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Carboxylation of a Polypentenamer and Preparation of Its Hydrogenated Derivatives

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Synopsis

Carboxylated three-membered ring derivatives of a polypentenamer (PP) that contained 82% trans and 17% cis double bonds were prepared by carbene addition of ethyldiazoacetate with a copper catalyst to the double bonds and subsequent hydrogenation of the residual unsaturation. In this way derivatives that contained approximately either 5 or 10 mole % three-membered rings with ester side groups were obtained. These side groups were further reacted by hydrolysis or neutralization to form carboxylic acid and cesium salts of carboxylic acid. Reaction conditions were chosen so that no backbone degradation occurred and side reactions that led to crosslinking were avoided. The derivatives were characterized by gel permeation chromatography (GPC), thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC), infrared (IR) spectroscopy, and nuclear magnetic resonance (NMR) spectroscopy. It was found that an increase in substituent concentration decreased the melting point (T_m) in hydrogenated derivatives and increased the glass transition temperature (T_g) in unhydrogenated derivatives. The cesium salts of carboxylic acid were the least thermally stable among those studied and the hydrogenated derivatives were generally more stable than the unhydrogenated.

INTRODUCTION

We have already reported the chemical modification of a polypentenamer by hydrogenation,¹ addition of thioglycolate side groups,² hydroformylation,³ and phosphonylation.⁴ The purpose of these studies was the preparation of derivatives that contained side groups of differing chemical nature and concentration but with identical chain backbones. Thus it was necessary to carry out the reaction under conditions that prevent backbone modification by scission or crosslinking. This restriction drastically limits the number of possibilities. In addition to those mentioned above, we were able to carry out a carbene addition by reacting ethyldiazoacetate with the polypentenamer which resulted in the carbene addition of CHCOOEt to the double bonds. The residual double bonds in the polypentenamer can be subsequently hydrogenated, as in other derivatives, to yield a crystalline backbone. It is difficult to obtain polymers with carboxyl side groups by modifying polybutadiene or other unsaturated polymers. Therefore most of these polymers have been prepared by copolymerization of vinyl compounds and acrylic derivatives. Lishanskii recently reported the carbene addition of ethyldiazoacetate to polybutadiene or other polymers with double bonds.⁵ *Cis*-polybutadiene and *cis*-isoprene may be

Addition of EDA to PP

A 16-g portion of PP was dissolved in 1600 ml of *p*-xylene that contained 0.8 g of copper powder in a 2-liter, three-necked, round-bottomed flask fitted with a condenser, a thermometer, and a nitrogen gas inlet. A 36-g portion of ethyldiazoacetate (EDA) was added to the solution at a ratio of 5 ml/10 min at 127–130°C. After this addition the reaction mixture was kept under refluxing conditions with stirring in a nitrogen atmosphere for a given period. After reaction the derivatives were recovered by pouring the solution into a 10-volume excess of methanol.

The derivative (PP ∇ COOEt) was purified by reprecipitation, dried at room temperature *in vacuo* for 48 hr, and stored under dry nitrogen with refrigeration.

Hydrogenation of (PP ∇ COOEt) with TSH

A 25-g portion of TSH was added to 4.2 g of PP ∇ COOEt in 350 ml of monochlorobenzene under nitrogen. The resulting mixture was heated with stirring at 135°C for 3 hr. The hydrogenated polymer was isolated by precipitation from methanol, and the polymer was purified by reprecipitation from *p*-xylene into methanol.

Hydrolysis of Ester Groups in PP ∇ COOEt and Hydrogenated PP ∇ COOEt (Hy-PP ∇ COOEt) to Prepare Carboxylic Acid Substituted PP(PP ∇ COOH) and Carboxylic Acid Substituted HY-PP(Hy-PP ∇ COOH)

The hydrolysis of PP ∇ COOEt and Hy-PP ∇ COOEt was carried out with sodium ethoxide in *p*-xylene and a small amount of water. A typical hydrolysis procedure was as follows: 1 g of PP ∇ COOEt, which contained almost 5 mole % of combined carboalkoxy groups was dissolved in 250 ml of *p*-xylene under nitrogen; 50 ml of ethanol which contained 1.5 g of sodium ethoxide and 1.5 ml of water was added to this polymer solution under refluxing conditions for 15 min, after which the reaction mixture was refluxed with stirring at 88°C. After 3 hr the mixture was neutralized with 15 ml of concentrated hydrochloric acid under refluxing conditions and stirred for 10 min. The resulting polymer was isolated by precipitation from methanol and purified by reprecipitation from *p*-xylene into methanol. The degree of hydrolysis was determined by infrared (IR)⁻ and elemental analysis.

Preparation of the Cesium Salts of PP ∇ COOH, Hy-PP ∇ COOH (PP ∇ COOCs), and (Hy-PP ∇ COOCs)

Cesium salts were prepared from PP ∇ COOH and Hy-PP ∇ COOH by reaction with cesium hydroxide-ethanol solution.

A 0.45-g portion of PP ∇ COOH was dissolved in 130 ml of *p*-xylene to which cesium hydroxide-ethanol solution (2 g in 25 ml of ethanol) that contained 0.2 ml of water was added with stirring under refluxing conditions in nitrogen. After 2 hr the reaction mixture was poured into a large amount of ethyl ether and the crude polymer was washed with methanol, water, methanol, and ethyl ether, in

that order. The resulting polymer was dried *in vacuo* at room temperature for 2 days.

The preparation of cesium salts of the hydrogenated polymers (Hy-PP ∇ COOCs) was carried out by the above-mentioned method for the synthesis of PP ∇ COOCs. The polymer salts were dried *in vacuo* at 60°C for 2 days.

Preparation of Hy-PP with Double Bonds in the Polymer Backbones

Some polymers were prepared in which the hydrogenation was not allowed to go to completion. The methods discussed for the preparation of Hy-PP ∇ COOEt were used and the residual unsaturation was quantitatively assessed by IR analysis.

Preparation of Hydrobrominated, Hydrogenated Polypentenamer (Hy-PP-H-Br)

A 0.02*M* solution of polypentenamer was prepared in dry toluene to which was added a solution of HBr in toluene. The reaction was allowed to proceed at room temperature and the degree of substitution was controlled by the concentration of the HBr solution. The bromide content of the polymer was determined by proton NMR and elemental analysis. Hydrogenation of these brominated derivatives was carried out with TSH in *p*-xylene according to the procedures described above. A summary of the reaction conditions is presented in Table I(b).

TABLE I

(a) Preparation of PP ∇ COOEt							
PP	Substrate (g)	Solvent ^a (ml)	Initiator (g)		Condition		Adduct ^b combined ∇ COOEt (mole %)
	N ₂ CH ₂ COOEt				Temperature (°C)	Time (hr)	
4.1	2.3	80 ^(c)	Cu	0.1	125	24	1
10.0	20.0	1000	Cu	0.5	125	24	3.8
10.0	40.0	1000	Cu	0.5	125	24	9.8
4.1	20.0	100	CuBrP(OEt) ₃		55	3	...
16.0	36.0	1600	Cu	0.8	128	6	4.0
15.0	32.0	1500	Cu	0.8	128	6	4.5
(b) Preparation of PP-H-Br							
Substrate PP (moles)	HBr, ratio to PP (mole %)				Condition		Combined Br (mole %)
					Temperature (°C)	Time (hr)	
0.02	22			25		24	15
0.02	29			25		24	19
0.02	48			25		24	37
0.02	66			25		24	50
0.02	82			25		24	73
0.02	100			25		24	79

^a *p*-Xylene or monochlorobenzene as solvent.

^b Calculated by using a calibration curve drawn from the results of IR and NMR.

^c Half of the polymer was crosslinked during the reaction.

Characterization

The samples were characterized by elemental, IR, NMR, and GPC analysis.

Elemental Analysis

Elemental analyses of the samples were performed by the Microanalytical Laboratory, University of Massachusetts. The contents of carboxyl ester groups in the polymers were estimated from the results obtained.

Infrared Analysis

Film samples of the polymers for IR measurement were prepared by solvent casting on a NaCl or glass plate. IR analyses were carried out on a Perkin-Elmer grating IR spectrophotometer, model 283. The determinations of the carboxyl content and the residual double bonds in the polymer were made on the basis of the absorption band at 720 cm^{-1} (cis C=C) and 1350 cm^{-1} (trans C=C) or 1730 cm^{-1} (ester carbonyl), 1690 cm^{-1} (carboxylic acid carbonyl), and 1470 cm^{-1} (CH_2), and the crystallinity of the polymers was estimated from the ratio of the absorption bands at $730\text{ cm}^{-1}/720\text{ cm}^{-1}$, as with polyethylene.⁸

NMR Analysis

NMR measurements of the samples were carried out on a Perkin-Elmer model R-32 NMR spectrometer in carbon tetrachloride with TMS as the internal standard.

Gel Permeation Chromatography (GPC)

A Waters Associates GPC model 201 was used to determine the molecular weight distribution. The experimental conditions were as follows: solvents and temperature at room temperature in THF for the unsaturated polymers. Columns 10^5 , 10^4 , 10^3 , and $500\text{ \AA}$; sample concentration, 2 mg/ml; flow rate, 1 ml/min. The columns were calibrated with polystyrene standards of narrow molecular weight distributions.

Differential Scanning Calorimetry (DSC)

DSC measurements were carried out on a Perkin-Elmer instrument, model DSC-II. The scanning speed was $10^\circ\text{C}/\text{min}$ in all cases and cyclohexane and Indium were used as standards. The temperature range was -120 to ca. 150°C . The peak temperature of the melting endotherm was established as the melting point of the polymers.

Thermogravimetric Analysis (TGA)

TGA measurements were carried out in a nitrogen stream on a Perkin-Elmer instrument, TGA-1, thermobalance at a scanning speed of $20^\circ\text{C}/\text{min}$ in all cases.

RESULTS AND DISCUSSION

Esters, acids, and salt of the carbene addition derivatives of saturated or unsaturated backbones were prepared by the synthetic routes summarized in eqs. (2)–(4):

In what follows we discuss each reaction step separately.

Addition of EDA to PP

The reaction of ethyldiazoacetate (EDA) with an olefin under mild conditions results in the carbene addition of ethyldiazoacetate to the double bond.^{6,7} The carbene addition of EDA to PP represented in step A was carried out under various conditions described in Table I, which reveals that by careful control of concentration, temperature, and reaction time it is possible to control the concentration of combined EDA in amounts ranging from approximately 1 to 10 mole %. To prevent gelation it is necessary to use a dilute solution and to keep the temperature below 130°C during the addition of EDA. The concentration of polypentenamer in solution must be kept below 1% to avoid crosslinking.

The GPC measurements reveal no significant differences in the molecular weights and distributions for the PPVCOOR derivatives compared with the starting PP.

Hydrolysis of Ethyl Ester in PPVCOOEt and Hy-PPVCOOEt

The hydrolysis of most esters of polyacrylic acid derivatives can be carried out with sodium hydroxide at high temperatures. In this case the hydrolysis of PPVCOOEt and Hy-PPVCOOEt was accomplished with sodium ethoxide which can be dissolved instantly in ethylalcohol. The various reaction conditions in-

vestigated are summarized in Table II. It was found that the hydrolysis of the ester compound with sodium ethoxide is complete after 2–3 hr.

Preparation of Salts of PPVCOOH and Hy-PPVCOOH

Cesium salts of the derivatives were found to be readily prepared by using ethanolic cesium hydroxide in *p*-xylene. The conditions are summarized in Table III. In general it was possible to neutralize the derivatives completely or nearly so.

NMR and IR Characterization

Figure 1 shows the NMR spectrum of the 10% ethyl ester derivative. Four resonances are discernible in this spectrum. The methylene proton signal of the ethyl ester ($\text{COOCH}_2\text{CH}_3$) is well resolved in the vicinity of $\delta = 4.1$.

The IR spectra of the ester, acid, and cesium salt derivatives of the PPVCOOR series are collected in Figure 2, whereas those for the corresponding hydrogenated derivatives are shown in Figure 3. It was found that a good correlation exists between the ratio of the peak intensity of 720 cm^{-1} (cis double bond) to the 1350

TABLE II
Hydrolysis of Pendant PPVCOOEt and Hy-PPVCOOEt

Sample	Reagent		Solvent			Temperature (°C)	Time (hr)	Degree of hydrolysis	
	(g)	Na (g)	<i>p</i> -Xylene	EtOH	Water			IR ^a	Elemental ^b
PPVCOOEt(5)	1	1	250	50	1.5	88	5	100	
PPVCOOEt(5)	1.5	1.5	320	50	2	90	3	100	
PPVCOOEt(10)	1	1	250	50	1.5	88	3	98	
PPVCOOEt(10)	1.5	1.5	300	50	2	88	3	100	
Hy-PPVCOOEt(5)	1	1	250	50	1.5	88	3	90	100
Hy-PPVCOOEt(5)	10	5	1250	250	8	91	3	98	
Hy-PPVCOOEt(10)	1	1	250	50	1.5	88	3	84	100
Hy-PPVCOOEt(10)	10	5.5	1350	100	8	92	2	98	

^a Calculated from IR analysis ($D = 1690\text{ cm}^{-1}/D = 1470\text{ cm}^{-1}$ to $D = 1732\text{ cm}^{-1}/D = 1470\text{ cm}^{-1}$).

^b Calculated from elemental analysis.

TABLE III
Preparation of Cesium Salts of PPVCOOH and Hy-PPVCOOH

Acid combined COOEt (mole %)	Reagent					Temperature (°C)	Time (hr)	Cation content (%)	
	(g)	CsOH (g)	EtOH (ml)	Water (ml)	<i>p</i> -Xylene (ml)			IR ^a	Elemental ^b
PPVCOOH(5)	4.3	0.45	2	25	0.2	130	88	2	100
PPVCOOH(10)	9.8	0.50	2	25	0.2	130	88	2	74
Hy-PPVCOOH(5)	4.3	0.45	2	25	0.2	130	88	2	55
Hy-PPVCOOH(5)	4.2	10	40	350	20	1100	83	3	90
Hy-PPVCOOH(10)	9.8	0.40	2	25	0.2	130	88	2	82
Hy-PPVCOOH(10)	10.2	8.5	34	80	5	1100	83	3	94

^a Calculated from IR analysis ($D = 1730\text{ cm}^{-1}/D = 1720\text{ cm}^{-1}$).

^b Elemental analysis.

Fig. 1. NMR spectrum of PP ∇ COOEt(10), 5 wt % carbon tetrachloride solution.

Fig. 2. IR spectra of PP ∇ COOR derivatives.

cm^{-1} (trans double bond) band and the concentration of combined carboxyl groups. This correlation is illustrated in Figure 4. It is evident that the elemental analysis and NMR results agree quite well with the IR results. It may be noted also that a good correlation exists between the ratio of the peak intensity at 1730 cm^{-1} (ester carbonyl) to the 1470 cm^{-1} ($-\text{CH}_2-$) band and the combined three-membered ring with ester group substituents. It was found that cis double bonds are more reactive to free radical addition than trans double bonds in the thioglycolate² and phosphonylated derivatives⁴ and it is clear that this is also true for the EDA carbene addition reaction.

Fig. 3. IR spectra of Hy-PP ∇ COOR derivatives.

Fig. 4. Dependence of residual cis double-bond concentration on combined- ∇ COOR concentration in the PP ∇ COOR derivatives. (●) NMR, (○) D_{1730}/D_{1470} of Hy-PP ∇ COOEt by IR, (Δ) elemental analysis, (◐) D_{720}/D_{1350} of PP ∇ COOH by IR.

Properties

The properties of the PP ∇ COOR and Hy-PP ∇ COOR derivatives are summarized in Table IV. Increasing substituent concentration has the effect of increasing the T_g s of the PP ∇ COOR derivatives and decreasing the T_m s of the Hy-PP ∇ COOR derivatives. The type of substituent, whether ester, acid, or salt, has relatively little effect, however. These observations parallel those made earlier for the thioglycolate derivatives² (PP-S). The magnitudes of the effects

TABLE IV
 Properties of PP ∇ COOR and Hy-PP ∇ COOR Derivatives

Sample	Combined ∇ COOR ^a (mole %)	Ionization ^b (%)	T_g^c (°C)	T_m^c (°C)	Crystallization point ^c (°C)
PP	0		-98	11	
PP ∇ COOEt(5)	4.3		-93	12	-46
PP ∇ COOH(5)	4.3		-92	11	-41
PP ∇ COOCs(5)	4.3	100	-93	1	-43
PP ∇ COOEt(10)	9.8		-91		
PP ∇ COOH(10)	9.8		-83		
PP ∇ COOCs(10)	9.8	73.4			
Hy-PP	0			132	
Hy-PP ∇ COOEt(5)	4.3			119	
Hy-PP ∇ COOH(5)	4.3			121	
Hy-PP ∇ COOCs(5)	4.3	90		122	
Hy-PP ∇ COOEt(10)	9.8			103	
Hy-PP ∇ COOH(10)	9.8			107	
Hy-PP ∇ COOCs(10)	9.8	82		114	

^a Calculated from IR analysis.^b Percent ionization from IR analysis.^c Determined by DSC.

are approximately the same for the EDA derivatives as the PP-S derivatives. Figure 5 illustrates this point. The slope of the lines in Figure 5 which represent the dependence of T_g in the PP ∇ COOR series on pendant group concentration are 0.7, 1.5, and 1.1 deg (mole %)⁻¹ for PP ∇ COOEt, PP ∇ COOH, and PP ∇ COOCs, respectively, whereas that of the line that represents the dependence of the T_g of the PP-S series on pendant group concentration is 1.2 deg (mole %)⁻¹. For hydrogenated derivatives the slopes of the lines that represent the depen-

Fig. 5. Pendant group concentration dependencies of T_m and T_g for the PP ∇ COOR derivatives and the thioglycolate derivatives. (O) PP ∇ COOEt, Hy-PP ∇ COOEt; (Δ) PP ∇ COOH, Hy-PP ∇ COOH; ($\square$) PP ∇ COOCs, Hy-PP ∇ COOCs; (---) PP-S; (---) Hy-PP-S.

dence of T_m on pendant group concentration are -2.9 , -2.5 , and -1.8 deg (mole %) $^{-1}$ for Hy-PP ∇ COOEt, Hy-PP ∇ COOH, and Hy-PP ∇ COOCs, respectively, for the Hy-PP ∇ COOR series and -2.2 deg (mole %) $^{-1}$ for the Hy-PS series. The three-membered ring appears to "stiffen" the chain to a comparable extent in the thioglycolate group. This may be caused by the strain on the ring.

Figures 6 and 7 summarize the results of the TGA analysis for both series of derivatives. In the PP ∇ COOR series the thermal stabilities decrease in the following order: PP > PP ∇ COOEt(5) > PP ∇ COOH(10) $\geq$ PP ∇ COOH(5) $\geq$ PP ∇ COOEt(10) > PP ∇ COOCs(5). PP ∇ COOCs(10) is not directly comparable because of the crosslinking in this derivative. In general, the ester derivative has more stability than the acid and salt derivatives and the orders of stabilities are PP ∇ COOEt > PP ∇ COOH > PP ∇ COOCs.

In the Hy-PP ∇ COOR series the thermal stabilities decrease in the following order: Hy-PP ∇ COOCs(10) > Hy-PP ∇ COOH(5) $\geq$ Hy-PP ∇ COOCs(5) > Hy-PP ∇ COOEt(5) > Hy-PP ∇ COOH(10) > Hy-PP ∇ COOEt(10) > Hy-PP.

Fig. 6. TGA curves for the PP ∇ COOR derivatives. (1) PP, (2) PP ∇ COOEt(5), (3) PP ∇ COOH(5), (4) PP ∇ COOCs(5), (5) PP ∇ COOEt(10), (6) PP ∇ COOH(10), (7) PP ∇ COOCs(10).

Fig. 7. TGA curves for the Hy-PP ∇ COOR derivatives. (1) Hy-PP, (2) Hy-PP ∇ COOEt(5), (3) Hy-PP ∇ COOH(5), (4) Hy-PP ∇ COOCs(5), (5) Hy-PP ∇ COOEt(10), (6) Hy-PP ∇ COOH(10), (7) Hy-PP ∇ COOCs(10).

For the hydrogenated series the cesium salt derivative possesses more thermal stability than the acid or ester derivatives. The hydrogenated series polymers are generally more stable than the unsaturated, as might be expected. In fact, they are at least equal to the unsaturated hydrogenated derivatives (Hy-PP) in stability. This is definitely not the case for the hydrogenated thioglycolate derivatives, among which the Hy-PP polymer is the most stable of the series.² This behavior, however, is similar to that shown by the phosphonylated derivatives.⁴

The crystallinity of the hydrogenated derivatives is summarized in Table V. The crystallinities of these polymers were estimated by IR measurement by using the ratio of the absorption bands at $730\text{ cm}^{-1}/720\text{ cm}^{-1}$.

In general, the derivatives that contain smaller substituent concentrations are more crystalline than those that contain the greater substituent concentrations, as would be expected. Figure 8 summarizes the results of crystallinity of the hydrogenated derivative, Hy-PP (with various contents of double bonds in the polymer backbone), Hy-PP-HBr (the hydrogenated compounds of the hydrobrominated polypentenamer which contain double bonds), and Hy-PP ∇ COOEt. It would appear that the Hy-PP derivatives have greater crystallinities than the other derivatives, perhaps because of the presence of bulky side group substituents in the latter.

TABLE V
Crystallinity of Hy-PP ∇ COOR

Sample	Combined ∇ COOR ^a (mole %)	T_m^b (°C)	Weight fraction crystallinity ^c
Hy-PP ∇ COOEt	4.3	119	0.87
Hy-PP ∇ COOH(5)		121	0.85
Hy-PP ∇ COOCs(5)		122	0.89
Hy-PP ∇ COOEt(10)	9.8	103	0.72
Hy-PP ∇ COOH(10)		107	0.73
Hy-PP ∇ COOCs		114	0.54

^a Calculated from IR analysis.

^b Determined by DSC.

^c Calculated from IR analysis ($D = 730\text{ cm}^{-1}/D = 720\text{ cm}^{-1}$).

Fig. 8. Percent crystallinity versus substituent concentration in hydrogenated derivatives. (O) Hy-PP (residual trans double bond), (Δ) Hy-PP-HBr, ($\square$) Hy-PP ∇ COOEt.

In summary, methods have been developed to introduce carboxyl groups into polypentenamer, an unsaturated polymer, by carbene addition of ethyldiazoacetate. Reaction conditions are elucidated under which substituent concentrations of as much as 10 mole % may be obtained without backbone degradation or crosslinking. The polymers are readily hydrogenated with *p*-toluenesulfonyl hydrazine and such hydrogenated derivatives possess excellent thermal stability.

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