of 2-alkanamide derivatives of methyl propenoate was synthesized in which side chains were derived from linear alkyl acids with 2–18 carbons, perfluorooctanoic or 10-undecenoic acid. Free radical polymerization gave high molecular weight for all polymers as evidenced by viscosity; for example, the C_{18} polymer with $[\eta]$ = 1.59 dL/g gave a light scattering molecular weight of 1.74 million. Wide-angle X-ray diffraction confirmed order in this series; i.e., a plot of the long D spacing values versus the number of side-chain carbon atoms gave a slope of 1.25 Å/CH_2 segment and an intercept of 8.96 Å corresponding to approximately seven atoms of the core backbone. Only the C_{18} derivative displayed side-chain crystallinity with a d_4 spacing of 4.2 Å, consistent with hexagonal packing similar to that observed for the other comb polymers.

Introduction

We have previously described the synthesis and characterization of the vinyl polymer of methyl 2-decanamidopropenoate (*N*-decanoyl dehydroalanine methyl ester).[1] Monomer synthesis involved a mild, high-yield reaction between decanoyl chloride and β-chloroalanine methyl ester (Figure 1). Radical polymerization took place readily in hexane to give a series of polymers varying in molecular weight. The viscosity–molecular weight correlation gave values for the Mark–Houwink constants K and a of 2.63×10^{-4} and 0.63, respectively.

We were surprised at the ready polymerizability of this monomer. Not only was it difficult to prevent spontaneous polymerization even at −5 °C, but also one polymer sample was estimated to possess a molecular weight of approximately 15 million.[1] In contrast, the *N*-methyl derivative of the butanamide analogue displayed reduced activity and would only copolymerize and not homopolymerize.[2] We have also found that the longer alkyl derivatives form monolayers and vesicles which undergo spontaneous polymerization as well as polymerization initiated by UV light or thermal radical initiators.[3]

During the course of this investigation, we became acquainted with the concept of captodative radical stabilization[4] (first postulated by Dewar[5] and also called push–pull stabilization[6] and merostabilization[7]). The basic concept, as applied to dehydroalanine derivatives, involves synergistic interaction of the electron-withdrawing (capto) substituent and the electron-donating (dative) substituent possessing a lone pair of electrons.[4] Additional resonance structures and a lower energy molecular orbital are thus available to stabilize the carbon radical (Figure 2).

Based on facile monomer synthesis and the ease of polymer formation, we have examined the homologous series of 2-alkanamide derivatives given in Figure 1. In this paper, we evaluate the effect of alkyl side-chain length on the properties of dehydroalanine polymers.

Experimental Section

Materials. 2,2′-Azobis(isobutyronitrile) (AIBN) or 2,2′-azobis(2-methylbutyronitrile) (Vazo-67, Du Pont) were used as radical initiators. All solvents and reagents were used as obtained. Monomer synthesis involved the procedures previously described for the C_{10} amide derivative[1] and utilized the methyl ester of β-chloroalanine and the appropriate acid chloride (Figure 1). Synthesis reactions were followed by capillary gas chromatography which was also used to establish final monomer purity. The C_4–C_9 *N*-acyl derivatives did not crystallize even at temperatures as low as −80 °C. Relatively pure products of these monomers could be obtained by using small scale silica column chromatography. All other derivatives could be recrystallized to high purity from hexane except for the acetyl derivative which was recrystallized from a 1:2:7 mixture of 1-propanol/ethanol/petroleum ether. Monomer melting points are included in Table I and show a monotonic increase with increasing hydrocarbon chain length for the C_{10}–C_{18} derivatives. Monomers were generally characterized by FTIR and ^{13}C NMR.

Table I
Summary of Polymerization Results for the Homologous Series of Poly(methyl 2-alkanamidopropenoates)

monomer	side-chain carbon no.	monomer mp, °C	polymer, % yield	$[\eta]$, dL/g	$k' - k''$
1	2	52.3–53.0	51	0.56	0.45
2	4		90	0.64	0.47
2[a]	4			2.2	0.48
3	6		46	0.41	0.54
4	7			1.00	0.50
5	8		46	1.48	0.48
6	9		74	2.07	0.46
7	10	10.3–11.5	66	2.28	0.46
8	12	25.3–26.4		2.30	0.51
9	14	39.0–39.5	74	1.30	0.49
10	16	44.7–46.0	57	0.91	0.52
11[b]	18	53.6–54.5	73	1.59	0.49
12	8[c]	39.5–40.2	48	0.54	0.05[d]
13	11[e]	34.1–34.9		2.70	0.53

[a] Sample had autopolymerized during monomer workup. [b] MW = 1 740 000 by LALLS (THF, 25 °C). [c] Perfluorooctanoyl derivative. [d] Hexafluoro-2-propanol; k' and k'' were 0.02 and −0.03, respectively. [e] 10-Undecenoyl derivative: $CH_2{=}CH(CH_2)_8CO{-}$.

Polymerizations. Polymerizations were carried out at 60 °C in 20% methanol in hexanes (C_4–C_7 side chains), or neat hexanes (C_2, C_8, and higher, and perfluorooctanoyl side chain). Polymer precipitation or solution gelation was observed for most systems. Some samples occasionally underwent spontaneous bulk polymerization, and one example is the third entry in Table I. Most crude polymers were dissolved in THF and precipitated into cold methanol; the perfluoroocatanamide polymer was precipitated from hexafluoro-2-propanol. For side chains below C_8, the polymers had significant solubility in methanol at room temperature and were precipitated into a mixture of 20% diethyl ether/petroleum ether from methanolic solutions. Polymerization results for the homologous series are summarized in Table I.

Characterization. Infrared spectra were recorded on a Nicolet 5DX FTIR. Solution NMR spectra were obtained on a Bruker MSL-200 in $CDCl_3$. Intrinsic viscosities were determined at 25.0 °C in methanol (C_2–C_6) or THF (C_7–C_{18}). Values of k' and k'' are the calculated Huggins and Kraemer constants, respectively. Thermal behavior was observed with a Leitz polarizing microscope equipped with a Mettler hot stage. X-ray data was obtained at room temperature on a Philips PW1720 diffractometer with nickel-filtered Cu K_α X-rays and a custom-built camera. All

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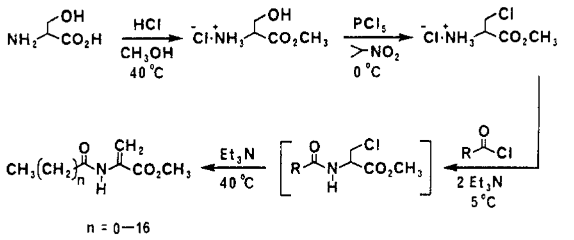

Figure 1. General dehydroalanine monomer synthesis.

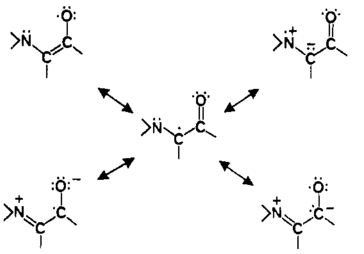

Figure 2. Captodative stabilization of dehydroalanine radicals.

polymer films used displayed optical birefringence under cross-polarization microscopy. Low-angle laser light scattering (LALLS) was performed with a Chromatix KMX-16 and KMX-6 using THF at 25 °C to give a dn/dc value of 0.823 for polymer from monomer 11.

Results and Discussion

Monomer Synthesis. The synthetic procedure employed for these monomers is simple, straightforward and gives yields of 70–95%. The lower yields were obtained from noncrystalline monomers due to loss during chromatography. Very high purity was obtained for the crystalline materials after two or three low-temperature recrystallizations.

Monomer characterization involved GLC analysis of purity, along with FTIR and ^{13}C and occasionally ^1H NMR spectroscopic characterization. Residual starting material seldom interfered with polymer formation. In fact, it was often difficult to prevent premature polymerization during monomer isolation and purification.

Polymer Synthesis and Characterization. Polymerizations usually occurred in fair to excellent yield over a 4–12-h period, often with polymer precipitation or solution gelation. Molecular weights of the polymers were high as evidenced by intrinsic viscosities and light scattering molecular weight determination of the polymer from monomer 11 (Table I). This C_{18} polymer possessed an intrinsic viscosity of 1.59 dL/g and a molecular weight of 1.74 million. On the basis of the Mark-Houwink values for the C_{10} polymer,[1] the lowest viscosity observed here (0.41 dL/g) should correspond to at least 100 000 molecular weight.

As was found for the C_{10} polymers, near-ideal viscosity behavior was observed for this entire series of polymers. Generally, the correlation coefficients for both the Huggins and Kraemer plots were 0.99 or better, and the differences between the Huggins and Kraemer constants were close to 0.5 (last column of Table I). The exception is the perfluorooctanoyl derivative which displayed near-zero slopes for viscosity plots and low solubility in general.

Films of all polymers were cast from solvent and analyzed by FTIR. Three of these are compared in Figure 3. The spectra are similar except for the increasing absorptions between 2800 and 2990 cm^{-1}. This data, along with ^1H and ^{13}C spectra, confirm that the polymers obtained from the homologous series of monomers have the same basic structure and differ only in the number of methylene units in the side chains.

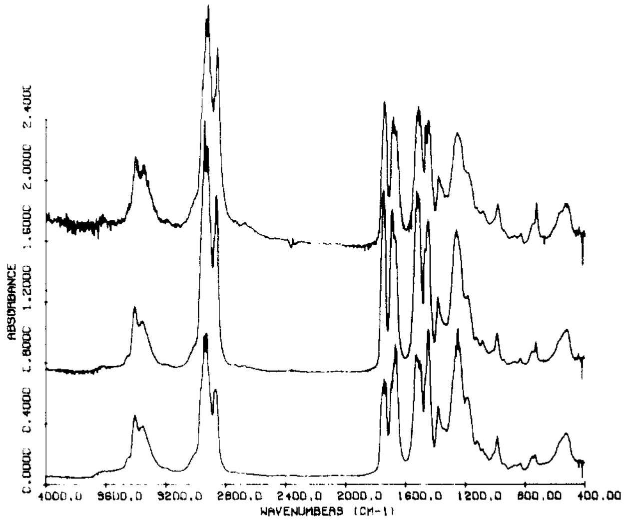

Figure 3. FTIR spectra of dehydroalanine polymers containing side chains with 7 (bottom scan), 12 (middle), and 18 (upper) carbon atoms.

Table II
X-ray Diffraction Data for the Homologous Series of Poly(methyl 2-alkanamidopropenoate)

	interplanar distances, Å					
sample	D^a	d_1	d_2	d_3	d_4	d_5
BUTA			10.4	4.6		2.7
HEX	17.2		8.2	4.7		2.7
OCT	19.3		8.2	4.5		2.7
DEC	19.3		8.2	4.5		2.6
DODEC	24.9		8.7	4.5		
TETRADEC	25.7	14.1	8.7	4.5		
HEXADEC	30.8	14.7	8.7	4.5		
OCTADEC	30.8	15.5	8.7	4.5	4.2	
PL-18^b	43.0	15.2	8.2	4.6	4.2	
PVOD^c	30.8	15.5	7.5		4.2	

[a] Long d spacing (low angles). [b] ε-Alkanamide derivatives of poly-L-lysine.[9] [c] Commercial samples of poly(vinyl octadecanoate).

Wide-Angle X-ray Spectrometry (WAXS). Wide-angle X-ray spectrometry was used to confirm crystallinity and determine interplanar spacing (d) for these polymers using the Bragg equation

$$n\lambda = 2d \sin \theta$$

which relates the wavelength λ, the interplanar spacing d, and one-half the angle of deviation of the diffracted rays from the incident X-rays, θ. The integer n is usually 1, corresponding to a first-order reflection from a given plane.[8] Results are summarized in Table II.

The WAXS photographs confirm that this series of polymers have crystalline order, although the exact unit-cell dimensions could not be calculated from the patterns obtained. A strong diffuse band was seen for all samples which corresponds to the d_3 spacings listed in Table II. Previous studies on comb polymers have shown this band to be independent of alkyl chain length.[9] Similar values were reported for alkyl-substituted poly(acrylates), poly(methacrylates), poly(vinyl ethers), poly(maleimides), and amorphous poly(α-olefins).[10] This diffuse band is presumedly due to short-range ordering of side-chain methylene groups.

The diffraction rings closer to the center of the photographs are the long D spacings related to side-chain length. As the side chain length increases, there is an increase in the D spacing. A linear plot of D versus number of side chain carbons (Figure 4) gives a correlation coefficient of 0.97 with a slope of 1.25 Å/chain segment and intercept

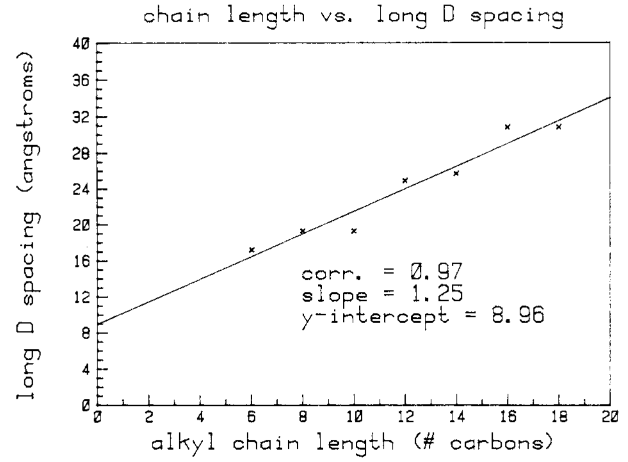

Figure 4. Plot of long D spacing versus the number of side-chain carbon atoms n.

of 8.96 Å. The slope corresponds to the side-chain length increment for each methylene group (e.g., for a planar zigzag conformation, it should equal 1.27 Å). The intercept provides an indication of the diameter of the common backbone unit.[10] A value of 8.9 is calculated if the backbone unit is considered to be seven atoms × 1.27 Å in diameter. The data suggest that the side chains are in close proximity to each other laterally and are arranged in fully extended arrays.

The octadecyl derivative shows a very strong band with a d_4 spacing of 4.2 Å. This is strong evidence that this polymer has hexagonal packing in the side chain since the same value (±0.15 Å) has been observed (and calculated) for a variety of alkyl-substituted polymers, including the poly(vinyl octadecanoate) shown in Table II.[10]

N-Alkanamide derivatives of poly-L-lysine have been prepared which possess side-chain structure similar to that of the polymers studied here; i.e., hydrogen bonding involving pendent groups can stabilize side-chain association. The WAXS data for the C_{18} polypeptide in Table II shows structural similarity to the C_{18} dehydroalanine polymer. The lysine poly(amino acid) derivatives probably exist in the β-sheet conformation with a perpendicular arrangement of the lateral chains in a hexagonal lattice.[9] In the dehydroalanine polymer, structural regularity in the backbone could involve syndio or isotactic arrangement. It is not clear at this time whether such stereoregularity exists or is required for the type of side-chain order observed here.

Conclusions

A series of high molecular weight comb polymers have been synthesized from dehydroalanine monomers available through a facile and general synthetic route. Polymers formed easily in bulk and in solution by using radical initiation. WAXS data for the homologous series studied here is similar to that of akyl comb polymers described in the literature and is consistent with extended pendent groups determining intermolecular distances. However, the C_{18} polymer is the only one of this series which exhibits side-chain crystallinity at room temperature.

Thermal analysis (DSC) and variable-temperature ^{13}C solid-state NMR experiments are in progress to further investigate side-chain crystallinity and backbone ordering in these highly functional and strongly interactive polymers.

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Registry No. **1**, 35356-70-8; **1** (homopolymer), 111209-75-7; **2**, 108414-60-4; **2** (homopolymer), 108414-61-5; **3**, 106158-82-1; **3** (homopolymer), 106158-83-2; **4**, 106133-28-2; **4** (homopolymer), 111209-76-8; **5**, 106133-29-3; **5** (homopolymer), 111209-77-9; **6**, 111209-73-5; **6** (homopolymer), 111209-78-0; **7**, 101979-26-4; **7** (homopolymer), 101979-27-5; **8**, 106133-25-9; **8** (homopolymer), 111209-79-1; **9**, 106133-31-7; **9** (homopolymer), 106158-84-3; **10**, 111209-74-6; **10** (homopolymer), 111209-80-4; **11**, 106133-27-1; **11** (homopolymer), 106158-81-0; **12**, 106133-30-6; **12** (homopolymer), 111209-81-5; **13**, 106133-26-0; **13** (homopolymer), 111209-82-6.

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