

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

### POLY(10-UNDECENOIC ACID) AND SOME OF ITS DERIVATIVES

Gyorgy Deak<sup>a</sup>; Otto Vogl<sup>b,c</sup>; Leszek B. Kiliman<sup>b</sup>

<sup>a</sup> Department of Applied Chemistry, Kossuth Lajos University, Debrecen, Hungary <sup>b</sup> 6 MetroTech Center, Polytechnic University, Brooklyn, NY, U.S.A. <sup>c</sup> Department of Polymer Science and Engineering, University of Massachusetts, Amherst, MA, U.S.A.

Online publication date: 28 February 2001

**To cite this Article** Deak, Gyorgy , Vogl, Otto and Kiliman, Leszek B.(2001) 'POLY(10-UNDECENOIC ACID) AND SOME OF ITS DERIVATIVES', *Journal of Macromolecular Science, Part A*, 38: 3, 221 – 231

**To link to this Article:** DOI: 10.1081/MA-100103344

**URL:** <http://dx.doi.org/10.1081/MA-100103344>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

## POLY(10-UNDECENOIC ACID) AND SOME OF ITS DERIVATIVES

Gyorgy Deak,<sup>†</sup> Otto Vogl,<sup>\*</sup> and Leszek B. Kiliman

Polytechnic University, 6 MetroTech Center, Brooklyn, NY 11201

### ABSTRACT

Commercially available 10-undecenoic acid was esterified with 2,5-dimethylphenol. After the supply of ester was properly complexed, it was polymerized in quantities and in high yield to high molecular polymers. The polymeric esters were hydrolyzed with base to the acid salt, which were converted to the acids. Reactions with 1,1'-carbonyldiimidazole gave polyethylene-based polymeric imidazolids.

*Key Words:* 10-Undecenoic acid; 2,5-Dimethylphenyl 10-undecenoate; Poly(10-undecenoic acid); Polymer reactions; Poly(10-undecenoyl) imidazolid.

### INTRODUCTION

For a long time, successful olefin coordination polymerization was limited to the normal olefins (1), such as ethylene, propylene, etc. Functional groups in the monomer, such as ester groups, prevented polymerization because they complexed the coordination catalysts effectively and deactivated its activity.

Approximately 20 years ago, we found that by proper selection of the ester group (it turned out to be the 2,6-dimethylphenol ester) and complexation of the monomer with diethylaluminum chloride regular  $\alpha$ -olefin polymerization of olefinic esters could be accomplished (2). The standard coordination catalyst sys-

---

<sup>\*</sup>Corresponding author. Otto Vogl, Department of Polymer Science and Engineering, University of Massachusetts, Amherst, MA 01003-4350. E-mail: vogl@polysci.umass.edu

<sup>†</sup>Present address: Department of Applied Chemistry, Kossuth Lajos University, Debrecen, H-1040 Hungary.

tem of  $\text{TiCl}_3$ .AA with diethylaluminum chloride, which is used in various forms for propylene polymerization, could be applied for the polymerization of  $\omega$ -alkenoates.

As was found for the polymerization of  $\omega$ -epoxyesters with triethylaluminum/water/acetylacetone  $\omega$ -epoxyalkanoates, the esters where the carboxylate group is near the polymerizing group, polymerization gave low yields or did not occur (3). Separating the carboxylate from the epoxy double bond by a minimum of three methylene groups was also essential (4, 5).

For the polymerization of 10-undecenoates, the 2,5 dimethylphenylester of 10-undecenoic acid (DMPU) is preferred; the phenyl ester was also polymerizable but not the aliphatic esters. Aromatic solvents, such as toluene, were good solvents, but aliphatic solvents were poor. Precomplexing of the monomer was essential and was best done at room temperature. Diethyl-, or even better, diisobutylaluminum chloride are good complexing agents but not trialkylaluminum compounds. The ratio of aluminum compounds to the transition metal  $\text{TiCl}_3$ . AA is important, but not essential as long as there is a sufficient amount of the dialkylaluminum chloride present (6-9).

One of the critical reaction conditions for the polymerization is the reaction time. A two-week reaction time at room temperature is necessary to obtain optimal yields, but even shorter times give high molecular polymer, but in lower yields. These studies were carried out in polymerization tubes closed with a rubber septum in 0.01-mol quantities of monomer.

In the meantime, novel coordination polymerizing systems have been uncovered based on systems of metallocenes and rare earth catalysts that allow the polymerization and copolymerization of olefins with ester functionalities (10).

It was the objective of this work to first prepare the polymeric esters in large quantities by our olefin polymerization technique (11). It was desirable to improve on the efficiency of complexation without changing the known efficient catalyst system, although potentially more effective systems might now be available. The further objective was to hydrolyze the polymeric esters to poly(10-undecenoic acid) and to prepare the polymeric imidazolids (12). The polymeric imidazolids were expected to be the basic reagents to form under mild reaction conditions, esters and amides with mesogenic functionalities. This work will be reported in a subsequent article.

## EXPERIMENTAL

### Reagents and Solvents

10-Undecenoic acid (UA) was esterified to methyl 10-undecenoate (MU) with methanol. For the the 2,5-dimethylphenol (DMP) ester the trifluoroacetic anhydride method was used (2, 13).

1,1'-Carbonyldiimidazole ( $\text{Im}_2\text{CO}$ ) (Staab reagent) (14, 15) was provided by PPG Industries and was used as received. It reacts readily with water and must be handled in a dry box.

Dichloromethane (DCM) was distilled (b.p. 40°C) from calcium hydride and stored under nitrogen.

N,N-Dimethylacetamide (DMAc) was stirred over phosphorous pentoxide for 12 h, and then distilled under reduced pressure (b.p. 58–58.5°C/10 mm Hg). It was stored under purified nitrogen in a drying column filled with 4 × Linde molecular sieves.

1,4-Dioxane (b.p. 100°C) and tetrahydrofuran (b.p. 65°C) were distilled from lithium aluminum hydride.

All chemicals, including trifluoroacetic acid anhydride, were obtained from the Aldrich Chemical Company. The solvents and reagents were used as received.

## Measurements

### General Procedures and Methods

The infrared (IR) spectra were recorded on the Perkin-Elmer Model 727 spectrophotometer. Solid samples were measured as KBr pellets. The IR spectra of most of the polymers were measured as thin films cast directly onto a single NaCl plate from chloroform or from 1,4-dioxane solutions. The peak assignments were made to the nearest 5 cm<sup>-1</sup>.

The inherent viscosities were measured at 30°C or 60°C using Ubbelohde viscometers and are the average values of three to five determinations. Solution concentrations were 0.1 or 0.5 g/dL in the appropriate solvent.

Microanalyses were carried out by the Microanalytical Laboratory, Office of Research Services, University of Massachusetts, Amherst, Massachusetts.

## Preparations

### Monomer Preparations

#### *2,6-Dimethylphenyl 10-Undecanoate [DMPU]*

UA (292 g, 1.6 mols) and trifluoroacetic anhydride (500 g) were charged into a dry 3-L, three-neck round-bottom flask. The reaction mixture was maintained at or below 20°C using an ice bath. Liquid DMP (194 g, 1.6 mol) was added dropwise over a period of 50 min. The reaction mixture was kept between 0° to 5°C for 1 h and then at room temperature for 5 more hours, benzene (1 L) was added and the solution was washed with an aqueous sodium bicarbonate solution and again with water. The benzene solution was dried, filtered, and the solvent evaporated leaving a dark orange oil. Crude DMPU was distilled at a boiling range of 150° to 160°C. Polymerization grade DMPU was obtained in 80% yield after two distillations under reduced pressure (0.05 mm Hg) (see also Tab. 1).

**Table 1.** Esterification of UA

#	UA g/mol	TFA g/mol	DMP g/mol	Yield g/%
1	40.2/0.2	42.4/0,3	24.4/0.2	57.6(62) 100
2	292/1.59	500/2.38	194/1.59	460(78) ~100
3	292/1.59	500/2.38	194/1.59	460(76) ~100

IR (neat) showed absorptions at 3070  $\text{cm}^{-1}$  (C-H stretch, olefinic), 2970, 2930, 2855  $\text{cm}^{-1}$  (C-H stretch), 1758  $\text{cm}^{-1}$  (C=O stretch, ester), 1640  $\text{cm}^{-1}$  (C=C stretch, monosubstituted olefin).

Elem. Anal: Calcd. for  $\text{C}_{19}\text{H}_{28}\text{O}_2$ : C, 79.17%; H, 9.72%. Found: C, 78.95%; H, 9.90%.

## Polymerizations

### *2,6-Dimethylphenyl 10-Undecanoate Poly[DMPU]*

A 2-L (“a”) and a 1-L (“b”) round-bottom flask were dried. Flask “a” was fitted with a magnetic stirring bar and a rubber septum. This assembly was then flamed out and, under a nitrogen stream, was allowed to cool to room temperature. A 100-mL dried graduated cylinder was fitted with a rubber septum and was charged with DEAC (105 mL, 0.84 mol).

In a dry box, flask “a” was opened and charged with titanium trichloride (aluminum activated) [ $\text{TiCl}_3$ .AA 1.1] (12 g, 60 mmol) and it was closed with a rubber septum. To flask “a” was added toluene (500 mL) and from flask “b” DEAC (30 mL, 0.24 mol) were added. The flask labeled “b” was charged with DEAC (75 mL, 0.6 mol). DMPU (173 g, 0.6 mol) was also placed in the same flask. The contents of this flask were warm and had a yellow color. The mixture was allowed to react for half an hour and it was then transferred into the flask labeled “a”.

Flask “a”, which contained the polymerization mixture, was fitted with a rubber septum. It was then removed from the dry box; stirring was started and was continued under nitrogen at room temperature for 2 days. The reaction mixture had become very viscous and was left without stirring for one additional week. To terminate the polymerization, the content of the polymerization vessel was discharged into a 2-L beaker and 300 mL of methanol (containing 5% of hydrochloric acid) was slowly added.

Upon addition of methanol, gas evolved and the temperature of the mixture increased, which was controlled by cooling the container with an ice bath. The mixture was concentrated to ~500 mL and then slowly added to 3 L of methanol. After two more hours, the polymer had precipitated; had a chewing gum consistency. The supernatant liquid was decanted and the polymer was then washed with

400 mL of methanol. The yield of crude poly[DMPU] was 121 g (65%) (see also Tab. 2).

Extracting it with acidified methanol (4% of hydrochloric acid) until the methanol solution became colorless purified the polymer; it was washed with methanol and dried. A slightly yellow, rubbery polymer was obtained with an inherent viscosity of 2.7 dL/g (0.5% in benzene, 30°C).

The IR spectrum (thin film 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).

Elem. Anal.: Calcd. for  $-(\text{C}_{19}\text{H}_{28}\text{O}_2)_n-$  C, 79.17%; H, 9.72% Found: C, 78.90%; H, 9.60%.

#### *Polymerization of Methyl 10-Undecenoate with $\text{TiCl}_3$ -AA*

1.1/Al(IsoBu)<sub>2</sub>Cl as initiator and  $\text{BCl}_3$  as the complexing agent. In a dry box a 100-mL one-neck round-bottom flask was charged with  $\text{TiCl}_3$ -AA 1.1 (0.2 g, 10 mmol), toluene (8 mL, 75 mmol), and DIBAC (0.8 mL, 40 mmol). A toluene solution (8 mL, 75 mmol),  $\text{BCl}_3$  (10 mL, 10 mmol), and methyl 10-undecenoate (MU) (2.8 mL, 10 mmols) had been prepared to complex the monomer. This mixture was transferred to the polymerization flask and the resulting purple slurry was allowed to polymerize. After 2 weeks, a thick suspension had formed. The polymerization was terminated by the slow addition of methanol (150 mL). After

**Table 2.** Polymerization of UA Esters

	DMPU g/mol	TiCl <sub>3</sub> /AA g/mol	BIBAC g/mol	Time days	Vessel Type	Yield g/%	$\eta_{\text{inh}}$ v
1	88/0.3	15/0.12	6/0.03	7	kettle	39/44	0.75
2	88/0.3	37.5/0.30	DEAC				
2	88/0.3	6.6/0.03	15/0.12	7	kettle	31/40	0.79
		37.5/0.30	DEAC				
			polymer solution				
3	98/0.37	6.6/0.033	15/0.12	7	kettle	73/75	0.93
		42/0.34	DEAC.				
4	184/0.65	12/0.06	30/0.24	12	kettle	121/65	0.86
		75/0.60	DEAC				
5	194/0.67	13/0.065	25/0.2	10	kettle	4.3/2.2	0.46
		80/0.64	DEAC				
6	162/0.56	12/0.06	47/0.24	13	kettle	77/48	3.5
		117/0.60	DIBAC				
7	160/0.56	12/0.06	47/0.24	18	kettle	98/60	5.2
		117/0.60	DIBAC				
8	144/0.50	14/0.07	47/0.24	5	kettle	63/44	2.7
		117/0.60	DIBAC				

several washings with fresh methanol (200 mL) the polymer was isolated and dried.

*Polymerization of 2,6-Dimethylphenyl 10-Undecenoate with  $TiCl_3$ .AA*

1.1/Al(isoBu)<sub>2</sub>Cl as initiator and BCl<sub>3</sub> as the complexing agent. A dry 100-mL one-neck round-bottom flask, equipped with a magnetic stirring bar and a rubber septum, was charged with TiCl<sub>3</sub>.AA. 1.1 (0.2 g, 1.0 mmol) in a dry box, toluene (8 mL, 75 mmol), and DIBAC (0.8 mL, 4 mmol). A dry 50-mL one-neck round-bottom flask was charged with toluene (8 mL, 75 mmol), DMPU (3 mL, 10 mmol) and BCl<sub>3</sub> (10 mL, 10 mmol), to precomplex DMPU. The two mixtures were combined and the polymerization was allowed to proceed for 2 weeks. The polymerization was terminated by slowly adding HCl containing methanol (150 mL). The solid polymer was isolated repeatedly washed with methanol and dried.

Polymeric Acid Preparation

*Poly(10-Undecanoic Acid Sodium Salt). Poly[UA<sup>-</sup>Na<sup>+</sup>]*

A 250-mL round-bottom flask was charged with poly(DMPU) (90 g, 0.31 mol) and 1,4-dioxane (3 L). The mixture was heated gently to 85°C to dissolve the polymer. Half of the solution of sodium hydroxide (50 g, 1.25 mol) dissolved in distilled water (150 mL) was added to the reaction mixture. The second half of the sodium hydroxide solution was added 30 min later when the solution had become very viscous. The sodium salt of the polymer, which had formed during the reaction, precipitated as a white solid. This mixture was stirred for another day at ~80°C. The polymer was isolated by filtration, repeatedly washed with methanol, and dried. Yield of the polymer was 42 g (98%).

The inherent viscosity of the polymer (0.5% in water, 30°C) was 1.2 dL/g. The IR spectra (KBr) showed absorptions at 2925, 2855 cm<sup>-1</sup> (C-H stretch); 1560, 1415 cm<sup>-1</sup> (COO<sup>-</sup> stretch, carboxylate anion).

*Poly(10-Undecenoic Acid) [Poly(UA)]*

A three-neck, 3-L round-bottom flask was charged with an aqueous (2.5 L) solution of poly(UA<sup>-</sup>Na<sup>+</sup>) (40 g, 195 mmol). The polymer was dissolved with stirring. Acetic acid (150 mL, 2.6 mol) was added dropwise, and the resulting suspension was stirred at 25°C for 3 h. The polymer was filtered, washed, and dried. Yield was 31 g (80%).

The IR spectrum (film from 1,4-dioxane) showed absorptions at 3400-2400 cm<sup>-1</sup> (-OH stretch, carboxylic acid); 2930, 2853 cm<sup>-1</sup> (C-H stretch); 1708 cm<sup>-1</sup> (C=O stretch, carboxylic acid); 1440 cm<sup>-1</sup> (C-OH bend); 1290 cm<sup>-1</sup> (C-O stretch).

Elem. Anal.: Calcd. for  $-(C_{11}H_{20}O_2)-$ : C, 71.74%; H, 10.87% Found: C, 71.50%; H, 10.51%.

### Polymeric Imidazolids

Polymeric imidazolids of poly(HxA) and poly(UA) were prepared by allowing to react ~10 mmol of poly(HxA) or poly(UA) under nitrogen in DMAc (200 mL) solutions with  $Im_2CO$  (13 mmol) (30% excess) for 2 h at room temperature.

### Test Reactions

#### *Biphenyl 10-Undecenoamide*

Into a 500-mL round-bottom flask, was added purified DMAc (100 mL) directly from a drying column (filled with molecular sieves). Freshly distilled 10-undecenoic acid (5 g, 27 mmol, 5.5 mL) was added with a syringe followed by  $Im_2CO$  (5.5 g, 34 mmol). The solution was stirred for 2 h. 4-aminobiphenyl (5 g, 30 mmol) was added and the solution was stirred at room temperature. After 1 day, the solvent was removed under reduced pressure and the resulting solid was dried.

Elem. Anal.: Calcd. for  $C_{23}H_{29}NO$ : C, 82.39%; H, 8.66%; N, 4.18% Found: C, 82.08%; H 8.75%; N, 4.31%.

#### *Biphenyl 10-Undecenoate*

Into a 500-mL round-bottom flask was added purified DMAc (200 L) and 10-undecenoic acid (5 g, 27 mmol, 5.5 mL) with a syringe, followed by  $Im_2CO$  (5.4 g, 34 mmol) After 2h, 4-hydroxybiphenyl (5 g, 29 mmol) was added to the reaction mixture with small amounts of sodium ethoxide and the solution was continued to be stirred at room temperature. After 1 day, the solvent was removed and the solid was dried.

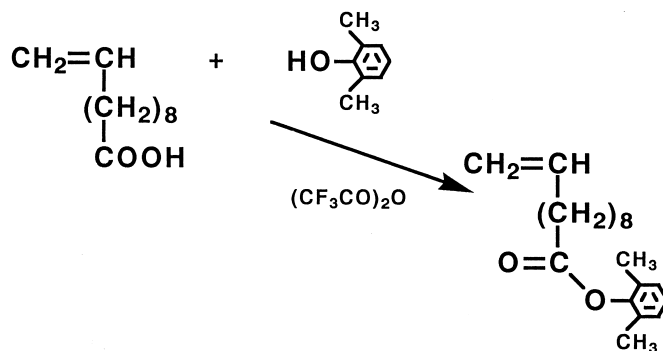
Elem. Anal.: Calcd. for  $C_{23}H_{28}O_2$ : C, 82.14%; H, 8.33%. Found: C, 81.89%; H, 8.4%.

## RESULTS AND DISCUSSION

DMPU was synthesized from 10-undecenoic acid and 2,6-dimethylphenol using trifluoroacetic anhydride according to the method developed by Tedder (13) and later perfected by Purgett (2), (Eq. 1). Equimolar amounts of UA and trifluoroacetic anhydride were first allowed to react to prepare the mixed anhydride and then 2,6-dimethylphenol was added

The polymerization of DMPU was carried out with transition metal initiating system using  $TiCl_3 \cdot AA$  1.1 and diethyl or diisobutylaluminum chloride in toluene as the solvent.

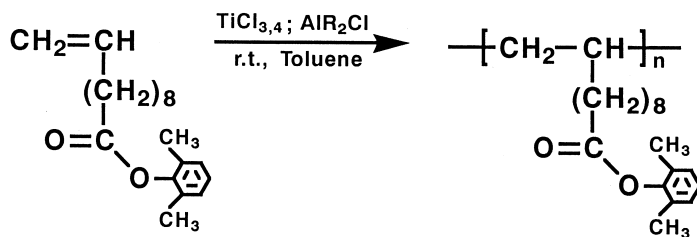




Equation 1. Synthesis of 2,6-dimethylphenyl 10-undecanoate.

In previous investigations, Purgett (2) had polymerized a number of functional alkenoates in sealed tubes and on a small scale (0.01 mol). In those investigations, the importance of the precomplexation of the monomer with equimolar amounts of the appropriate aluminum alkyls was pointed out. The selection of the transition metal derivative and the aluminum alkyl, their ratio in the initiating mixture, the monomer/titanium ratio was very important. The type of solvent, reaction temperature, reaction time, and the type of the olefin ester monomer all influenced the outcome of the polymerizations. The polymerizations were carried out at room temperature for 10–14 days (Eq. 2). DMPU has been polymerized using  $\text{TiCl}_3 \cdot \text{AA}$  1.1/ $\text{Al}(\text{iOBu})_2\text{Cl}$  initiating systems in toluene at 25°C; and high molecular weight polymers ( $n_{\text{inh}} = 2.88$  dL/g) were obtained in high yields (Eq. 2).

In our work, we succeeded in scaling up the polymerization of DMPU, using  $\text{TiCl}_3 \cdot \text{AA}$  1.1/ $\text{Al}(\text{isoBu})_2\text{AlCl}$  or  $\text{TiCl}_3 \cdot \text{AA}$  1.1/ $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$  initiating systems in a resin kettle. The monomers had been precomplexed with an equimolar amount of the dialkyl aluminum chlorides and the polymerizing mixtures were allowed to react for 1–2 weeks. The results of this polymerization are displayed in Table 2. The inherent viscosity of the polymers obtained varied between 0.76 dL/g and 5.2 dL/g and the yields were between 45 and 75% in all our polymerizations.



Equation 2. Polymerization of 2,6-dimethylphenyl 10-undecanoate.

Poly(DMPU) Was Hydrolyzed to the Corresponding Polyacids

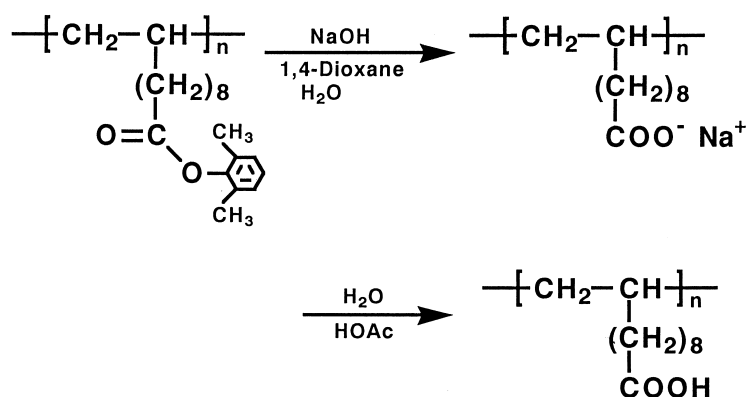
*Synthesis of Poly(10-Undecenoic Acid) [Poly(UA)]*

Poly(DMPU) has previously been shown to be readily converted to the corresponding poly(10-undecenoic acid sodium salt) [poly(UA<sup>-</sup>Na<sup>+</sup>)] by the reaction with a strong base (threefold excess of OH<sup>-</sup> to ester). Poly(UA<sup>-</sup>Na<sup>+</sup>) was then neutralized with glacial acetic acid to poly(UA). The conversion of the pendant ester groups of poly(DMPU) to the sodium carboxylate form and then to the polymeric carboxylic acid was accomplished under analogous reaction conditions (Eq. 3).

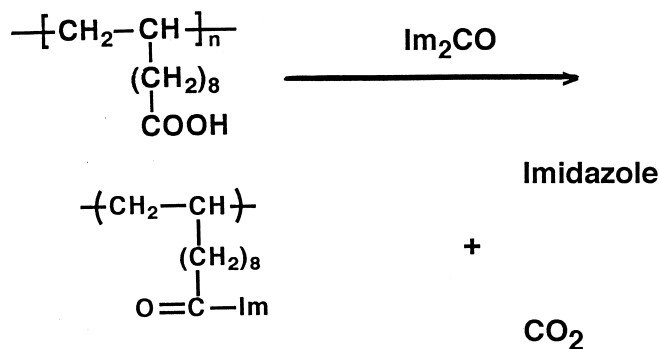
Poly(UA<sup>-</sup>Na<sup>+</sup>) precipitated from the reaction mixture and was easily recovered in yields of over 90%. Poly(UA<sup>-</sup>Na<sup>+</sup>) was converted to the polyacid form as shown by the reaction in Equation 3. The acidification was carried out at room temperature in aqueous solution with a 15-fold excess of glacial acetic acid.

The IR spectra of poly(UA) and poly(UA<sup>-</sup>Na<sup>+</sup>) differed from each other and also from the IR spectra of their ester-substituted precursor poly(DMPU). The carbonyl (C=O) stretching frequency of poly(DMPU) appeared at 1760 cm<sup>-1</sup>. Poly(UA<sup>-</sup>Na<sup>+</sup>) showed a strong carboxylate anion stretch at 1540 cm<sup>-1</sup>. Poly(UA), obtained by neutralization of poly(UA<sup>-</sup>Na<sup>+</sup>), showed the carboxylic acid C=O stretch at 1710 cm<sup>-1</sup> in addition to the broad O-H stretch in the region of 3400 to 2400 cm<sup>-1</sup>. The IR spectrum of poly(UA) was identical to the IR spectrum of poly(UA) reported earlier.

Im<sub>2</sub>CO was allowed to react at room temperature with an equimolar quantity of carboxylic acids in THF, chloroform, or similar inert solvents. Within a few minutes, in an almost quantitative yield, an imidazolid was obtained, with a liberation of 1 mol of CO<sub>2</sub> and 1 mol of imidazole. Isotope experiments had previously provided conclusive proof that in this reaction a mixed anhydride of the imidazole-*N*-carboxylic acid and the carboxylic acid is first formed and then the imidazolid is formed through an intermolecular transacylation.



Equation 3. Synthesis of poly(10-undecenoic acid).



Equation 4. Synthesis of UA imidazolid.

Highly reactive carboxylic acid imidazolids can give esters or amides when alcohols or amines are added to the reaction mixture. Substitution reactions with typical hydroxy- and amino-substituted biphenyls using the 10-undecenoic acid imidazolid were carried out successfully. For the preparation of the *polymeric imidazolids* of poly(ImHxA) and poly(ImUA) (Eq. 4), we used DMAc as the solvent. This work will be reported in a subsequent article.

#### ACKNOWLEDGMENTS

This work was supported by the Mark Chair of the Polytechnic University and the National Science Foundation. We are very grateful to Dr. Kania of PPG Industries for providing us with a generous supply of Im<sub>2</sub>CO. We are also grateful to Lyn Roberts for her help in the finalization of this article.

#### REFERENCES

1. Boor, J. Ziegler. *Natta Catalysts as Polymerizations*; Academic Press: New York, 1979.
2. Purgett, M.D. Ph.D. Thesis. University of Massachusetts: Amherst, MA, 1984.
3. Muggee, M.J. Ph.D. Thesis. University of Massachusetts: Amherst, MA, 1982.
4. Vogl, O.; Okahata, Y.; Bansleben, D.A.; Muggee, J.; Purgett, M. J. *Macromol. Sci., Chem Ed.* **1984**, *21(8&9)*, 1217.
5. Vogl, O.; Muggee, J.; Bansleben, D. *Polym. J.* **1980**, *12(9)*, 677.
6. Purgett, M.D.; Vogl, O. J. *Polym. Sci., Polym. Chem. Ed.* **1987**, *26(3)*, 677.
7. Purgett, M.D.; S.S. Xie; D. Bansleben; Vogl, O. J. *Polym. Sci., Polym. Chem. Ed.* **1988**, *26(3)*, 657.
8. Purgett, M.D.; Vogl, O. J. *Polym. Sci., Polym. Chem. Ed.* **1988**, *26(3)*, 677.
9. Purgett, M.D.; Vogl, O. J. *Macromol. Sci., Chem. Ed.* **1989**, *27(3)*, 2051.
10. Schellekens, M.A.J.; Klemperman, B. J. *Macromol. Sci., Rev. Macromol. Chem., Phys.* **2000**, *C40(2 & 3)*, 167.

11. Kiliman, L.B. Ph.D. Thesis, Polytechnic University: Brooklyn, NY, 1993.
12. Vogl, O.; Kiliman, L.B. J. Macromol. Sci., Pure & Appl. Chem. **2001**, *A38(2)*, *in press*.
13. Bourne, E.J.; Stacey, M.; Tatlow, J.C.; Tedder, J.M.J. Chem Soc. **1949**, 2976.
14. Staab, H.A.; Wendel, K. Ber. **1960**, *93*, 2910.
15. Staab, H.A.; Lüking, M.; Dürr, F. H. Ber. **1962**, *95*, 1275.

Received: September 10, 2000