

# Functional Polymers. XLVIII.

## Polymerization of $\omega$ -Alkenoate Derivatives\*

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### Synopsis

Esters of  $\omega$ -alkenoic acids have been homopolymerized with transition metal initiating systems. The key to the successful polymerization was the complexation of the monomer prior to its addition to the initiating system. Titanium trichloride, aluminum activated, was found to be best as the transition metal part of the initiator systems, with diethyl-, or better, diisobutylaluminum chloride as the reducing agents and *n*-hexane or toluene as the solvents. Best results for polymerizations were obtained with 2,6-dimethylphenyl esters of the functional  $\alpha$ -olefin monomers; however, other phenyl esters also polymerized well. Attempts to polymerize methyl 10-undecenoate gave the corresponding polymer in only low yields. Polymers of the 2,6-dimethylphenyl esters, obtained in high molecular weight, were characterized. Polymers were also obtained from 2,6-dimethylphenyl 7-octenoate, but not from  $\omega$ -alkenoates with less than three methylene units between the ester group and the terminal olefin group.

Poly(2,6-dimethylphenyl 10-undecenoate) was hydrolyzed in an aqueous sodium hydroxide/1,4-dioxane solution to poly(sodium 10-undecenoate) that in turn was neutralized with acetic acid to poly(10-undecenoic acid).

### INTRODUCTION

$\alpha$ -Olefins with at least one hydrogen atom attached to the carbon atom next to the polymerizable carbon-carbon double bond can only be polymerized with coordination initiators of certain transition metals. The driving force for the polymerization is the instability of the transition metal alkyl or its polymeric analog with respect to the transition metal alkyl that has one more  $\alpha$ -olefin units inserted between the carbon-transition metal bond.<sup>1-5</sup>

The scope of the coordination polymerization, also called Ziegler-Natta polymerization, is extensive, and initiator combinations and reaction conditions have been developed that allow the polymerization not only of  $\alpha$ -olefins but also of dienes, cycloolefins, and acetylenes.<sup>6-10</sup>

Transition metals used most successfully, and with a wide range of activity, are those of titanium, vanadium, and zirconium, chromium, and molybdenum. Very effective coordination initiators have also been made from cobalt, nickel, scandium, hafnium, and tungsten as well as from uranium and most rare earth metals.<sup>11</sup> Although halides have received the most attention as ligands for the transition metal part of the initiating systems, other ligands, including alkox-

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yl, phenyl, acetylacetonyl, and cyclopentadienyl have also been used to provide the transition metal ions with the proper surrounding of ligands. This delicate balance of transition metal in the proper valence state with the appropriate ligands ultimately gave the optimum stability/instability of the (complexed) transition metal ion.<sup>12</sup> To provide the proper space filling surrounding about the transition metal and to allow stereospecific coordination of the  $\alpha$ -olefin and stereospecific insertion into the already formed polyolefin chain which is still attached by carbon-transition metal bond to the transition metal complex.<sup>13,14</sup> This transition metal complex is now allowed to react with an organometallic component that reduces the transition metal complex to the proper valence state and coordination number using the ligands from the mixtures.<sup>15</sup> Together with the polymerizable  $\alpha$ -olefin, this complex combination gives the proper transition metal initiating system that is capable of polymerizing not only normal but also functional  $\alpha$ -olefins.

In the traditional coordination systems of transition metal initiators, for  $\alpha$ -olefin polymerization, not more than 1–2% of the transition metal was actually in a state to promote coordination polymerization because the transition metal ions exist in cluster form. Modern systems ("high yield" initiating systems) have 30–50% of the transition metal compounds capable of polymerizing ethylene or  $\alpha$ -olefins because they are separated eventually to individual ions in a solid matrix, usually magnesium chloride.

Experimental techniques for the combination of all components to produce an effective coordination initiating system vary widely. The systems may have, in addition to the transition metal compound, the reducing agents, and the monomer, other necessary components: activators, deactivators, and agents that enhance polymerization rate, increase stereospecificity, prevent the formation of amorphous fractions, or influence the molecular weight and molecular weight distribution of the final polymer.<sup>16–20</sup> Polymerization processes for  $\alpha$ -olefins utilizing these variations of reactive conditions may result in homogeneous, colloidal, or heterogeneous systems. Polymerizations may be carried out in solution, slurry, in the gas phase, or in fluidized bed reactors. The broad spectrum of initiator components, methods of their combination, and polymerization conditions result in wide variations in the initiating system that effects activity, efficiency, and stereospecificity and often effects the morphology of the resulting polymers.<sup>21,22</sup>

$\alpha$ -Olefins that have electron donating atoms or groups in the molecule pose difficulty in polymerizations with coordination initiators because both the polymerizable olefinic double bond and the heteroatoms of the functional groups of the monomer can interact with the initiating system. Coordination complexes of a functional group with the transition metal part of the initiating systems are often more stable than complexes that involve only the pi-electrons of the vinyl double bond.

A number of approaches can be taken to minimize or eliminate the unfavorable interactions of functional groups with the transition metals. (1) Insulate the olefin double bond from the functional group by placing a spacer group, for example, of several methylene units, between the functional and the polymerizable groups. (2) Increase the steric hindrance around the functional group. (3) Decrease the electron-donating character of the heteroatom of the functional group by attaching electron-withdrawing substituents onto the

functional group. (4) Select the components of the coordination initiator system in such a way that they are less likely to react with the functional group. (5) Decrease the reactivity of part of the organometallic component by precomplexing it with a Lewis base as donor molecules. (6) Precomplex the functional monomer with a Lewis acid, often the same type as that used for the reduction of the transition metal salt to form the active centers. (7) Use polar solvents that complex the "undersirable acidic" active centers and permit penetration, coordination, and polymerization of the vinyl monomer.<sup>23</sup>

By proper design of the initiating system/complexation of the functional monomer these conditions could be achieved by one or more of the above techniques, and polymerization of the functional monomer at active sites could be accomplished.

It has been reported that some  $\alpha$ -olefins with functional groups could be polymerized. Silicon-containing monomers (allyl silanes) were found to give low molecular weight polymers,<sup>24-26</sup>  $\omega$ -halo-1-olefins, including fluoro-, chloro-, and bromo-substituents;<sup>27,28</sup> nitrogen-containing monomers,<sup>29,30</sup> particularly vinylpyridines,<sup>31</sup> and silylated alcohols (4-penten-1-ol or 10-undecen-1-ol)<sup>30</sup> gave polymers.

The patent literature of particular interest for our work described some polymerizations and copolymerizations of polar-substituted  $\alpha$ -olefins. The claims in the patents include the polymerization of aliphatic esters, alkoxides, phenoxides, amides, phosphonates, phosphinates, and aluminum tris(alkenoxides).<sup>32</sup> In other patents even the polymerization by coordination initiators of acrylic esters,<sup>33</sup> methacrylonitrile, and also of other oxygen- or nitrogen-containing monomers was claimed.

In some cases, methylene spacer groups have been used in attempts to separate the functional group from the polymerizable olefin group to effect the polymerization of functional olefins at reasonable rates, and to form polymers of attractive properties.<sup>27-33</sup>

It was the object of this work to evaluate the polymerizability of functional  $\alpha$ -olefins, especially of  $\omega$ -alkenoates, to identify initiator systems, transition metal compounds, ligands, solvents, and the appropriate monomers to establish clearly and beyond any reasonable doubt the polymerization of functional  $\alpha$ -olefins of the  $\omega$ -alkenoate type, to determine the limitations of their polymerizability, and to characterize the polymers.

## EXPERIMENTAL

### Materials

Solvents were distilled through a 45 cm column packed with 0.5 cm sections of glass tubing. Distillations of reagents and monomers were carried out on either a 13 cm Vigreux column or a short-path microdistillation apparatus. All distillations, at either atmospheric or reduced pressure, were carried out with magnetic stirring under a nitrogen atmosphere.

Tetrahydrofuran (THF) was distilled (bp 62.5°C) from lithium aluminum hydride (LAH) immediately before use.

*n*-Heptane was washed successively with concentrated sulfuric acid, distilled water, 10% aqueous sodium carbonate, and distilled water and then

dried over anhydrous calcium chloride. It was then distilled from phosphorus pentoxide with a center cut taken at 97°C and stored under nitrogen.

Toluene was washed in the same manner, predried over magnesium sulfate, distilled (bp 109.5°C) from phosphorus pentoxide, and stored under dry nitrogen.

All other solvents and reagents were used as received.

The reagents were received from the following sources and used as received: acetic acid, benzene, chloroform, decahydronaphthalene, and tetrahydrofuran (THF) from Fisher Scientific Company; diethylaluminum chloride (DEAC), diisobutylaluminum chloride (DIBAC), triethylaluminum (TEA), and triisobutylaluminum (TIBA) from the Ethyl Corporation; titanium tetrachloride from Alpha Products; and various grades of titanium trichloride, in part aluminum activated, from the Stauffer Chemical Company.

### Measurements

Infrared spectra were recorded on Perkin-Elmer, spectrophotometers models 727 and 783; solid samples were cast as films onto NaCl plates from chloroform, toluene, or decahydronaphthalene solutions. KBr pellets and Fluorolube® mulls were prepared from insoluble solid samples. Peak assignments were recorded to within 5 cm<sup>-1</sup>.

<sup>1</sup>H-NMR spectra of monomers, intermediates, and selected polymers were obtained on a 60 MHz T-60 or 90 MHz R-32 Perkin-Elmer NMR spectrometer.

The <sup>13</sup>C-NMR spectra were recorded on a Varian CFT-20 Fourier-Transform spectrometer operating at 22.6 MHz. Sample concentrations were typically 20–40% (w/v) in CDCl<sub>3</sub>, benzene-d<sub>6</sub> or 1,2,4-trichlorobenzene, benzene-d<sub>6</sub> (3/1 by volume). At least 20,000 transients were accumulated for polymer samples. Typical instrument parameters include a pulse width (PW) of 5–15 μ seconds, a pulse delay (PD) of 0–15 s, and an acquisition time of 1.023 s.

Inherent viscosity measurements were run at 30°C in benzene and at 135°C in decalin using Ostwald-type viscometers. Solution concentrations were 0.5 g/dL, and reported values are the average of at least three trials.

Gel permeation chromatography was conducted on a Waters Associates Model 210 liquid chromatograph utilizing a set of 5 MicroStyragel® columns (nominal pore size 500, 10<sup>3</sup> (two), 10<sup>4</sup>, and 10<sup>5</sup> Å). Tetrahydrofuran was used as solvent, with a flow rate of 1.47 mL/min. Solutions were 0.15% (w/v) in THF. The instrument was calibrated using a set of four narrow-distribution polystyrenes supplied by Pressure Chemicals and Water Associates.

Microanalyses were performed by the Microanalytical Laboratory at the University of Massachusetts, Amherst, Massachusetts.

### Procedures

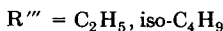
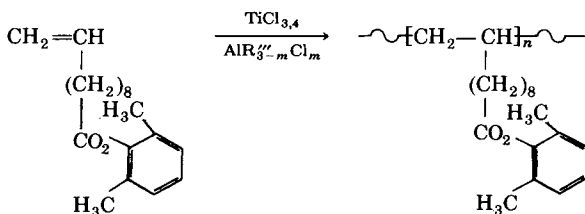
#### *Coordination Polymerization of 2,6-Dimethylphenyl 10-Undecenoate (Scheme 1)*

*General Polymerization Procedure.* A large (20 × 2.5 cm) polymerization tube was washed with a soap solution, rinsed with acetone and distilled water,

and dried in an oven for 2 days at 200°C. The hot reaction tube was allowed to cool to room temperature at  $10^{-6}$  mm. The tube was then transferred to a dry box and charged with the specified weight (normally 0.1–0.2 g) of  $\text{TiCl}_3\text{AA}$ , a magnetic stirring bar, and a rubber septum. The tube was removed from the dry box, safety wired, and placed in a desiccator. The reaction tube was charged with the appropriate solvent, aluminum alkyl, monomer, and/or monomer-aluminum alkyl complex utilizing gas-tight dry syringes fitted with TFE-tipped needles. The precomplexed mixture was transferred to the polymerization tube, which also contained the initiator mixture. The reaction mixture was magnetically stirred at the appropriate temperature up to 65°C. After the specified polymerization time, the reaction was terminated by *slow* addition of 40 mL methanol to the vented reaction tube. Caution is required since vigorous degassing generally occurs. The precipitated polymer was allowed to stir in methanol for 1 h and the liquid decanted. Methanol (60 mL) was then added, and the polymer was allowed to stir for 12 h. The polymer was isolated by decanting the methanol solution and dried, and a crude yield was obtained. Homopolymers of functionally-substituted olefins were reprecipitated by dissolution of the polymer in toluene followed by dropwise addition of the solution into methanol.

*Polymerization of 2,6-Dimethylphenyl 10-Undecenoate with  $\text{TiCl}_3\text{AA}$   
1.1 /  $\text{Al}(\text{isoBu})_2\text{Cl}$  Initiator.*

A dry  $20 \times 2.5$  cm polymerization tube fitted with a magnetic stirring bar and a rubber septum was charged with  $\text{TiCl}_3\text{AA}$  1.1 (0.1 g, 0.5 mmol Ti) under a nitrogen atmosphere. The reaction tube was equipped with nitrogen inlet and outlet needles, and toluene (4.0 mL, 37.5 mmol) and DIBAC (0.39 mL, 2.0 mmol) were added using nitrogen-purged gas-tight syringes. To this heterogeneous mixture was added a solution of toluene (4.0 mL, 37.5 mmol), DIBAC (0.97 mL, 5.0 mmol), and DMPU (1.47 mL, 5.0 mmol) that had been mixed in a similarly equipped reaction tube. The resulting purple-colored mixture was stirred at 25°C for 1 week, during which time the viscosity of the reaction increased to form a plug. The polymerization was terminated by slowly adding 30 mL of methanol to the well-vented tube. During this addition the color of the plug changed from dark purple-brown to ivory. The contents of the polymerization tube were added to a beaker containing methanol (200 mL) and allowed to stir for 12 h. The polymer was isolated by decanting the



Scheme 1.

methanol solution and was dried by evacuation at 0.01 mm for 2 days; 1.27 g (88%) of poly-DMPU were obtained. The polymer was dissolved in toluene (40 mL) and reprecipitated by dropwise addition of methanol. The resulting polymer was white and opaque. The inherent viscosity of the polymer (0.5% in benzene, 30°C) was 2.9 dL/g; this corresponds to average molecular weights  $\bar{M}_n = 3.06 \times 10^5$  and  $\bar{M}_w = 2.59 \times 10^6$  (based on polystyrene calibration standards) as determined by gel permeation chromatographic analysis of poly-DMPU in THF solution (0.15%, w/v). The infrared spectrum (thin film cast from toluene) showed absorptions centered at  $3040\text{ cm}^{-1}$  (C—H stretch, aromatic),  $2938, 2860\text{ cm}^{-1}$  (C—H stretch),  $1762\text{ cm}^{-1}$  (C=O stretch, ester),  $1470, 1375\text{ cm}^{-1}$  (C—H bend, methylene and methyl, respectively),  $768\text{ cm}^{-1}$ .

The  $^1\text{H}$ -NMR showed  $\delta$ : 0.50–2.18 ppm ( $-\text{CH}_2-\text{CH}-\text{CH}_2-$ , 7H), 2.04 ppm ( $-\text{CH}_3$ , 6H, singlet), 2.45 ppm ( $-\text{CH}_2-\text{CO}_2-$ , 2H, triplet), 6.83 ppm (phenyl hydrogens, 3H, singlet). The  $^{13}\text{C}$ -NMR spectrum ( $\text{CDCl}_3$ ) showed  $\delta$ : 16.34 ppm ( $-\text{CH}_3$ ), 25.28 ppm ( $-\text{CH}_2-\text{CH}_2-\text{CO}_2-$ ), 26.83 ppm ( $-\text{CH}_2-\text{CH}-\text{CH}_2-\text{CH}_2-$ ), 29.54, 29.87, 30.50 ppm ( $-\text{CH}_2-$ ), 32.41 ppm ( $-\text{CH}_2-\text{CH}-$ ), 34.08 ppm ( $-\text{CH}_2-\text{CO}_2-$ ), 35.06 ppm ( $-\text{CH}_2-\text{CH}-\text{CH}_2-$ ), 40.14 ppm ( $-\text{CH}-\text{CH}-$ ), 125.75, 128.60, 130.11, 148.42 ppm

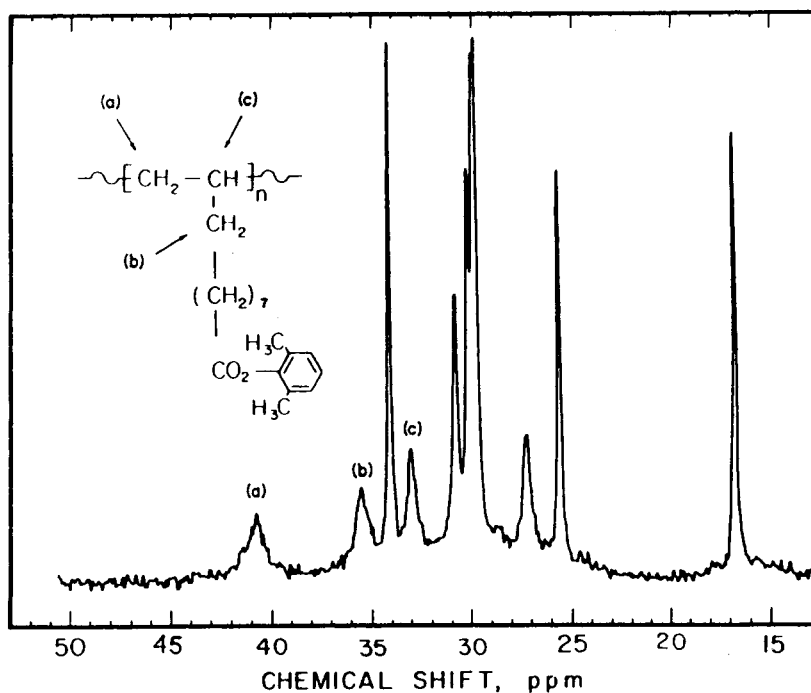


Fig. 1.  $^{13}\text{C}$ -NMR spectrum of poly(2,6-dimethylphenyl 10-undecenoate).

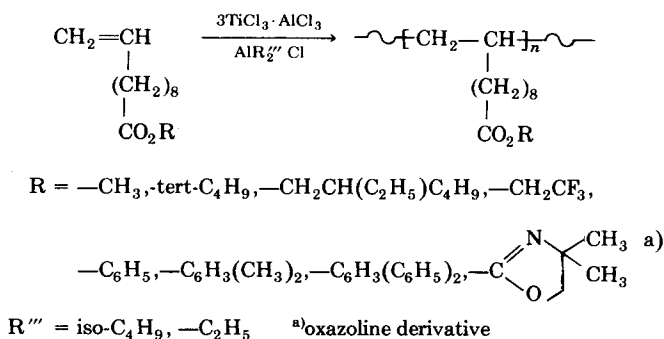
(phenyl carbons *p*, *m*, *o*, and  $-\text{CO}_2-\text{C}-$ , respectively), 171.13 ppm ( $\text{C}=\text{O}$ ) (Fig. 1).

ANAL. Calcd for  $-(\text{C}_{19}\text{H}_{28}\text{O}_2)_n-$ : C, 79.12%; H, 9.79%. Found: C, 78.76%; H, 9.71%.

*Polymerization of 10-Undecenoates with  $\text{TiCl}_3\text{AA}$  1.1 /  $\text{AlEt}_{1.5}\text{Cl}$  as the Initiator (Scheme 2)*

**General Procedure for polymerization of the 10-Undecenoate Series.** Reaction apparatus and polymerization techniques as described above were utilized for this polymerization series. Sixteen reaction tubes were prepared. Eight tubes, designated as initiator tubes, were charged with  $\text{TiCl}_3\text{AA}$  1.1 (0.2 g, 1.0 mmol  $\text{TiCl}_3$ ), toluene (10.0 mL, 94 mmol), and DEAC (0.5 mL, 4.0 mmol). The eight remaining tubes, designated as precomplexation tubes, were charged with 1 of the 8 prescribed 10-undecenoates (10.0 mmol), toluene (6.0 mL, 56 mmol), and DEAC (1.25 mL, 10.0 mmol). The solutions in the complexation tubes were then transferred to the initiator tubes using nitrogen-purged gas-tight syringes. The eight polymerizations were then stirred at  $65^\circ\text{C}$  for 10 days, allowed to cool, and terminated by slow addition of acidic methanol (5%  $\text{HCl}$ , 5 mL) to the vented tubes. The contents of the tubes were transferred to beakers containing methanol (200 mL) and allowed to stir for 12 h. The polymers were then isolated by decanting or suction filtration with a sintered glass funnel. The solvent was removed by evacuation in a desiccator to constant weight at 0.01 mm/ $25^\circ\text{C}$ . The polymers were reprecipitated by dissolving in toluene (30 mL) and dropwise addition of methanol. The polymers were again dried under reduced pressure.

**Polymerization of 2,6-Diphenylphenyl 10-Undecenoate.** A dry  $20 \times 2.5$  cm polymerization tube was charged with  $\text{TiCl}_3\text{AA}$  1.1 (0.2 g, 1.0 mmol); toluene (10.0 mL, 94.1 mmol) and DEAC (0.5 mL, 4.0 mmol) were then introduced with gas-tight syringes. Precomplexation was done with toluene (6.0 mL, 57 mmol), diphenylphenyl 10-undecenoate (4.0 mL, 10.0 mmol), and DEAC (1.25 mL, 10.0 mmol). After mixing, the polymerization was carried out at  $65^\circ\text{C}$  for 10 days, during which time a plug formed. After treatment with methanol (10 mL methanol, 0.5 mL conc. hydrochloric acid), washing by decantation with



Scheme 2.

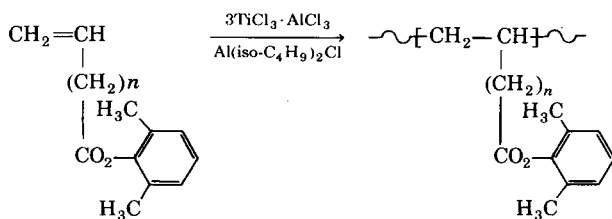
methanol, and drying, the polymer was dried for 2 days at 0.01 mm. Yield of the ivory-colored, slightly elastic poly(2,6-diphenylphenyl 10-undecenoate) was 3.2 g (77%). The polymer was reprecipitated by dissolving it in toluene (20 mL) and adding the solution dropwise into methanol; inherent viscosity (0.5% in benzene, 30°C) was 0.8 dL/g. The infrared spectrum (thin film from toluene) showed absorptions centered at 3053  $\text{cm}^{-1}$  (C—H stretch, aromatic), 2920, 2850  $\text{cm}^{-1}$  (C—H stretch), 1950, 1885, 1805  $\text{cm}^{-1}$  (overtone or combination bands), 1762  $\text{cm}^{-1}$  (C=O, ester), 1598, 1500  $\text{cm}^{-1}$  (C—C ring stretch), 1463  $\text{cm}^{-1}$  (C—H bend, methylene).

The  $^1\text{H}$ -NMR spectrum showed  $\delta$ : 1.03 ppm ( $-\text{CH}_2-\text{CH}-\text{CH}_2-$ , 17H), 1.85 ppm ( $-\text{CH}_2-\text{CO}_2-$ , 2H), 7.14 ppm (phenyl hydrogens, 13H). The  $^{13}\text{C}$ -NMR spectrum ( $\text{CDCl}_3$ ) showed  $\delta$ : 24.40 ppm ( $-\text{CH}_2-\text{CH}_2-\text{CO}_2-$ ), 26.67 ppm ( $-\text{CH}_2-\text{CH}-\text{CH}_2-\text{CH}_2-$ ), 28.83 ppm, 29.40 ppm, 29.64 ppm, 30.47 ppm ( $-\text{CH}_2-$ ), 32.43 ppm ( $-\text{CH}_2-\text{CH}-$ ), 33.85 ppm ( $-\text{CH}_2-\text{CO}_2-$ ), 35.15 ppm ( $\text{CH}_2-\text{CH}-\text{CH}_2-$ ), 40.85 ppm ( $-\text{CH}_2-\text{CH}-$ ), 126.28 ppm, 127.35 ppm, 127.75 ppm, 128.12 ppm, 129.12 ppm, 130.02 ppm, 130.51 ppm, 136.03 ppm, and 138.02 ppm (phenyl carbons), 145.22 ppm ( $\text{CH}_2-\text{CO}_2-\text{C}$ ), 171.27 ppm (C=O).

ANAL. Calcd for  $-\text{C}_{29}\text{H}_{32}\text{O}_2-$ : C, 84.43%; H, 7.82%. Found: C, 83.95%; H, 7.89%; ash, 0.2%.

**Polymerization of Phenyl 10-Undecenoate.** The initiator/polymerization tube was charged with  $\text{TiCl}_3\text{AA}$  1.1 (0.2 g, 1.0 mmol), toluene (8.0 mL, 75 mmol), and DIBAC (0.78 mL, 4.0 mmol). The precomplexation tube was charged with toluene (8.0 mL, 75 mmol), DIBAC (1.94 mL, 10.0 mmol), and phenyl 10-undecenoate (2.6 mL, 10.0 mmol), mixed, and allowed to polymerize at 25°C for 1 week.

**Polymerization of the 4,4-Dimethyl-2-oxazoline Derivative of 10-Undecenoic Acid.** The initiator/polymerization tube was charged with  $\text{TiCl}_3\text{AA}$  1.1 (0.2 g, 1.0 mmol), toluene (14.0 mL, 130 mmol), and DEAC (0.5 mL,



$n$	% Yield
1	—
3	—
6	60
8	95

Scheme 3.



4.0 mmol). The precomplexation tube was charged with toluene (6.0 mL, 56 mmol), DEAC (1.25 mL, 10 mmol), and the oxazoline derivative (2.7 mL, 8.85 mmol). The contents of the precomplexation tube were transferred to the initiation tube, and the polymerization was allowed to proceed at 25°C for 1 week; the inherent viscosity ( $\text{H}_2\text{O}$ , 30°C) of the product was 0.24 dL/g. The infrared spectra (film cast from methanol) showed absorptions at 3500–2800  $\text{cm}^{-1}$ , 2070  $\text{cm}^{-1}$  (N—H stretch and combination band), 2950  $\text{cm}^{-1}$ , 2870  $\text{cm}^{-1}$  (C—H stretch), 1740  $\text{cm}^{-1}$  (C=O stretch, ester), 1600  $\text{cm}^{-1}$ , 1505  $\text{cm}^{-1}$  (NH band, asymmetric and symmetric), 1390  $\text{cm}^{-1}$ , 1372  $\text{cm}^{-1}$  (gem-dimethyl C—H band). The  $^{13}\text{C}$ -NMR spectrum ( $\text{D}_2\text{O}$ , 60°C) showed  $\delta$ : 175.39, 69.70, 55.25, 35.14, 30.95, 30.65, 29.92, 26.16, and 23.83 ppm.

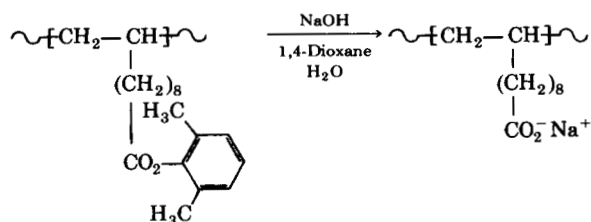
*Polymerization of  $\omega$ -Alkenoates with Variation of the Methylene Chain Length (Scheme 3)*

**Polymerization of 2,6-Dimethylphenyl 10-Undecenoate.** The dry initiator/polymerization tube (20  $\times$  2.5 cm), equipped with magnetic stirring bar and rubber septum, was charged with  $\text{TiCl}_3\text{AA}$  1.1 (0.2 g, 1.0 mmol), toluene (8 mL, 75 mmol), and DIBAC (0.78 mL, 4.0 mmol). The precomplexation tube was charged with toluene (8 mL, 75 mmol), DIBAC (1.94 mL, 10.0 mmol), and DMPU (2.94 mL, 10.0 mmol). The contents of the precomplexation tube were transferred to the polymerization tube, and the resulting purple heterogeneous slurry was allowed to stir at 25°C for 7 days. The polymer obtained was 2.8 g (94%); the inherent viscosity (0.5% in benzene, 30°C) was 2.88 dL/g. The infrared spectrum (film from toluene) and the  $^{13}\text{C}$ -NMR spectrum ( $\text{CDCl}_3$ ) were identical to that described earlier.

**Polymerization of 2,6-Dimethylphenyl 8-nonenolate.** The dry initiator/polymerization tube was charged with  $\text{TiCl}_3\text{AA}$  1.1 (0.2 g, 1.0 mmol), toluene (8 mL, 75 mmol), and DIBAC (0.78 mL, 4.0 mmol); the precomplexation tube was charged with toluene (8 mL, 75 mmol), DIBAC (1.94 mL, 10.0 mmol), and 2,6-dimethylphenyl 8-nonenolate (2.65 mL, 10.0 mmol). The contents of the precomplexation tube were transferred to the polymerization tube, and the resulting heterogeneous slurry was allowed to stir at 25°C for 7 days. The polymer obtained was 1.5 g (57%). The inherent viscosity (0.5% in benzene, 30°C) was 2.84 dL/g. The infrared spectrum showed absorptions at 3030  $\text{cm}^{-1}$  (C—H stretch, aromatic), 2922, 2858  $\text{cm}^{-1}$  (C—H stretch, aliphatic), 1760  $\text{cm}^{-1}$  (C=O stretch, ester), 1479 (C—H bend). The  $^{13}\text{C}$ -NMR spectrum ( $\text{CDCl}_3$ ) showed peaks at  $\delta$ : 16.34 ppm ( $-\text{CH}_3$ ), 25.27 ppm ( $-\text{CH}_2-\text{CH}_2-\text{CO}_2-$ ), 26.58 ppm ( $-\text{CH}_2-\text{CH}-\text{CH}_2-\text{CH}_2-$ ), 29.54 ppm, 30.12 ppm ( $-\text{CH}_2-$ ), 32.15 ppm ( $-\text{CH}_2-\text{CH}-$ ), 33.96 ppm ( $-\text{CH}_2-\text{CO}_2-$ ), 34.92 ppm ( $-\text{CH}_2-\text{CH}-\text{CH}_2-$ ), 40.07 ppm ( $-\text{CH}_2-\text{CH}-$ ), 125.73 ppm, 128.54 ppm, 130.00 ppm (phenyl carbons *p*, *m*, *o*, respectively), 148.21 ppm ( $\text{CH}_2-\text{CO}_2-\text{C}$ ), 171.21 ppm ( $\text{C}=\text{O}$ ).

ANAL. Calcd. for  $-\text{C}_{17}\text{H}_{24}\text{O}_2-$ : C, 78.42%; H, 9.29%. Found: C, 78.22%; H, 9.36%; ash, < 0.1%.

**Attempted Polymerization of 2,6-Dimethylphenyl 5-Hexenoate.** The initiator/polymerization tube was charged with  $\text{TiCl}_3\text{AA}$  1.1 (0.2 g, 1.0 mmol), toluene (8 mL, 75 mmol), and DIBAC (0.78 mL, 4.0 mmol); the precomplexa-



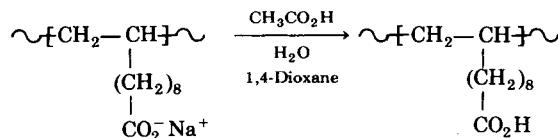
Scheme 4.

tion tube was charged with toluene (8 mL, 75 mmol), DIBAC (1.94 mL, 10.0 mmol), and 2,6-dimethylphenyl 5-hexenoate (2.22 mL, 10.0 mmol). The contents of the polymerization tube were transferred to the polymerization tube, and the resulting slurry was allowed to stir for 7 days at 25°C. No polymer was obtained.

**Attempted Polymerization 2,6-Dimethylphenyl 3-Butenoate.** The initiator/polymerization tube was charged with  $\text{TiCl}_3\text{AA}$  1.1 (0.2 g, 1.0 mmol), toluene (8 mL, 75 mmol), and DIBAC (0.78 mL, 4.0 mmol). The precomplexation tube was charged with toluene (8 mL, 75 mmol), DIBAC (1.94 mL, 10 mmol), and 2,6-dimethylphenyl 3-butenate (1.94 mL, 10.0 mmol). The contents of the precomplexation tube were transferred to the polymerization tube, and the resulting heterogeneous slurry was allowed to stir at 25°C for 7 days. No polymer was obtained.

#### Modifications of $\omega$ -Functionally Substituted Polyolefins

**Preparation of Polyolefin Ionomers and Polyelectrolytes (Scheme 4): Saponification of Poly(2,6-dimethylphenyl 10-Undecenoate).** A 3-neck, 500 mL round bottom flask equipped with magnetic stirrer, condenser, thermometer, and argon inlet and outlet needles connected to an oil bubbler was charged with poly-DMPU (1.42 g, 4.9 mmol) and purified 1,4-dioxane (250 mL). This solution was heated gently at 85°C until all polymer was dissolved. A 4N aqueous sodium hydroxide solution (0.6 g sodium hydroxide in 3.7 mL distilled water) was then added, resulting in the formation of a two-phase system. This mixture was stirred at 85°C for 1 h, followed by addition of distilled water (4.5 mL) and 4N aqueous sodium hydroxide solution (0.6 g sodium hydroxide in 3.7 mL distilled water) and continued for 12 h during which time the polymer precipitated as a granular powder. The polymer was collected by filtration, washed repeatedly with methanol, and dried for one day at 0.01 mm over phosphorus pentoxide; yield: 1.0 g (99%). To ensure total conversion to the carboxylate salt, the product was charged to distilled water (200 mL) and sodium hydroxide (0.67 g, 16.8 mmol). The polymer dissolved readily, and the resulting solution was stirred for 3 h at 70°C, suction filtered to remove insoluble material, and divided into two equal portions. One portion was set aside for conversion to the polyacid derivative. The second portion was precipitated by the addition of 1,4-dioxane (180 mL). The product was isolated by filtration, washed with methanol, and dried for 1 day at 0.01 mm over phosphorus pentoxide. A white, free-flowing powder (0.45 g, 90%) was obtained. The inherent viscosity of the polymer (0.5% in water, 30°C) was 0.48 dL/g. The infrared spectra (KBr) showed absorptions at 2925  $\text{cm}^{-1}$ , 2855



Scheme 5.

$\text{cm}^{-1}$ , 2855  $\text{cm}^{-1}$  (C—H stretch), 1560  $\text{cm}^{-1}$ , 1415  $\text{cm}^{-1}$  ( $\text{CO}_2^-$  stretch, carboxylate anion). The  $^{13}\text{C}$ -NMR spectrum ( $\text{D}_2\text{O}$ , 60°C) showed peaks at  $\delta$ : 27.73 ppm ( $-\text{CH}_2-\text{CH}_2-\text{COO}^-\text{Na}^+$ ), 30.39, 30.61, 30.98, and 31.13 ppm ( $-\text{CH}_2-$ ), 34.95 ppm ( $-\text{CH}_2-\text{CH}-$ ), 36.18 ppm ( $-\text{CH}_2-\text{CH}-\text{CH}_2-$ ), 39.23 ppm ( $-\text{CH}_2-\text{COO}^-\text{Na}^+$ ), 42.57 ppm ( $\text{CH}_2-\text{CH}-$ ), 184.39 ppm ( $-\text{COO}^-\text{Na}^+$ ).

ANAL. Calcd. for  $(\text{C}_{11}\text{H}_{19}\text{O}_2\text{Na} \cdot 4\text{H}_2\text{O})_n$ : C, 47.47%; H, 9.78%; Na, 8.26%. Found: 47.38%; H, 7.32%; Na, 8.7%.

#### *Preparation of Polyolefin Carboxylic Acids (Scheme 5): Poly(10-Undecenoic Acid)*

A 3-neck, 500 mL round bottom flask was charged with a solution of poly(10-undecenoic acid sodium salt) (0.8 g, 3.9 mmol), sodium hydroxide (0.34 g, 8.4 mmol), and distilled water (115 mL). Glacial acetic acid (3 mL, 52.0 mmol) was added dropwise, and the resulting solution was stirred at 25°C for 3 h. The polymer product was isolated and dried for 2 days at 0.005 mm over phosphorus pentoxide; yield: 0.54 g (76%). The infrared spectrum (film cast from 1,4-dioxane) showed absorptions at 3400–2400  $\text{cm}^{-1}$  (—OH stretch, carboxylic acid), 2930  $\text{cm}^{-1}$ , 2853  $\text{cm}^{-1}$  (C—H stretch), 1708  $\text{cm}^{-1}$  (C=O stretch, carboxylic acid), 1440  $\text{cm}^{-1}$  (C—OH bend), 1290  $\text{cm}^{-1}$  (C—O stretch).

ANAL. Calcd. for  $-\text{C}_{11}\text{H}_{20}\text{O}_2-$ : C, 71.70%; H, 10.49%. Found: C, 70.32%; H, 11.30%; Na, < 0.1%.

## RESULTS AND DISCUSSION

Polymerization of DMPU and other  $\omega$ -alkenoates was accomplished with transition metal initiators of the coordination type, particularly titanium. Success was achieved only when it was recognized that the functional monomer had to be precomplexed, a factor that had not been recognized in previous attempts at polymerization of functional olefin monomers.

The nature and properties of polymers obtained using Ziegler–Natta initiators, and indeed the success of the polymerization, are functions of a great number of interrelated variables. The crystallinity, stereoregularity, yield, molecular weight, molecular weight distribution, copolymer composition, nascent morphology, and other physical properties are strongly influenced by the selection, stoichiometry, and techniques for the introduction and reaction of initiator components and monomers. Specifically, the following factors must be considered: transition metal derivatives; choice of metal, valence, ligands, and crystal modification; organometallic component; choice of metal; alkyl or halogen substituents; selection of third component(s); inert gas and solvent; stoichiometry of the preceding components; use of aging and heat treatments for initiators and monomer precomplexes; reaction conditions;

time, temperature, method, and sequence of component addition; stirring technique and polymer work-up. In addition, preparative and purification techniques must be optimized and scrupulously maintained to ensure experimental repeatability.

### Selection of the Transition Metal Derivative

The role of the transition metal component in coordination polymerization has been examined extensively.<sup>3</sup> Although individual factors, including the choice of metal, ligand, valence, mode of reaction, etc., are extremely important, Natta<sup>35-37</sup> recognized early that it is the combined effects of these factors that ultimately determine the contribution of the transition metal compound.<sup>3</sup> Although nearly all the transition metals have been shown to form active metal salts for one or more monomers, the commercially important results have been obtained with only a small number of metals. The early extensive use of titanium derivatives was certainly a result of the ready availability of  $\text{TiCl}_4$  at low cost and of high purity. The same holds true for the extensive use of the aluminum-based alkyls. In due course, other transition derivatives of scandium, vanadium, chromium, niobium, zirconium, and tungsten have been evaluated and are available. Salts of vanadium, including  $\text{VCl}_4$ ,  $\text{VCl}_3$ , and  $\text{VOCl}_3$ , have received much attention owing to their ability to generate random copolymers as compared with the blocky products obtained using titanium systems.

The variation in the reported ligand structure is great, including halogen, oxychloride, acetylacetonate, alkoxyl, cyclopentadienyl, oxides, phosphate, sulfate, and others. Note that exchange with the aluminum alkyl is possible, so that the ligand structure of the active center may be different from the starting salt. Choices for both metal and ligand become restricted when discussion turns from ethylene to propylene and to higher  $\alpha$ -olefins, due to differences in activity and steric restrictions. The major portion of the

TABLE I  
Polymerization of 2,6-Dimethylphenyl 10-Undecenoate (DMPU) with Variation of the Transition Metal Derivative (TMD)<sup>a</sup>

Experiment	Charged monomer (g)	Solvent	TMD	Mole ratio <sup>b</sup> Al/Ti/monomer	Reaction temperature (°C)	Polymer yield (%)
1	1.4	Heptane	$\text{TiCl}_4$	3.7 + 11.4/1.0/11.4	45	Oligomer
2	3.0	Heptane	$\text{TiCl}_4$	30.0/1.0/25	45	Oligomer
3	2.9	Toluene	$\text{TiCl}_3^b$	4.0 + 10.0/1.0/10.0	25	0
4	2.9	Toluene	$\text{ZrCl}_4$	4.0 + 10.0/1.0/10.0	25	0
5	2.9	Toluene	$\text{TiCl}_3 \text{AA}^c$ 1.1	4.0 + 10.0/1.0/10.0	65	76 <sup>d</sup>
6	2.9	Toluene	$\text{TiCl}_3 \text{AA}$ 1.2	4.0 + 10.0/1.0/10.0	65	78 <sup>d</sup>
7	2.9	Toluene	$\text{TiCl}_3 \text{AA}$ 1.3	4.0 + 10.0/1.0/10.0	65	62 <sup>d</sup>
8	2.9	Toluene	None	4.0 + 10.0/0.0/10.0	65	0

<sup>a</sup> Reaction conditions: 25–65°C, 10 days;  $\text{AlR}_2\text{Cl} = \text{AlEt}_2\text{Cl}$ ; mole ratio Ti/solvent = 1.0/150.

<sup>b</sup>  $\text{TiCl}_3$ , hydrogen reduced;  $\text{AlR}_2\text{Cl} = \text{Al}(\text{isoBu})_2\text{Cl}$ .

<sup>c</sup>  $\text{TiCl}_3 \text{AA} = \text{TiCl}_3 \cdot 1/3\text{AlCl}_3$ .

<sup>d</sup> Yield after reprecipitation.

research on the polymerization of  $\alpha$ -olefins, especially monomers with some functionality, reports the use of halogen-substituted titanium, specifically  $\text{TiCl}_3$  preparations obtained by reduction of  $\text{TiCl}_4$ . The  $\delta$  form of  $\text{TiCl}_3$  demonstrates the highest activity and stereospecificity. On this basis several commercially available  $\text{TiCl}_4$  and  $\text{TiCl}_3$  preparations were selected for study. Table I shows the results of homopolymerizations of 2,6-dimethylphenyl 10-undecenoate. As indicated, good yields were obtained only in experiments utilizing  $\text{TiCl}_3\text{AA}$  ( $\text{TiCl}_3 \cdot 0.33\text{AlCl}_3$ ) prepared by aluminum metal reduction of  $\text{TiCl}_4$  under specific conditions followed by ball-milling to increase active site concentration per unit surface area. Three grades were evaluated, with comparable results.  $\text{TiCl}_3\text{AA}$  1.1 and 1.2 differ only in crystallite size, which is closely related to the activity, the smaller size being reported as more active due to higher surface area and thus a higher concentration of active sites.  $\text{TiCl}_3\text{AA}$  1.3 has been treated with low molecular weight polar molecules. Note that no polymer was obtained with  $\text{TiCl}_3$  prepared by hydrogen reduction of  $\text{TiCl}_4$  or with  $\text{ZrCl}_4$ , and only an oily oligomer was obtained using  $\text{TiCl}_4$  directly.

### Variation of the Aluminum Alkyl

Not all metals in groups I to III of the periodic table form active metal alkyls, as shown in the patent literature. The aluminum alkyls have been by far the most extensively studied owing to availability, cost, and solubility properties. The most widely used aluminum alkyls are triethylaluminum (TEA), triisobutylaluminum (TIBA), and some of the alkylaluminum chlorides such as diethylaluminum chloride (DEAC) and diisobutylaluminum chloride (DIBAC).

Substitution of one or two alkyl groups by halogens generally alters the activity and stereoregulating ability of the aluminum alkyl. It was shown that this substitution consistently results in decreased activity and increased stereospecificity. The loss in activity can be restored by addition of electron donor molecules. As shown in Table II, TEA, TIBA, DEAC, and DIBAC were

TABLE II  
Polymerization of 2,6-Dimethylphenyl 10-Undecenoate (DMPU) with Variation of the Aluminum Alkyl<sup>a</sup>

Experiment	Charged monomer (g)	Type $\text{AlR}_3$	Mole ratio <sup>b</sup> $\text{Al/Ti/monomer}$	Polymer yield (%)	$\eta^{\text{inhc}}$ (dL/g)
1	2.9	None	0/1.0/10.0	0	—
2	2.9	$\text{AlEt}_3$	3.7 + 10.0/1.0/10.0	4	—
3	2.9	$\text{Al(isoBu)}_3$	3.7 + 10.0/1.0/10.0	7	—
4	2.9	$\text{AlEt}_2\text{Cl}$	3.7 + 10.0/1.0/10.0	78	<sup>d</sup>
5	2.9	$\text{Al(isoBu)}_2\text{Cl}$	3.7 + 10.0/1.0/10.0	82	<sup>d</sup>

<sup>a</sup> Reaction conditions:  $\text{Ti} = \text{TiCl}_3\text{AA}$  1.1, solvent = toluene, 60°C/10 days.

<sup>b</sup> Mole ratio  $\text{Ti/solvent} = 1.0/150$ ; monomer precomplexed with aluminium alkyl, 1:1.

<sup>c</sup> A 0.5% solution in benzene, 30°C.

<sup>d</sup> Major portion of product is insoluble.

TABLE III  
Polymerization of 2,6-Dimethylphenyl 10-Undecenoate with Variation of the Mole Ratio Al/Ti<sup>a</sup>

Experiment	Charged monomer (g)	Type AlR <sub>3</sub>	Mole ratio <sup>b</sup> Al/Ti	Polymer yield (%)	$\eta_{inh}^c$ (dL/g)
1	2.9	AlEt <sub>2</sub> Cl	0/1.0	0	—
2	2.9	AlEt <sub>2</sub> Cl	3.6/1.0	5	—
3	2.9	AlEt <sub>2</sub> Cl	3.6 + 10.0/1.0	93	d
4	2.9	AlEt <sub>2</sub> Cl	7.4 + 10.0/1.0	89	d
5	2.9	AlEt <sub>2</sub> Cl	11.1 + 10.0/1.0	95	d

<sup>a</sup> Reaction conditions: 60°C/10 days, Ti = TiCl<sub>3</sub>AA 1.1, solvent = toluene.

<sup>b</sup> Mole ratio Ti/solvent = 1.0/150.

<sup>c</sup> A 0.5% solution in benzene, 30°C.

<sup>d</sup> Major portion of product is insoluble.

utilized for the study of the polymerization of  $\omega$ -alkenoates. Low yields of polymers were obtained with TEA and TIBA. In contrast, very good yields (80%) were achieved using both DEAC and DIBAC.

#### Variation of the Aluminum/Titanium Mole Ratio

Alkylation of the transition metal derivative by the metal alkyl results in the formation of active centers. The literature contains reports of these components being combined in mole ratios from less than 1 to 30 and higher. It is now recognized that the mole ratio of the organometallic component to the transition metal derivative is a most important variable in Ziegler-Natta polymerization and affects the polymer reaction rate, yield, stereospecificity, and molecular weight.<sup>38</sup> For most nonpolar hydrocarbon monomers, the optimum Al/Ti mole ratio for maximum yield falls in the range from 1 to 3 for heterogeneous systems but can be as high as 10. It is important to note that the Al/Ti mole ratio that gives the best yield does not necessarily result in the optimum stereoregularity.<sup>39</sup> Quite the opposite has been demonstrated for a system polymerizing 1-butene.<sup>40</sup> In addition, different initiator combinations result in different optimum Al/Ti mole ratios for the same monomer.

The literature indicates that polymerizations involving monomers containing heteroatoms invariably require significantly higher Al/Ti mole ratios. In many cases, the monomer is precomplexed with an equimolar amount of the aluminum alkyl before addition to an initiator prepared using more conventional mole ratios in the range of 3–4. In other publications, Al/Ti mole ratios as high as 30 are reported, with subsequent addition of the functional monomer. It appears probable to this experimenter that in this case also the result is a 1:1 complexation of the monomer with sufficient uncomplexed aluminum alkyl remaining to initiate polymerization if alkylation has not already occurred before monomer addition.

Given this information, the homopolymerization of 2,6-dimethylphenyl 10-undecenoate (DMPU) was conducted using various Al/Ti mole ratios, as detailed in Table III. With no aluminum alkyl present, no polymerization was observed. With a mole ratio of 3.6, a yield of 5% was obtained. By precomplexing the DMPU with an equimolar amount of DEAC, the yield increased

TABLE IV  
Polymerization of 2,6-Dimethylphenyl 10-Undecenoate with Variation  
of the Monomer/Ti Mole Ratio<sup>a</sup>

Experiment	Mole ratio monomer/Ti	Wt % Ti in reaction	Polymer yield (%)	$\eta_{inh}^b$ (dL/g)
1	10.0/1.0	1.03	97	2.86
2	20.0/1.0	0.53	65	2.77
3	40.0/1.0	0.33	42	2.27

<sup>a</sup>Reaction conditions: 25°C, 7 days; Ti = TiCl<sub>3</sub>AA 1.1; AlR<sub>2</sub>Cl = Al(isoBu)<sub>2</sub>Cl; solvent = toluene.

<sup>b</sup>A 0.5% solution in benzene, 30°C.

dramatically to 93%. In experiments 4 and 5, further increase did not adversely affect the polymer yield but did result in decreased molecular weight, as evidenced by loss of properties of the products, which were tacky flowing solids. The molecular weight determinations by dilute solution viscometry of the polymer product was not successful. This problem was remedied by conducting the polymerizations at 25°C rather than at 65°C.

#### Variation of the Monomer/Titanium Mole Ratio

Homopolymerizations of monomers containing heteroatoms claim monomer/Ti mole ratios considerably lower than those reported for nonpolar hydrocarbon systems. For example, key publications report the following monomer/Ti mole ratios: polymerization of monomers containing nitrogen and oxygen,<sup>41,42</sup> monomer/Ti = 11.4; polymerization of halogen-containing monomers,<sup>29</sup> monomer/Ti = 20; polymerization of vinyl pyridines,<sup>43</sup> monomer/Ti = 20; polymerization of nitrogen-, phosphorus-, and oxygen-containing monomers,<sup>32</sup> monomer/Ti = 25–50.

On the basis of these findings, the polymerization of 2,6-dimethylphenyl 10-undecenoate was conducted using monomer/Ti mole ratios from 10 to 40 (Table IV). It is clear that best results were obtained with a mole ratio of 10, which gave a very high polymer yield (97%) whose inherent viscosity was 2.86 dL/g. Increase of the monomer/Ti mole ratio to 20 resulted in a significant drop in the yield (65%) but did not significantly affect the molecular weight. Further increase in the mole ratio to 40 continued the trend, resulting in a 42% yield of polymer with a moderate decrease in inherent viscosity.

As the monomer/Ti mole ratio is increased, the weight percent of transition metal component (and so the number of potentially active sites) is decreased. It follows that the yield would decrease, but not the molecular weight.

It is apparent that these results are in general agreement with previous findings. Note, however, that the inherent viscosity values of the polymers prepared in this study are considerably higher than those generally cited; the optimized reaction conditions include use of DIBAC as the aluminum alkyl and reaction at 25°C rather than at 65°C.

#### Variation of Solvent

Any solvent that does not react with the initiator components in a deleterious manner can be used for Ziegler–Natta polymerization. The proper choice

TABLE V  
Polymerization of 2,6-Dimethylphenyl 10-Undecenoate in *n*-Heptane<sup>a</sup>

Experiment	Charged monomer (g)	Type AlR <sub>2</sub> Cl	Reaction temperature (°C)	Mole ratio <sup>b</sup> Al/Ti	Polymer yield (%)	$\eta^{inh}$ <sup>b</sup> (dL/g)
1	2.9	AlEt <sub>2</sub> Cl	60	2.0 + 10/1.0	28	
2	2.9	AlEt <sub>2</sub> Cl	60	4.0 + 10/1.0	36	1.09
3	2.9	AlEt <sub>2</sub> Cl	60	20.0 + 10/1.0	39	
4	1.5	Al(isoBu) <sub>2</sub> Cl	25	4.0 + 10/1.0	58	2.94

<sup>a</sup> Reaction conditions: 6 days, Ti = TiCl<sub>3</sub> AA 1.1.

<sup>b</sup> Mole ratio Ti/monomer/solvent = 1.0/10.0/100.

<sup>c</sup> A 0.5% solution in benzene, 30°C.

depends on the initiator system and polymerization conditions. Solubility of the monomer and polymer, boiling point of the solvent, purity, and purifiability must be considered.<sup>3</sup> Aliphatic and aromatic hydrocarbons are used primarily as solvents.

Toluene (bp 111°C) and *n*-heptane (bp 98°C) were selected on the basis of their boiling points and the fact that they would provide solvents of different degrees of solvation for homopolymerization of the  $\omega$ -alkenoates. Tables I and V show the comparison of the polymerizability of DMPU in toluene and in *n*-heptane. Using the heterogeneous TiCl<sub>3</sub>AA/AlR<sub>2</sub>Cl systems, the polymerization reactions prepared with both toluene and *n*-heptane were deep-purple slurries at the start of the reaction. However, after only a few minutes, the appearance of the tubes varied as a function of the solvent. Agglomerates of dark-colored particulate appeared in the experiment conducted using *n*-heptane, which soon settled out, resulting in a two-phase system that stirred poorly. Upon further reaction, a dark-purple plug settled on the bottom of the polymerization vessel. The size of this plug increased over the course of the reaction, while the solvent phase remained nonviscous. In *n*-heptane, poly-DMPU is insoluble and precipitates out of solution, resulting in a plug as polymerization proceeds; relatively low and erratic yields (28–58%) were noticed when *n*-heptane was used.

In contrast, the experiments using toluene as solvent remained as a uniform purple-colored slurry, which stirred well until increased viscosity of the single phase resulted in plug formation. Consistently high yields (75–100%) were obtained using toluene. The experimental series conducted in *n*-heptane also showed the effectiveness of DIBAC as the aluminum alkyl; a reaction temperature of 25°C results in optimum yield and molecular weight (see Table V). Results also indicate that although the use of *n*-heptane affects the yield adversely, the molecular weight of poly-DMPU obtained in *n*-heptane is comparable to that obtained in toluene.

#### Variation of Reaction Temperature and Monomer/Aluminum Alkyl Precomplexation Techniques

Reaction temperatures from –90°C to 200°C have been reported for polyolefins prepared with Ziegler–Natta initiators.



TABLE VI  
Polymerization of 2,6-Dimethylphenyl 10-Undecenoate with Variation of the Aluminum Alkyl  
and Reaction and Precomplexation Temperature<sup>a</sup>

Experiment	Type AlR <sub>3</sub>	Reaction temperature (°C)	Precomplex ageing (°C/min)	Polymer yield (%)	$\eta^{inh\ b}$ (dL/g)
1	AlEt <sub>2</sub> Cl	25	22/20	84	1.21
2	AlEt <sub>2</sub> Cl	60	22/20	90	<sup>c</sup>
3	AlEt <sub>2</sub> Cl	25	60/45	74	0.89
4	AlEt <sub>2</sub> Cl	60	60/45	79	<sup>c</sup>
5	Al(isoBu) <sub>2</sub> Cl	25	22/20	88	2.51
6	Al(isoBu) <sub>2</sub> Cl	60	22/20	88	<sup>c</sup>
7	Al(isoBu) <sub>2</sub> Cl	25	60/45	89	2.86
8	Al(isoBu) <sub>2</sub> Cl	60	60/45	74	<sup>c</sup>

<sup>a</sup>Reaction conditions: Ti = TiCl<sub>3</sub>AA 1.1; mole ratio Al/Ti/monomer/solvent = 4.0 + 10/1.0/10.0/150, reaction time = 7 days, solvent = toluene.

<sup>b</sup>A 0.5% solution in benzene, 30°C.

<sup>c</sup>Major portion of product is insoluble.

Boor<sup>3</sup> reported that the polymerization temperature can affect the rate, stereoregularity, and molecular weight in ways that are not always predictable and are best experimentally established for a particular system. Combs<sup>41</sup> showed that stereoregularity varied with temperature and that the molecular weight distribution can become more narrow as the reaction temperature is increased.

The polymerizations conducted in the course of this study were carried out at either 25°C or 65°C. Initial homopolymerizations were all done at 65°C, resulting in yields of 80% and better. However, although the polymers were found to swell greatly in toluene or benzene and to form a microgel, a significant portion of the polymer did not dissolve. As a result, molecular weight estimates via dilute solution viscometry could not be obtained. Variation in the work-up procedures, including treatments with aqueous or alcoholic acid solutions, did not improve the solubility in most cases. Poly-DMPU samples prepared at 65°C, as described in Table VI, were elastic solids with little toughness. However, when the polymerization was conducted at 25°C, the resulting polymer was totally soluble in benzene and toluene and had a tough, rubberlike appearance with no tackiness.

Many studies addressing the polymerization of functional monomers utilize precomplexation, aging, and/or heat treatments of the initiator components or monomer with aluminum alkyl. Modifications of this type were investigated in the present study, as detailed in Table VI. Four variations were evaluated utilizing initiator systems consisting of TiCl<sub>3</sub>AA/Al(isoBu)<sub>2</sub>Cl and TiCl<sub>3</sub>AA/AlEt<sub>2</sub>Cl, resulting in a total of eight experiments. In all cases, the monomer was precomplexed with an equimolar amount of the appropriate aluminum alkyl. In variation 1 the monomer precomplex was prepared and allowed to stir at 22°C for 20 minutes, which was the time required to prepare the initiator slurry. The precomplex and initiator tubes were then combined, and the resulting mixture was allowed to react at 25°C. Variation 2 called for preparation of the monomer precomplex as previously described, followed by

TABLE VII  
 Polymerization of 2,6-Dimethylphenyl 10-Undecenoate with Variation of Reaction Time<sup>a</sup>

Experiment	Monomer charge (g)	Reaction time (days)	Polymer yield (%)	$\eta^{inh\ b}$ (dL/g)
1	1.5	1	49	2.58
2	1.5	2	59	
3	1.5	3	65	2.79
4	1.5	7	94	
5	1.5	10	98	2.88

<sup>a</sup> Reaction conditions: 25°C, Ti = TiCl<sub>3</sub>AA 1.1, AlR<sub>2</sub>Cl = Al(isoBu)<sub>2</sub>Cl, solvent = toluene, mole ratio Al/Ti/monomer/solvent = 4.0 + 10/1.0/10/150.

<sup>b</sup> A 0.5% solution in benzene, 30°C.

transfer to the initiator tube and reaction at 60°C. Variation 3 involved preparation of the monomer/aluminum alkyl precomplex followed by aging at 60°C for 45 min prior to combination with the initiator tube and reaction at 25°C. Variation 4 required similar aging of the precomplex at 60°C for 45 min, followed by polymerization at 60°C.

The yields for all eight polymerizations were good, in the range of 75–90%. However, important variations in product solubility and molecular weights were observed. The four reactions conducted at 60°C, regardless of the precomplex aging technique, produced polymer that was substantially insoluble in toluene. In contrast, the four polymerizations run at 25°C, regardless of the precomplex aging temperature, produced toluene-soluble polymer. Comparison of both yield and inherent viscosity data demonstrates that best results were obtained using DIBAC as the aluminum alkyl and a polymerization temperature of approximately 25°C.

Comparison of experiments 1 and 3, run at 25°C and using DEAC, indicates that heat aging the monomer precomplex results in a decrease in the molecular weight. However, comparison of experiments 5 and 7, run at 25°C with DIBAC, suggests a slight increase in molecular weight with heat treatment. In either case, the differences are not enough for definite conclusions to be drawn on the effects of heat aging without further experimentation.

### Variation of Reaction Time

Batch-type polymerizations of ethylene or propylene are normally conducted over a period of 1–7 h, with times of 1–3 h being most typical. Longer times, up to 10 days, have been reported in the literature. Higher  $\alpha$ -olefins are less reactive and generally require longer reaction times. The homopolymerizations of some functional olefin or epoxide monomers were conducted for periods of 1–3 weeks.<sup>32,41,42,45</sup> In our hands, the polymerizations of DMPU and other  $\omega$ -alkenoates were carried out for 1 week or slightly longer with a TiCl<sub>3</sub>AA/Al(isoBu)<sub>2</sub>AlCl initiator system at 25°C. The results are included in Table VII. After only 1 day, a yield of 50% was obtained. Over the course of the next 9 days, the yield slowly increased to a maximum of 98%. A plot of polymer yield in percent versus time in days is presented in Figure 2. As might be expected, the molecular weights as reflected by inherent viscosity measure-

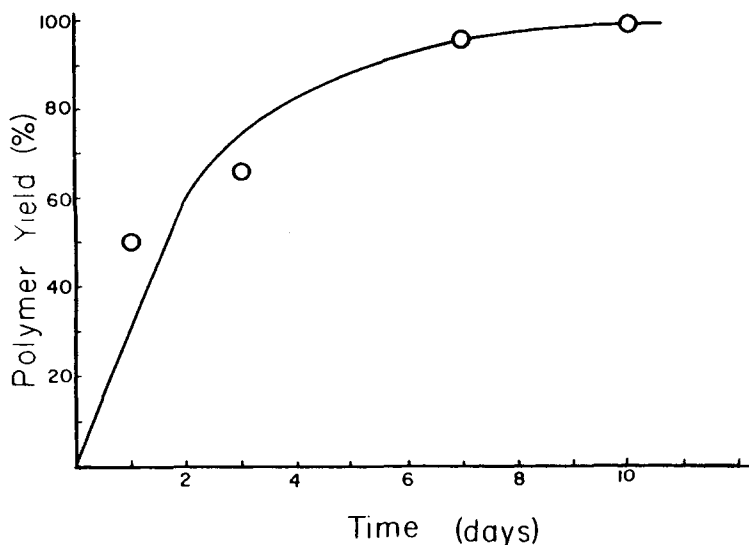


Fig. 2. Yield of poly(DMPU) as a function of reaction time.

ments were high after only one day, and further reaction resulted in only a slight increase.

#### Polymerization of 10-Undecenoates

As presented in Table VIII, eight different ester substituents and derivatives possessing widely different electronic and steric environments were evaluated; two polymerization series were investigated. The first series used DEAC, toluene, and a polymerization temperature of 65°C. The yields for most of the  $\omega$ -alkenoates including the methyl, tert-butyl, 2-ethyl-1-hexyl, trifluoroethyl, and phenyl esters were very poor: in the range from 2 to 6%. Note that in the case of the tert-butyl ester, a gaseous product, possibly isobutylene, evolved when the reaction mixture was first heated. Good yields (75%) were obtained for the 2,6-dimethylphenyl and 2,6-diphenylphenyl  $\omega$ -alkenoates.

The 4,4-dimethyl-2-oxazoline derivative of 10-undecenoic acid behaved in a manner different from the exhibited by the 10-alkenoates. The other seven polymerization reactions appeared initially as deep-purple-colored slurries that remained as a single phase while the viscosity increased. However, the polymerization of the 2-oxazoline derivative behaved differently: a black agglomerate formed early in the reaction; after 2 days, 2 phases had formed: a dark solid plug and a water-thin clear liquid, probably toluene solvent. From infrared analysis of the product, vinyl absorption at  $1645\text{ cm}^{-1}$  (C=C stretch) was absent, as was the  $\text{—C=N}$  stretch at  $1680\text{ cm}^{-1}$ , and from the  $^{13}\text{C}$ -NMR spectra it appears that polymerization had occurred and that the oxazoline ring had opened during the work-up. The inherent viscosity of the product in  $\text{H}_2\text{O}$  was 0.24 dL/g.

Subsequent polymerization experiments with DMPU demonstrated that DIBAC aluminum alkyl and a reaction temperature of 25°C resulted in higher yields and molecular weight (compare Tables V and III), and side reactions

TABLE VIII  
 Polymerization of 10-Undecenoates<sup>a</sup>

Experiment	R	Monomer charge (g)	Type AlR <sub>2</sub> Cl	Reaction temperature (°C)	Polymer yield (mol %)	$\eta^{inh}$ <sup>b</sup> (dL/g)
1	—CH <sub>3</sub>	2.0	AlEt <sub>2</sub> Cl	65	2	
2	—CH <sub>3</sub>	2.0	Al(isoBu) <sub>2</sub> Cl	25	8	
3	—tertC <sub>4</sub> H <sub>9</sub>	2.4	AlEt <sub>2</sub> Cl	65	2	
4	—CH <sub>2</sub> CH(C <sub>2</sub> H <sub>5</sub> )C <sub>4</sub> H <sub>9</sub>	3.0	AlEt <sub>2</sub> Cl	65	5	
5	—CH <sub>2</sub> CF <sub>3</sub>	2.7	AlEt <sub>2</sub> Cl	65	2	
6	—C <sub>6</sub> H <sub>5</sub>	2.6	AlEt <sub>2</sub> Cl	65	6	
7	—C <sub>6</sub> H <sub>5</sub>	2.6	Al(isoBu) <sub>2</sub> Cl	25	54	<sup>d</sup>
8	—C <sub>6</sub> H <sub>3</sub> (CH <sub>3</sub> ) <sub>2</sub>	2.9	AlEt <sub>2</sub> Cl	65	79	1.84
9	—C <sub>6</sub> H <sub>3</sub> (CH <sub>3</sub> ) <sub>2</sub>	2.9	Al(isoBu) <sub>2</sub> Cl	25	97	2.86
10	—C <sub>6</sub> H <sub>3</sub> (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	4.1	AlEt <sub>2</sub> Cl	65	77	0.80
11	—Oxazoline	2.8	AlEt <sub>2</sub> Cl	25	<sup>e</sup>	0.24 <sup>c</sup>

<sup>a</sup> Reaction conditions: 7 days; Ti = TiCl<sub>3</sub>AA 1.1; solvent = toluene; mole ratio Al/Ti/monomer/solvent = 4.0 + 10.0/1.0/10.0/150.

<sup>b</sup> A 0.5% solution in benzene, 30°C.

<sup>c</sup> A 0.5% solution in H<sub>2</sub>O, 30°C.

<sup>d</sup> Major portion of product is insoluble.

<sup>e</sup> Crude yield in excess of theoretical amount.

could occur. The methyl and phenyl esters and the oxazoline derivative were then polymerized in a second series, using optimized conditions. In the case of the phenyl ester, the yield increased from 6 to 54%. The methyl ester was obtained in an only slightly improved yield of 8%. The oxazoline derivative generated a quantitative yield of a water-soluble, apparently polymeric material. Note that poly(phenyl 10-undecenoate) was highly swollen in organic solvents but would not dissolve. This same insolubility was observed for poly-DMPU samples prepared at 65°C and may be due to crosslinking via a Friedel-Crafts alkylation of the phenyl rings.

On the basis of yield, inherent viscosity measurements, and solubility, DMPU was selected for further detailed characterization and reaction including copolymerization and polymer modifications.

### Polymerization of 2,6-Dimethylphenyl $\omega$ -Alkenoates

One of the objectives of this work was to study the polymerizability of  $\omega$ -alkenoates as a function of methylene spacer chain length. Interaction between the ester substituent and vinyl group, specifically inductive effects, must be taken into account. It is known that variation in the electron density of a vinyl group can alter its affinity toward coordination with active centers, which is a prerequisite for the insertion reaction. It was therefore considered necessary to "insulate" the vinyl group from the carboxylate function, in this case by a hydrocarbon chain consisting of methylene units. A series of 2,6-dimethylphenyl  $\omega$ -alkenoates with methylene spacers of one, three, six, and eight units were prepared.

The four monomers were polymerized using TiCl<sub>3</sub>AA/Al(isoBu)<sub>2</sub>Cl in toluene at 25°C. Results are recorded in Table IX. As previously dem-

TABLE IX  
Polymerization of 2,6-Dimethylphenyl  $\omega$ -alkenoates with Variation  
of the Methylene Chain Length<sup>a</sup>

Experiment	<i>n</i>	Monomer charge (mL)	Polymer yield (mol %)	$\eta_{inh}^b$ (dL/g)
1	1	1.94	—	—
2	3	2.22	—	—
3	6	2.65	57	2.84
4	8	2.94	94	2.88

<sup>a</sup> Reaction conditions: 25°C, 10 days; Ti = TiCl<sub>3</sub> AA 1.1; AlR<sub>2</sub>Cl = Al(isoBu)<sub>2</sub>Cl; solvent = toluene; mole ratio Al/Ti/monomer/solvent = 4.0 + 10/1.0/10/150.

<sup>b</sup> A 0.5% solution in benzene, 30°C.

onstrated the  $n = 8$  ester polymerized in high yield (95%). A good yield of the  $n = 6$  ester (57%) was similarly obtained. The inherent viscosities of these two polymers were very similar, approximately 2.9 dL/g. No polymer or oligomer was obtained for the  $n = 1$  or  $n = 3$  esters. This indicates that a spacer chain of greater than three and less than or equal to six units is required to insulate the double bond from the electronic and steric effects of the ester substituent. A quantitative estimate of the electronic effects of the ester functionality on the double bond may be found in the <sup>13</sup>C-NMR chemical shift data for the vinyl methylene and methine carbons, recorded in Table VI, Ref. 1. The chemical shift of the methylene carbon is known to be related to the electron density of the carbon-carbon double bond. Electron deficiency of the vinyl group is reflected in an increase in the chemical shift (downfield movement). This is clearly demonstrated in Table VI, Ref. 1, with a range from 114.28 to 119.10 ppm as the insulating spacer chain decreases from 8 to 1 units in length. The cutoff for polymerizability is apparently between 114.42 and 115.63 ppm.

Key infrared absorptions for these  $\omega$ -alkenoates are included in Table V, Ref. 1. As noted by Muggee<sup>42</sup> for a series of methyl  $\omega$ -alkenoates, the frequency of the lower vinyl C—H out-of-plane bending vibration was observed to decrease as the spacer group length increased.<sup>43</sup> This observation is consistent with established correlations between functional group electron density and infrared absorption frequency.<sup>46</sup>

The conclusion that a spacer group of greater than 3 methylene units is required to insulate the vinyl group is in agreement with the findings of other studies of functional monomers. It was found in the past that a spacer group of only one methylene unit was sufficient to insulate the effects of the less electronegative silicon atom.<sup>24,25</sup> Giannini reported that in the case of a series of *N,N'*-diisopropylamines, no polymerization occurred with  $n = 1$  methylene unit. For  $n = 2$ , polymerization proceeded very slowly and in low yields, for  $n = 3$  polymerization occurred readily. For polymerizations and copolymerizations involving oxygen-containing monomers, at least three and preferably four carbons were required.<sup>33,43</sup>

Recent work by Muggee<sup>47</sup> in this laboratory demonstrated that rates for the coordination polymerization of methyl  $\omega$ -epoxyalkenoates reached a constant value when a spacer group of more than three carbons was incorporated.

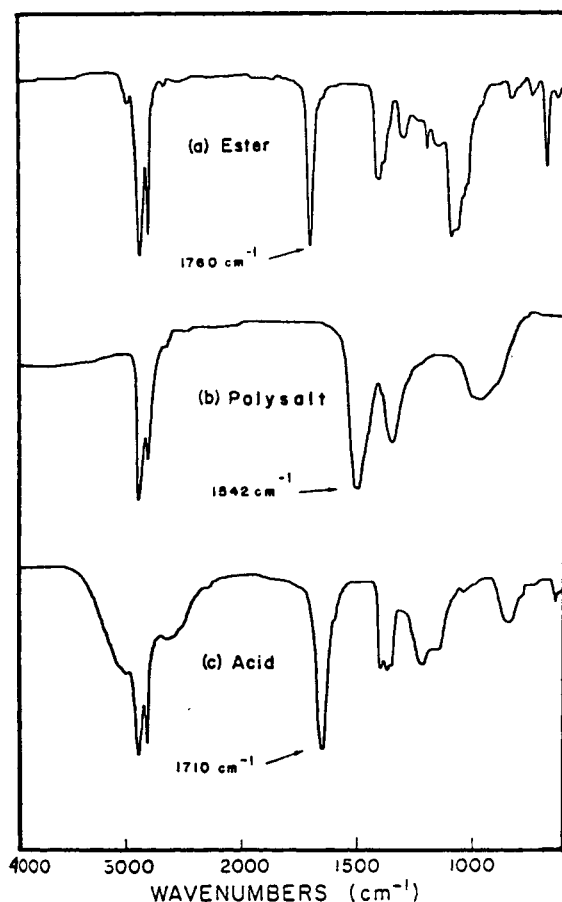


Fig. 3. Comparison of infrared spectra of functionally substituted polyolefins: (a) poly(DMPU), (b) poly(10-undecenoic acid sodium salt), and (c) poly(10-undecenoic acid).

### Modification Reactions of Poly(2,6-dimethylphenyl 10-Undecenoate)

Olefin polymers containing ester or acid functionality, such as ethylene-acrylic acid copolymers, are readily neutralized to carboxylate salts.<sup>46,47</sup> Poly(alkylene oxide) ionomers were prepared by base hydrolysis from methyl  $\omega$ -epoxyalkanoate oxirane copolymers.

Poly-DMPU ( $\eta$  of 2.9 dL/g) was subjected to base hydrolysis. It was found to be totally soluble in 1,4-dioxane; upon addition of a 4*N* aqueous sodium hydroxide solution, a second lower phase was formed that at first became a gel and then, as the hydrolysis proceeded, a granular paste. When a solution of poly-DMPU in 1,4-dioxane was used at strength greater than 0.6% (w/v), unstirrable gels were obtained. After 12 h at 85°C, a granular product precipitated, and the viscosity decreased. A quantitative yield of the poly(10-undecenoic acid sodium salt) was obtained. Infrared analysis of the initial reaction products indicated the presence of some residual ester functionality. To ensure total hydrolysis the initial product was redissolved in water and

again treated with base. After precipitation with 1,4-dioxane the resulting white, free-flowing, fine powder was isolated. The total recovery was still in excess of 90%. Infrared analysis in KBr or Fluorolube® mull indicated total conversion of the ester to the sodium salt, as evidenced by a shift in the carbonyl stretch absorption from 1760 to 1542  $\text{cm}^{-1}$  (Figure 3).  $^{13}\text{C}$ -NMR analysis also confirmed total conversion to the salt. The salt was somewhat hygroscopic.

Although poly-DMPU is totally soluble in 1,4-dioxane and unswellable in water, the reverse was true of the polysalt. Gentle heating was required to completely dissolve the polysalt in water, which gave an inherent viscosity of 0.48 dL/g. The relationship between ionic group concentration and dilute solution properties is of considerable interest, and the effects due to the presence of the hydrocarbon spacer chain will be studied in a separate effort.

Poly(10-undecenoic acid) was prepared readily by neutralization of the sodium salt with glacial acetic acid in 76% yield. The infrared spectra showed strong absorptions at 3400–2400  $\text{cm}^{-1}$  (OH stretch, carboxylic acid) and 1708  $\text{cm}^{-1}$  (C=O stretch, carboxylic acid). Ash analysis indicated that less than 0.1% residual sodium was retained in the polymer.

The elemental analysis of poly(10-undecenoic acid) showed the carbon value to be low and the hydrogen value to be slightly high, suggesting the presence of some residual water.

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