Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Functional Polymers. L Terpolymers of 10-Undecenoate Derivatives with Ethylene and Propylene

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To cite this Article Purgett, Mark D. and Vogl, Otto(1987) 'Functional Polymers. L Terpolymers of 10-Undecenoate Derivatives with Ethylene and Propylene', Journal of Macromolecular Science, Part A, 24: 12, 1465 — 1481
To link to this Article: DOI: 10.1080/00222338708078153
URL: http://dx.doi.org/10.1080/00222338708078153

J. MACROMOL. SCI.–CHEM., A24(12), pp. 1465-1481 (1987)

FUNCTIONAL POLYMERS. L.* TERPOLYMERS OF 10-UNDECENOATE DERIVATIVES WITH ETHYLENE AND PROPYLENE

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ABSTRACT

Terpolymers of 2,6-dimethylphenyl 10-undecenoate with ethylene and propylene have been synthesized. With titanium-based coordination initiator systems, a crystalline terpolymer was obtained which consists of blocks of ethylene and propylene, indicated by two distinct melting transitions. With vanadium-based systems, an amorphous ethylene/propylene terpolymer was obtained. The crystalline terpolymer was hydrolyzed to the sodium carboxylate salt, which was acidified to give the polymeric carboxylic acid. All polymers were characterized by their infrared, ^{1}H-, and ^{13}C-NMR spectra, by differential scanning calorimetry, elemental analysis, and dilute-solution viscometry. In addition the polymeric sodium salt was characterized by wide-angle x-ray diffraction.

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INTRODUCTION

Random, alternating, and block-type copolymers of α-olefins and ethylene have been prepared in the past with Ziegler-Natta type coordination initiators [1-3]. Most of the work on coordination polymerization has been directed toward the preparation of stereoregular crystalline homopolymers of the lower α-olefins [4]. However, a considerable amount of interest has been devoted to amorphous copolymers and terpolymers [5-7]. By far the most important α-olefin copolymers are those prepared from ethylene and propylene.

The architecture of copolymers of α-olefins prepared with coordination initiators is a function of many factors, including the selection and treatment of the transition metal coordination initiator. Previous studies indicated that soluble (and some colloidal) initiators, including $VOCl_3$ or VCl_4, generate random, amorphous, rubbery ethylene/propylene (EP) copolymers with 20-80 mol% of propylene [8]. Heterogeneous systems such as those based on $TiCl_3$ have been known to produce block copolymers with various degrees of crystallinity [4, 9].

A major incentive for investigating these copolymers was the development of elastomers from amorphous ethylene/propylene (EP). While saturated EP copolymers are used as such, ethylene/propylene terpolymers (EPT) incorporating reactive functional groups as curing sites for vulcanization were needed [10]. 1,4-Hexadiene, dicyclopentadiene, and alkylenenorbornenes have been used as termonomers to provide crosslinking sites for sulfur vulcanization [11-14]. Other curing methods have been used for other polymers. Halogen-containing polymers such as poly(2-chloro-1,3-butadiene) or fluorocarbon elastomers have been cured with metal oxides, diamines, and phosphonium salts [15].

Termonomers which might introduce other functional groups as crosslinking sites such as carboxylates have been considered, and derivatives of norbornene [16-20] have been used as termonomers for EPT polymerization.

Very recently, we reported the homopolymerization of ω-alkenoates and their copolymerization with α-olefins and ethylene [21-24]. It appeared that EPT with functional carboxylate groups separated by a flexible spacer group could provide a superior and more effective crosslinking group based on the carboxylic acid function.

The study of polymers containing ionizable groups and the resulting interactions in ion-containing polymeric materials is an area of rapid growth [25]. The ionic cluster formations in the macromolecules behave like thermally reversible ionic crosslinks, giving rise to unique and useful properties.

There are many practical uses as well as theoretical considerations for these ion-containing polymers. Examples of practical applications involve ion-exchange resins, reverse osmosis membranes, flocculants, electrostatics, and bacteriocidal films. Theoretical applications include the study of chain conformations as a function of the counterion type and concentration, the mechanism of ion selectivity by ion exchange, and catalytic effects as a function of electrostatic potential and hydrophobic interactions.

It was the objective of the current study to prepare ethylene/propylene terpolymers with 2,6-dimethylphenyl 10-undecenoate (DMPU) to convert these terpolymers to the corresponding carboxylate salts and carboxylic acid derivatives, and to characterize the resulting terpolymer series.

EXPERIMENTAL

Materials

Purification of Solvents and Reagents

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

2,6-Dimethylphenyl 10-undecenoate (DMPU) was prepared as previously reported.

Toluene was washed successively with concentrated sulfuric acid, distilled water, 10% aqueous sodium carbonate solution, distilled water, and then dried over anhydrous calcium chloride. It was then distilled from phosphorus pentoxide; a center cut (bp 109°C) was taken and stored under nitrogen.

Ethylene (c.p. 99.5%) and propylene (c.p. 99.0%) were used as received from Matheson.

Diethylaluminum chloride (DEAC) was obtained from the Ethyl Corporation; vanadium oxytrichloride ($VOCl_3$) from Aldrich Chemical Company, and various grades (including 1.1) of titanium trichloride, aluminum activated ($TiCl_3$ AA) from the Stauffer Chemical Company.

Measurements

Infrared spectra were recorded on Perkin-Elmer Models 727 and 783 spectrophotometers. Solid samples were measured as films cast onto

NaCl plates from chloroform, toluene, or decahydronaphthalene (decalin) solutions.

The ^{13}C-NMR spectra were obtained on a Varian CFT-20 Fourier-transform spectrometer operating at 22.6 mHz. Sample concentrations were typically 20-40% (w/v) in $CDCl_3/C_6D_6$ or 1,2,4-trichlorobenzene/C_6D_6 (3/1 v/v); at least 20,000 transients were accumulated.

Inherent viscosities were measured at 135°C in decalin, using Ostwald-type viscometers. Solution concentrations were 0.5 g/dL; the reported values were the average of at least three measurements.

The glass transition temperatures (T_g) and melting temperatures (T_m) for polymer samples were determined on a Perkin-Elmer DSC-2 differential scanning calorimeter at a heating rate of 20°C/min.

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

Procedures

Terpolymerization of Ethylene, Propylene, and DMPU

Copolymerization of Ethylene and Propylene with $TiCl_3AA/AlEt_2Cl$ as Initiator. The initiator/polymerization tube was charged with $TiCl_3$AA 1.1 (0.2 g, 1.0 mmol), toluene (16 mL, 150 mmol), and DEAC (0.46 mL, 3.7 mmol). A monomer feed consisting of propylene and ethylene (9/1 v/v) was introduced into the polymerization tube by means of an 18-gauge syringe needle positioned below the level of the reaction mixture. A gentle flow was maintained for 70 min at room temperature. The reaction was mildly exothermic and polymer began to precipitate immediately. A white copolymer powder (1.54 g) was obtained; inherent viscosity (0.5% in decalin, 135°C), 2.91 dL/g. The infrared spectrum (thin film cast from decalin) showed absorptions at 2950, 2918, and 2845 cm^{-1} (C—H stretch, methyl methylene), 1460 cm^{-1} (C—H bend, methylene), 1373 cm^{-1} (C—H bend, methyl, and 1258, 796, 725, and 715 cm^{-1}. The ^{13}C NMR (1,2,4-trichlorobenzene/benzene-d_6, 3/1 v/v, 120°C) showed peaks at 21.74 ppm ($-\underline{C}H_3$), 28.97 ppm $-\!(CH_2\overset{|}{\underline{C}}H)\!-$, 29.92 ppm $-\!(\underline{C}H_2-CH_2)\!-$, and 46.57 ppm $-\!(\underline{C}H_2-CH)\!-$.

Terpolymerization of Ethylene, Propylene, and DMPU with $TiCl_3AA/AlEt_2Cl$ as the Initiator. The initiator/polymerization tube was charged with $TiCl_3$AA 1.1 (0.2 g, 1.0 mmol), toluene (5.92 mL, 55.7 mmol), and DEAC (0.46 mL, 3.7 mmol). The precomplexation tube was charged with toluene (10.0 mL, 94.1 mmol), DEAC (1.24 mL, 10.0 mmol), and DMPU (2.94 mL, 10.0 mmol). A monomer feed consisting of propylene and ethylene (9/1 v/v) was introduced into the polymerization mixture by means of an 18-gauge syringe needle for 30 s, followed by addition of the contents of the precomplexation tube. A gentle flow was maintained at a rate which ensured a slight positive pressure in the polymerization tube. Reaction conditions: 25°C, 70 min; yield: 2.64 g of a white, slightly tacky, tough, elastic solid after work-up by reprecipitation. Inherent viscosity (0.5% in decalin, 135°C), 2.34 dL/g. The infrared spectrum (thin film cast from decalin) showed absorptions at 2950, 2925, and 2850 cm^{-1} (C–H stretch), 1762 cm^{-1} (C=O stretch, ester), 1460 cm^{-1} (C–H bend, methylene), 1378 cm^{-1} (C–H bend, methyl), 1168 cm^{-1} (–C–C(=O)–O stretch), and 764 cm^{-1}. The ^{13}C-NMR spectrum (trichlorobenzene/benzene-d_6, 3/1, 120°C) showed peaks at 16.22 ppm ($-CO_2-C_6H_3(\underline{C}H_3)_2$), 19.88, 20.62, and 21.72 ppm ($(-\!(CH_2-\overset{|}{C}H)\!-\underline{C}H_3)$), 25.37 ppm ($-\underline{C}H_2-CH-CO_2-$), 28.93 ppm ($(-\!(CH_2-\underline{C}H(CH_3))\!-)$) 29.58 ppm ($(-\!(\underline{C}H_2)\!-_n)$), 29.89 ppm ($(-\!(\underline{C}H_2-CH_2)\!-)$), 34.14 ppm ($-\underline{C}H_2-CO_2-C_6H_3$-$(CH_3)_2$), and 46.54 ppm ($(-\!(\underline{C}H_2-CH(CH_3))\!-)$).

The relative composition of the terpolymer was approximately 6 mol% DMPU, 47 mol% propylene, and 47 mol% ethylene.

Analysis. Calculated for $-\!(C_2H_4)\!-_{0.47}-\!(C_3H_6)\!-_{0.47}-\!(C_{19}H_{28}O_2)\!-_{0.06}$: C, 83.22; H, 12.96%. Found: C, 83.28; H, 12.70%.

Copolymerization of Ethylene and Propylene with $VOCl_3/AlEt_2Cl$ as the Initiator. The polymerization tube was charged with toluene (16 mL, 150 mmol), $VOCl_3$ (0.094 mL, 1.0 mmol), and DEAC (0.5 mL, 4.0 mmol). The ethylene/propylene monomer feed was added as described above in 70 min at 25°C. Yield: 0.23 g of a white, rubbery polymer. The infrared spectrum (film cast from decalin) showed absorptions at 2960 cm^{-1} (C–H stretch, methyl), 2920 and 2842 cm^{-1} (C–H stretch, methylene), 1460 cm^{-1} (C–H bend, methylene), 1380 cm^{-1} (C–H bend, methyl), and 1155 and 970 cm^{-1}. The ^{13}C-NMR spectrum (trichlorobenzene, 80°C) showed peaks at 20.02, 20.74, and 20.85 ppm ($-\underline{C}H_3$), 28.23 ppm $-\!(\underline{C}H_2-CH(CH_3))\!-$, 28.54 ppm $-\!(\underline{C}H_2-CH_2)\!-$, and 46.28 ppm ($-\!(\underline{C}H_2-CH(CH_3))\!-$).

Terpolymerization of Ethylene, Propylene, and DMPU with $VOCl_3/AlEt_2Cl$ as Initiator. The initiator/polymerization tube was charged with toluene (8.0 mL, 75 mmol), $VOCl_3$ (0.094 mL, 1.0 mmol), and DEAC (0.5 mL, 4.0 mmol). The precomplexation tube was charged with toluene (8.0

mL, 75 mmol), DEAC (1.24 mL, 10.0 mmol), and DMPU (2.94 mL, 10.0 mmol). A monomer feed consisting of propylene and ethylene (10/1 v/v) was introduced into the polymerization tube. Monomer gas flow was maintained for 60 min at 25°C, and for 80 min at a reaction temperature gradually increasing from 30 to 60°C. After work-up by reprecipitation, a yield of 0.08 g of a white, rubbery polymer was obtained. The infrared spectrum (film cast from decalin) showed absorptions at 2940, 2915, and 2840 cm^{-1} (C–H stretch), 1758 cm^{-1} (C=O stretch, aromatic ester), 1455 cm^{-1} (C–H bend, methylene), 1372 cm^{-1} (C–H bend, methyl), and 1165 cm^{-1} (C–C(=O)–O stretch).

Saponification of Poly(Ethylene-*co*-Propylene-*co*-2,6-Dimethylphenyl 10-Undecenoate)

A mixture of poly(ethylene-*co*-propylene-*co*-2,6-dimethyl 10-undecenoate) (0.48 g) and 1.4-dioxane (25 mL) was allowed to stir under nitrogen at room temperature for several hours and for 60 min at 85°C, after which a 4 *N* aqueous sodium hydroxide solution (0.2 g, 5 mmol sodium hydroxide in 0.7 mL distilled water) was added. The slurry was heated at 85°C for 3 h, allowed to cool, and filtered through a sintered glass funnel. The solid was washed with an ether/methanol solution (4/1, 200 mL), transferred to a beaker, and allowed to stir for one day in fresh ether/methanol. A tan powder was isolated by filtration and dried at 0.01 torr/100°C for 2 days. Yield: 0.40 g (84%). The infrared spectrum (KBr) showed absorptions at 2910 and 2850 cm^{-1} (C–H stretch), 1565 and 1420 cm^{-1} (CO_2 stretch, carboxylate anion), and 1460 and 1376 cm^{-1} (C–H bend).

Analysis. Calculated for $\text{-(}C_2H_4\text{)-}_{0.47}\text{-(}C_3H_6\text{)-}_{0.47}\text{-(}C_{11}H_{19}O_2Na\cdot H_2O\text{)-}_{0.06}$: C, 77.88; H, 12.94; Na, 2.97%. Found: C, 77.08; H, 13.08; Na, 3.01%.

Preparation of Poly(Ethylene-co-Propylene-co-10-Undecenoic Acid). A 3-neck, 100-mL round-bottomed flask equipped with magnetic stirrer, septum stoppers, and nitrogen inlet and exit needles, connected to an oil bubbler, was charged with poly(ethylene-*co*-propylene-*co*-10-undecenoic acid sodium salt) (0.5 g), 1,4-dioxane (50 mL), distilled water (21.0 mL), and glacial acetic acid (6.0 mL). This mixture was allowed to stir for 1 day at 25°C. The polymer suspension was then filtered, the solid resuspended and stirred in distilled water for 2 h, and again isolated and dried for 2 days at 100°C and 0.01 mm over phosphorus pentoxide. The yield was 0.4 g (82%) of a white, rubbery polymer. The infrared spectrum (film cast from decalin) showed absorptions at 3400-2500 cm^{-1} (–OH stretch, carboxylic acid), 2955, 2920, and

2855 cm^{-1} (C–H stretch), 1715 cm^{-1} (C–H stretch), 1715 cm^{-1} (C=O stretch, carboxylic acid), and 1465 and 1380 cm^{-1} (C–H bend).

Analysis. Calculated for $\text{-(}C_2H_4\text{)-}_{0.47}\text{-(}C_3H_6\text{)-}_{0.47}\text{-(}C_{11}H_{20}O_2\text{)-}_{0.06}$: C, 82.13; H, 13.51%. Found: C, 82.05; H, 14.08; Na < 0.1%.

RESULTS AND DISCUSSION

Terpolymerizations of DMPU with ethylene and propylene were carried out with titanium- and vanadium-based initiator systems. Copolymers of ethylene and propylene were prepared under the same conditions to provide a reference. With $TiCl_3AA/AlEt_2Cl$ as the initiator and toluene as the solvent, a slightly higher yield was consistently obtained than with *n*-heptane as the solvent (Table 1); infrared analysis indicated higher propylene incorporation. The copolymers were white and rubbery with inherent viscosities of approximately 2.9 dL/g. The infrared spectra absorptions at 725 and 715 cm^{-1} were indicative of polyethylene crystallinity.

The copolymerizations of ethylene and propylene with $VOCl_3/AlEt_2Cl$ as the initiator were carried out with Al/V mole ratios of 4.0 and 14.0 with a propylene/ethylene volume feed ratio of 10:1, the reverse of the approximate relative copolymerization parameters. The yield of copolymer was relatively low compared with polymers obtained with $TiCl_3AA/AlEt_2Cl$ as the initiating system. Infrared analysis of the rubbery products indicated the presence of both propylene and ethylene, but the absence of the crystalline absorption band at 725 cm^{-1}. DSC analysis indicated that the copolymer was essentially amorphous.

The terpolymerizations of DMPU, propylene, and ethylene with $TiCl_3AA/AlEt_2Cl$ (Table 1) were carried out in toluene and *n*-heptane as the solvent. Infrared analysis indicated that the relative proportions of DMPU, propylene, and ethylene in the terpolymer were very similar in the two samples. Approximately 6 mol% DMPU was incorporated in the tough, elastic terpolymer which had an inherent viscosity of 2.3 dL/g. The mole ratios of ethylene and propylene were estimated on the basis of the relative size of the crystalline melting transitions obtained by DSC analysis.

Terpolymerization of DMPU, propylene, and ethylene with $VOCl_3/AlEt_2Cl$ gave a rubbery terpolymer in low yield; infrared analysis revealed an ethylene/propylene mole ratio comparable to that obtained with titanium-based initiators, but a higher incorporation of DMPU, as evidenced by a stronger absorption band at 1758 cm^{-1} (C=O stretch, aromatic ester). The terpolymer was amorphous according to DSC analysis.

TABLE 1. Terpolymerization of Ethylene, Propylene, and 2,6-Dimethylphenyl 10-Undecenoate[a]

Experiment	DMPU		Solvent[b]	Mole ratio Al/Ti/DMPU	Polymer yield, g	Comonomer[c] units, mol%	η_{inh}, dL/g
	%	mmol					
1	0.0	0.0	Toluene	3.7/1.0/0.0	1.5	—	2.91
2	0.0	0.0	*n*-Heptane	3.7/1.0/0.0	1.2	—	
3	2.9	10.0	Toluene	3.7 + 10/1.0/10.0	2.6	6	2.34
4	2.9	10.0	*n*-Heptane	3.7 + 10/1.0/10.0	2.4	6	

[a] Reaction conditions: 25°C/70 min; Ti = $TiCl_3$ aluminum activated 1.1; AlR_3 = $AlEt_2Cl$; 90/10 v/v propylene/ethylene feed.

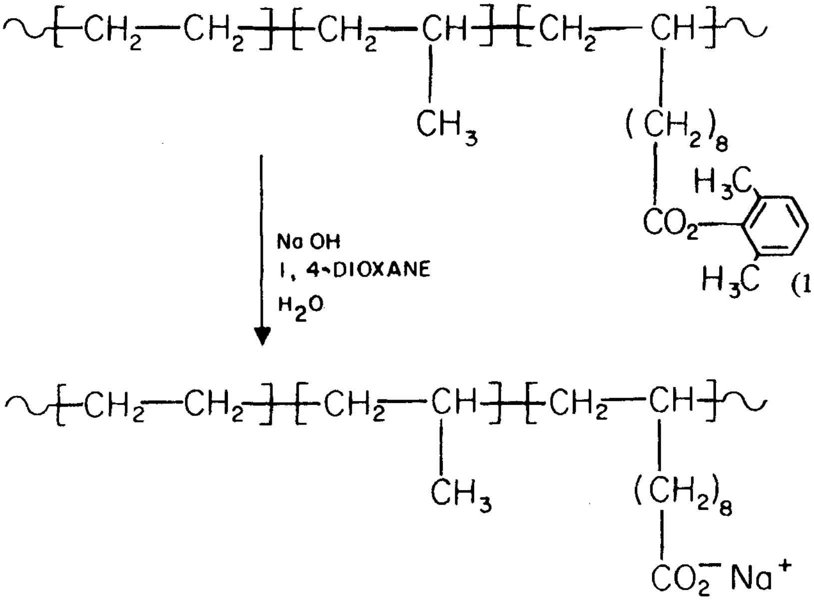
[b] 20 mL.

[c] Determined by elemental analysis.

Neither type of terpolymer of DMPU, propylene, and ethylene (initiated with titanium or initiated with vanadium initiating systems) has been fractionated. As a consequence, the polymers isolated from the polymerization reaction are probably not pure in the sense that each polymer chain does not contain all termonomers in the proportions that are evident from the termonomer feed. It cannot be excluded that certain amounts of ethylene/propylene copolymer, free of a terpolymer including DMPU units, are also present in the polymer obtained from the polymerization. It was not the objective of this work to demonstrate that the polymers obtained in this terpolymerization reaction are completely homogeneous, but rather that DMPU units could be incorporated into ethylene/propylene copolymers by coordination polymerization.

The terpolymer, poly(ethylene-*co*-propylene-*co*-2,6-dimethylphenyl 10-undecenoate), prepared with $TiCl_3 AA/AlEt_2Cl$ in toluene, with approximately 6 mol% of the DMPU unit in the polymer, was hydrolyzed under alkaline conditions to the sodium carboxylate salt, followed by acidification to liberate the polymeric carboxylic acid.

The ethylene/propylene/DMPU terpolymer was not soluble in 1,4-dioxane, but formed a suspension after stirring for 1 h at 85°C. This slurry was treated with 4 *N* aqueous sodium hydroxide, stirred at 85°C for 3 h, and the product isolated by filtration (Eq. 1).



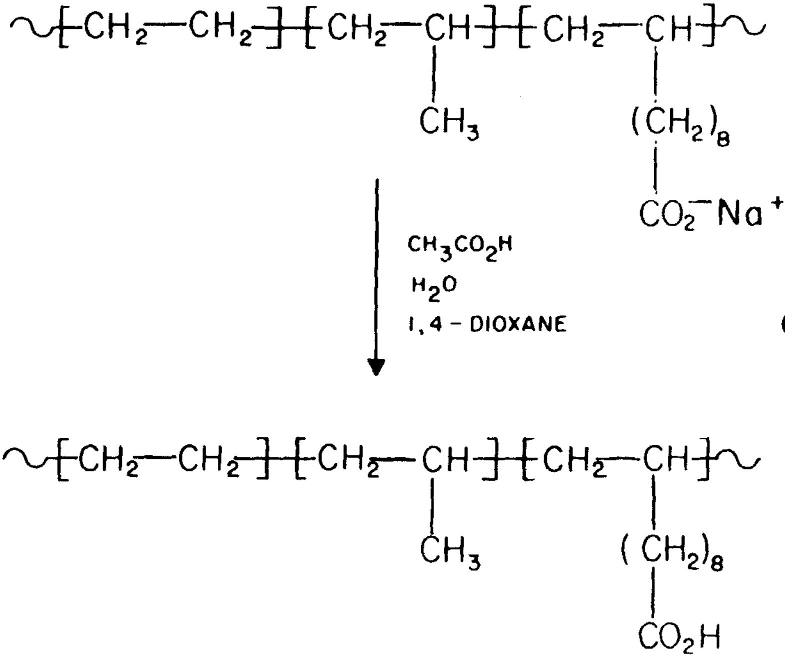
(1)

The washing procedure for this polymer is most critical; stirring the polymer in ether/methanol (4/1) and drying gave 84% of a light-tan powder.

The hydrolysis of the DMPU/propylene/ethylene terpolymers to the sodium salt and the additional treatment in the work-up seems to guarantee that the ionomer, obtained from the terpolymer with the functional DMPU units in the polymer and the polymeric acid, derived from the ionomer by neutralization with acetic acid is essentially free from any possible ethylene/propylene copolymers.

The infrared spectrum showed the typical 1565 cm^{-1} (C=O stretch) band of the carboxylate salt group (Fig. 1). The E/P/DMPU terpolymer was soluble in hot decalin, while the terpolymer salt $\mathrm{E/P/U^{-}Na^{+}}$ was not, confirming incorporation of the DMPU into the polyolefin. Infrared and elemental analysis of this sodium carboxylate-containing terpolymer indicated the presence of bound water, not removable by conventional drying techniques.

Poly(ethylene-*co*-propylene-*co*-10-undecenoic acid), a white, rubbery solid, was easily isolated in 82% yield by treating the terpolymer salt with acetic acid in a 1,4-dioxane/water solution (Eq. 2).



(2)

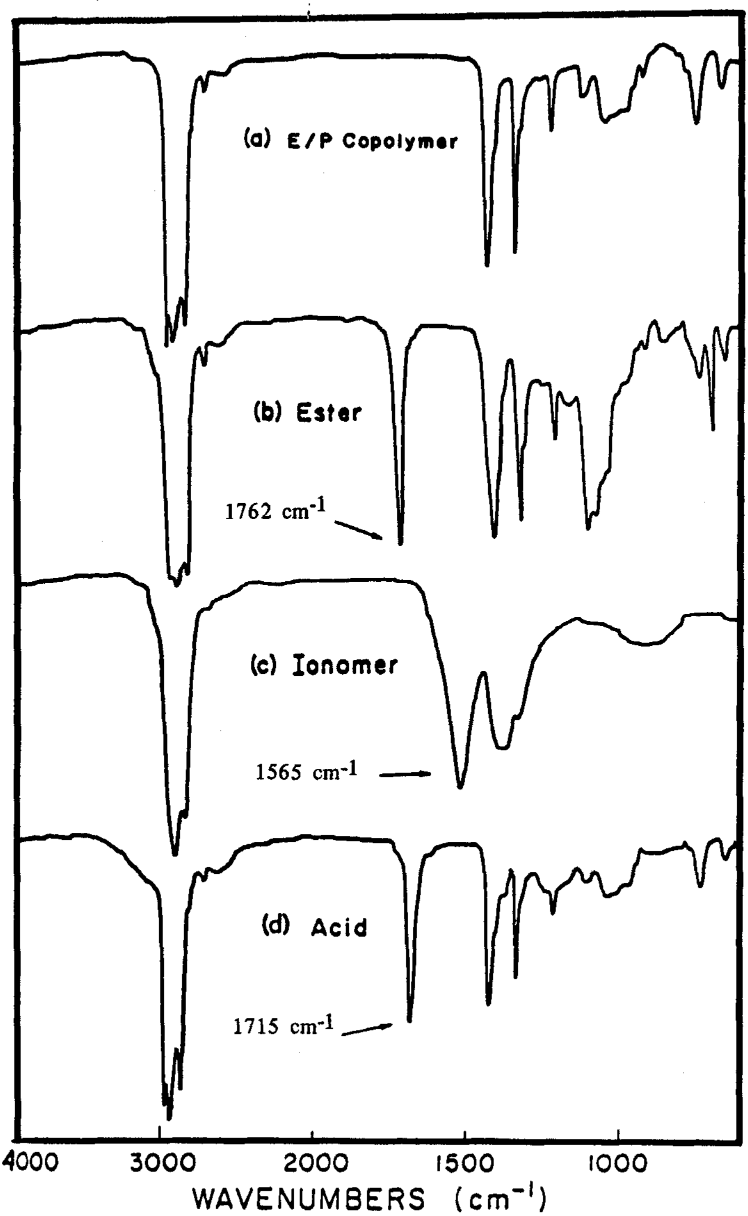


FIG. 1. Comparison of infrared spectra of functionally substituted polyolefin terpolymer: (a) poly(ethylene-*co*-propylene), (b) poly(ethylene-*co*-propylene-*co*-DMPU), (c) poly(ethylene-*co*-propylene-*co*-10-undecenoic acid sodium salt), and (d) poly(ethylene-*co*-propylene-*co*-10-undecenoic acid).

TABLE 2. Thermal Transition Temperatures[a]

Polymer	Transition metal derivative	R	T_g, °C[b]	T_g, °C[c]	T_m, °C
E/P	$TiCl_3$AA 1.1	–	-55	-30	122, 152
E/P	$VOCl_3$	–	-26	-22	–
E/P/DMPU	$TiCl_3$AA 1.1	$-C_6H_3(CH_3)_2$	-43	-33	101,[d] 123, 146
E/P/DMPU	$VOCl_3$	$-C_6H_3(CH_3)_2$	-31	-26	–
E/P/UA^-Na^+	$TiCl_3$AA 1.1	Na〉	-51	-11	120, 131, 252
E/P/UA	$TiCl_3$AA 1.1	H	-51	-1	122, 141

[a] Determined by DSC, heating rate 20°C/min, Run 2 of 3.

[b] Transition onset.

[c] Transition midpoint.

[d] Observed in initial scan only.

Infrared analysis indicated total conversion to the polycarboxylic acid, as demonstrated by a shift in the carbonyl absorption from 1565 cm^{-1} (C=O stretch, carboxylate salt) to 1715 cm^{-1} (C=O stretch, carboxylic acid). Poly(ethylene-*co*-propylene-*co*-2,6-dimethylphenyl 10-undecenoate), poly(ethylene-*co*-propylene-*co*-undecenoic acid sodium salt), and poly(ethylene-*co*-propylene-*co*-10-undecenoic acid) were characterized by IR analysis, as shown in Fig. 1.

The results of the DSC analysis for the members of this co- and terpolymer series are shown in Table 2 and Figs. 2 and 3. The reference copolymer prepared using the $TiCl_3AA/AlEt_2Cl$ initiator system exhibited a broad glass transition at -30°C (transition midpoint) and melting transitions at 122 and 152°C, compared to the literature values of 138 and 175°C for linear polyethylene and isotactic polypropylene, respectively [26]. These results indicate that our copolymer of ethylene and propylene is not a random copolymer, but, rather, contains crystalline blocks of polyethylene and polypropyl-

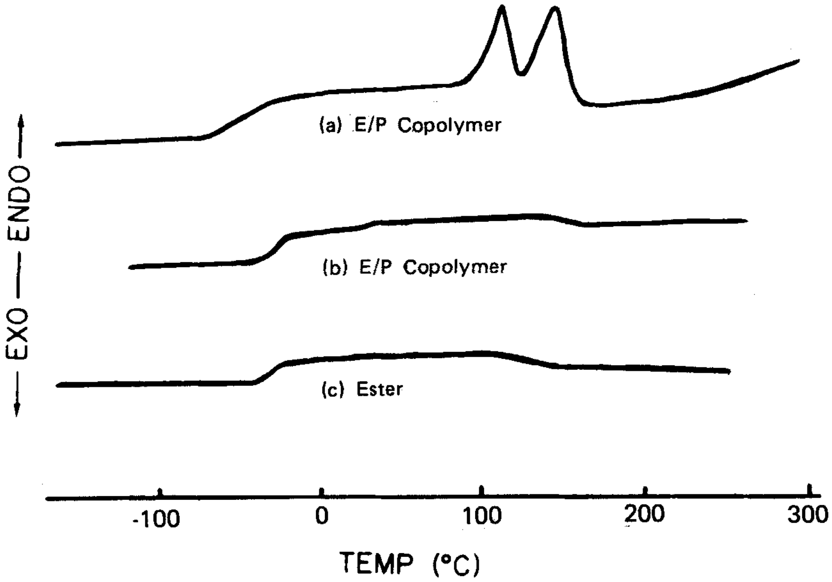


FIG. 2. DCS scans of (a) poly(ethylene-*co*-propylene) via $TiCl_3AA/AlEt_2Cl$, (b) poly(ethylene-*co*-propylene) via $VOCl_3/AlEt_2Cl$, and (c) poly(ethylene-*co*-propylene-*co*-2,6-dimethylphenyl 10-undecenoate) via $VOCl_3/AlEt_2Cl$.

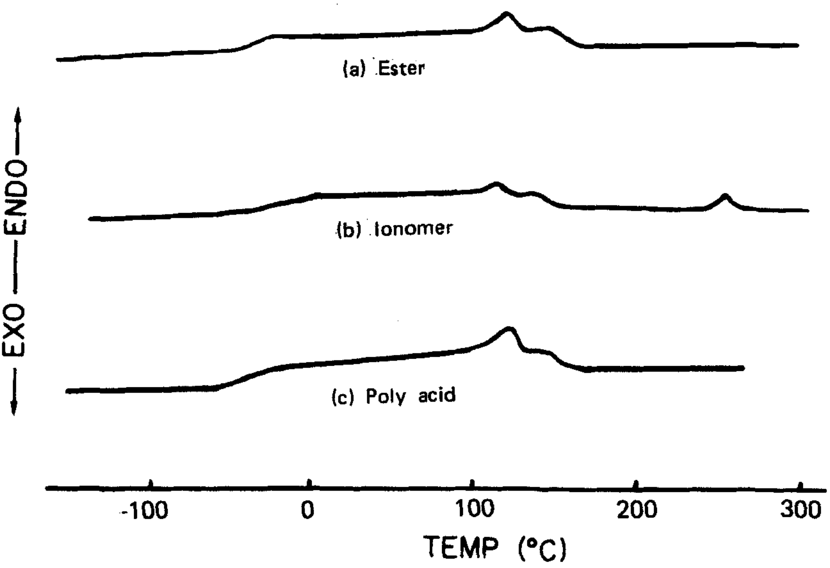


FIG. 3. DSC scans of (a) poly(ethylene-*co*-propylene-*co*-DMPU), (b) poly(ethylene-*co*-propylene-*co*-10-undecenoic acid sodium salt), and (c) poly(ethylene-*co*-propylene-*co*-10-undecenoic acid).

ene, as may be expected of a copolymer prepared with titanium-based initiators [9]. The terpolymer poly(E/P/DMPU) prepared with $TiCl_3AA/AlEt_2Cl$ showed a glass transition at -35°C and melting transitions at 101, 123, and 146°C. The position and character of these transitions suggest that incorporation of the ester-substituted monomer has partially inhibited the formation and crystallization of blocky domains.

The terpolymer salt, poly($E/P/UA^-Na^+$), exhibited a broad and higher glass transition, had lower crystallinity, and, most importantly, showed a high melting transition at 252°C, which had also been observed in the DMPU homopolymer sodium salt [27]. Upon cooling the terpolymer salt at 20°C/min, a crystallization exotherm at 244°C was observed. The results obtained to date indicate that this melting transition corresponds to the thermal disruption of the ionic aggregates.

The terpolymer acid, poly(E/P/UA), showed a glass transition similar to that of the salt as well as melting transitions at 122 and 141°C. There is some crystallinity due to polyethylene and polypropylene blocks in the copolymer

TABLE 3. Wide-Angle X-Ray

Polymer	Functionality	Angular position of peak (in degrees 2θ)	Spacings, Å
Poly (E/P/UA$^-$Na$^+$)	6 mol% sodium carboxylate	6.6, 14.0,* 16.9, 18.4, 21.4,* 23.7, 34.3	13.5, 6.3, 5.3, 4. 4.2, 3.8, 2.6

*Denotes major peaks in WAXD scan.

and all three terpolymers, with the relative degree of crystallinity appearing to decrease in the order: poly(E/P) > poly(E/P/DMPU) = poly(E/P/UA) > poly(E/P/UA$^-$Na$^+$).

The ethylene-propylene copolymer and the DMPU terpolymer prepared with $VOCl_3/AlEt_2Cl$ initiator systems showed sharp glass transitions at -22 and -26°C, respectively. In addition, both polymers exhibited only extremely weak melting transitions in the region from 117 to 142°C, indicating very low crystallinity, such as would be expected from a more random co- or terpolymer prepared with a vanadium-based initiator system (Fig. 2).

The scattering maxima and corresponding spacings obtained for the terpolymer salt poly(ethylene-*co*-propylene-*co*-10-undecenoic acid sodium salt) prepared with $TiCl_3/AA$ initiators are recorded in Table 3. Note the existence of the ionic peak at $2\theta = 6.6°$ which correlates to a domain spacing of 13 Å, which is in good agreement with that observed by Bansleben [28] for poly(alkylene oxide) ionomers with an identical spaces chain length of eight ethylene units and sodium carboxylate incorporation. The spacings at 2.6, 3.8, and 4.2 Å and at 4.8, 5.3, and 6.3 Å are assigned to crystallinity from polyethylene and polypropylene blocks, respectively. In the case of this terpolymer carboxylate salt, a core-shell ionic domain structure in concert with considerable main-chain crystallinity appears to be a reasonable model.

ACKNOWLEDGMENTS

This work was supported by Grant No. DMR-80-17050 from the National Science Foundation and from the Materials Research Laboratory of the University of Massachusetts. This paper is part of the PhD dissertation of Mark D. Purgett, University of Massachusetts, Amherst. We wish to thank Mrs Elizabeth Cary and Miss Liping Hu for their assistance in the preparation of this manuscript.

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Received January 13, 1987
Revision received May 26, 1987