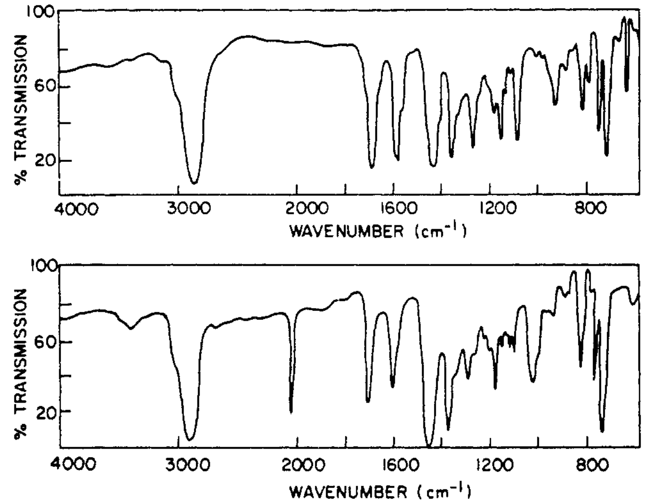

Figure 1. Ir spectrum of: (top) poly(2-vinylfluorenone) and (bottom) a copolymer of 2-vinylfluorenone:2-vinyl-9-diazofluorene.

groups in a polymeric environment leads to facile and efficient crosslinking and insolubilization. A control experiment with polystyrene containing 9-diazofluorene (2 mol % as in the test styrene copolymer) confirmed the efficiency of the crosslinking reactions.

Because of the thermal instability of the diazofluorene-containing polymers, the photocrosslinking reactions were not pursued in any detail and no sensitization experiments were made. Exposure of polymer films and polymer solutions to light of 3650 Å caused rapid insolubilization. The decrease in the intensity of the diazo band at 2060 cm^{-1} followed simple first-order kinetics and the quantum yield for carbene formation was estimated by conventional techniques to be in the range 0.6 to 0.9. Any attempt to define the mechanism of the reactions of the polymeric carbene (IV) would be highly speculative. Carbenes are known to undergo a wide range of abstraction, addition, coupling, and insertion reactions and most of these processes lead to free radical products, *e.g.*, $>\mathrm{C}: + \mathrm{RH} \rightarrow\ >\mathrm{CH}\cdot + \mathrm{R}\cdot$, which can participate in further abstraction, addition, and coupling reactions. Since each carbene, therefore, has the potential of generating more than one crosslink the overall photocrosslinking efficiency of such systems can be high.

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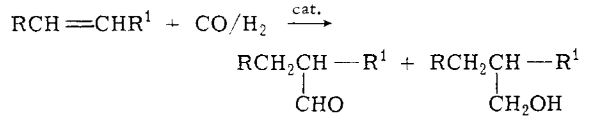
Communications to the Editor

Hydroformylation of a Polypentenamer and Preparation of Derivatives Therefrom

The oxo reaction for the conversion of olefins to aldehydes by the use of carbon monoxide and hydrogen, according to eq 1, has been known for a long time and is of considerable industrial importance in the manufacture of oxo alcohols.



$$\mathrm{RCH{=}CHR^1 + CO/H_2 \xrightarrow{cat.} RCH_2\underset{\displaystyle CHO}{CH}{-}R^1 + RCH_2\underset{\displaystyle CH_2OH}{CH}{-}R^1} \qquad (1)$$

However, the hydroformylation of unsaturated polymers by this technique has apparently been largely neglected.[1] The reasons for this are most likely because of the instability of the product, cross-linking occurring due to reactions of the aldehyde side groups, and probable main chain degradation during the course of the reaction. These difficulties stem in large measure from the fact that with the "traditional" catalyst, dicobalt octacarbonyl, it is necessary to employ high temperatures and pressures in order to obtain reasonable conversions in fairly short times. Thus, a typical set of conditions for the hydroformylation of polybutadiene are reported as a gas pressure of 2400 psi (H_2:CO = 1:1), a temperature of 145°, and a reaction time of 3 hr.[1]

More recently there has been considerable interest in rhodium complexes as hydroformylation catalysts. Many of the details of these reactions have been elucidated by Wilkinson and coworkers.[2-4] These rhodium complexes are effective under much milder conditions than the cobalt complexes. This report represents the first application of these complexes to the hydroformylation of olefinic polymers, in this case a polypentenamer. It has been possible to incorporate up to 20 mol % of formyl side groups into the starting polypentenamer without cross-linking or main chain degradation, using the rhodium catalyst. In addition, it has been possible to convert the formyl side groups of the modified polypentenamer to the aldoxime and thence to the nitrile derivatives. Also hydrogenation has been carried out to convert the amorphous, unsaturated nitrile derivative to the crystalline, saturated polymer. The reaction sequence may be schematically represented as follows

$$\mathrm{PP \xrightarrow[RhH(CO)(PPh_3)_3]{CO/H_2} PP{-}CHO \xrightarrow[pyridine]{HONH_2HCl}}$$
$$\mathrm{PP{-}CH{=}N{-}OH \xrightarrow[or\ P_2O_5]{Ac_2O} PP{-}CN \xrightarrow[TSH]{TPBSH} Hy{-}PP{-}CN} \qquad (2)$$

where PP = starting polypentenamer, PP–CHO = polypentenamer derivative with formyl side groups, PP—CH=NOH = polypentenamer derivative with aldoxime side groups, PP–CN = polypentenamer derivative with nitrile side groups, TPBSH = 2,4,6-triisopropylbenzenesulfonyl hydrazide, TSH = *p*-toluenesulfonyl hydrazide, Hy–PP–CN = hydrogenated polypentenamer derivative with nitrile side groups.

Direct oxidation of the formyl group and hydrolysis of the nitrile group to the carboxylic acid has also been carried out and will be reported subsequently.[5]

Table I
Hydroformylation of PP[a]

H_2/CO	Total pressure, psi	Temp, °C	Time, hr	Aldehyde content,[b] mol %
1	40	25	1	1
1	80	30	1	3
1	100	40	4	8
1	200	40	3	7.4
1	400	40	8	20
2	300	40	3	12.5
2	300	40	12	50

[a] Concentration of PP: 13.6 g/l.; solvent, toluene; catalyst, $RhH(CO)(PPh_3)_3$ = 1 mol %. [b] Estimated from the results of the nitrogen analysis of the corresponding aldoxime derivatives.

Experimental Section

(1) Materials. (a) Polypentenamer (PP). This polymer was kindly provided by the Goodyear Tire and Rubber Company and is identical with the polymer used in our previous studies.[6,7] It consists of 82% trans and 17% cis double bonds with less than 1% vinyl side groups.

(b) *p*-Toluenesulfonyl hydrazide (TSH) was purified by recrystallization from ethanol. 2,4,6-Triisopropylbenzenesulfonyl hydrazide (TPBSH) was prepared by treating a solution of 2,4,6-triisopropylbenzenesulfonyl chloride in tetrahydrofuran with hydrazine hydrate [yield, *ca.* 85%; mp 121°]. TPBSH was stored under nitrogen at 0° in the dark.

Hydridocarbonyltris(triphenylphosphine)rhodium(I), carbon monoxide, hydrogen, acetic anhydride, and phosphorous pentoxide were used as received.

(c) Solvents were purified by standard procedures.

(2) Hydroformylation of PP with Hydridocarbonyl Tris(triphenylphosphine)rhodium(I) (Preparation of PP-CHO). All experiments were carried out in a 1900-ml stainless-steel closed autoclave fitted with a heater, stirrer, and gas samplers.

In the autocalve, a solution of PP in toluene (13.6 g/l.) and 1 mol % of $RhH(CO)(PPh_3)_3$ were added. The air in the autoclave was replaced by hydrogen, and then carbon monoxide was introduced to reach the desired gas composition. The pressure was kept at the desired value within ±10% during the reaction period. (The hydroformylation reaction is appreciably exothermic and consequently within a few minutes or so of initiation temperature rises were observed.) After the reaction, the stirring and heating were stopped, the autoclave was cooled immediately, and a part of the reaction mixture was poured into methanol. Most of the reaction mixture was treated with sufficient hydroxylamine hydrochloride and pyridine to prepare the oxime derivatives.

The reaction conditions used and the results for hydroformylation of PP are summarized in Table I. From these results it was found that the rate of hydroformylation increases with increasing total pressure, reaction time, and temperature. Also, the use of H_2 rich gas mixtures (H_2:CO = 2:1) causes an increase in the rate of hydroformylation. However, it should be noted that, when the hydroformylation is carried out using H_2 rich gas mixtures, minor amounts of side reactions such as hydrogenation and isomerization of PP seem to take place simultaneously. If the hydroformylation is carried out at high concentrations of $RhH(CO)(PPh_3)_3$ for longer reaction times, polymers having greater than 50 mol % of formyl groups may be obtained even at 30 to 40°.

(3) Preparation of PP—CH=N—OH. Sufficient hydroxylamine hydrochloride and pyridine were added to the toluene solution (*ca.* 14 g/l.) of the hydroformylated polymers. The mixture was stirred at room temperature for 15 hr and then heated at 60° for 1 hr under nitrogen. The aldoxime was isolated by precipitation from methanol. After washing with methanol, distilled water, and methanol again, the product was purified by reprecipitation from benzene solution into methanol and then dried at room temperature *in vacuo* for 48 hr. The pendant group content in the polymers was estimated from the results of the elemental analysis (Table II). It should be pointed out that removal of residual catalyst from the PP—CN=OH is much easier than from PP-CHO.

(4) Preparation of PP-CN.[8] PP—CH=N—OH (14 g) was dissolved in a mixture of toluene (1000 ml) and pyridine (200 ml). A small amount of hydroxylamine hydrochloride was added to the solution in order to convert trace residual aldehyde to oxime. After the temperature of the resulting mixture reached 100°, acetic anhydride (500 g) was added slowly to the hot solution in portions. The mixture was heated with stirring at 100 to 110° for 5 hr under nitrogen. The reaction mixture was poured onto ice and then treated with sodium carbonate. The upper layer was washed with water and poured into methanol. The product was collected, washed with methanol, and dried at room temperature *in vacuo* for 15 hr.

In addition, the dried product was dissolved in a mixture of dry toluene (500 ml) and dry pyridine (100 ml). Phosphorus pentoxide (20 g) was added slowly to the solution, and the mixture was refluxed for 1 hr to convert the small amount of residual oxime to nitrile. The reaction mixture was washed with distilled water and poured into methanol. The product was isolated, washed with distilled water, and dried in the usual manner. The product was stored under nitrogen with refrigeration.

(5) Hydrogenation of PP-CN. It is well known that[9] TPBSH undergoes thermal decomposition much more readily than TSH and that it is an effective reagent for the hydrogenation of olefins at relatively low temperatures. However, it was found that complete hydrogenation of the PP-CN with TPBSH did not occur, maximum conversion being *ca.* 90%. Therefore, hydrogenation was carried out in two stages using both TPBSH and TSH as detailed below.

PP-CN (8 g) was dissolved in *p*-xylene (600 ml) at 70° under nitrogen. Sufficient TPBSH to give a greater than 2:1 mol ratio of TPBSH to double bonds in the PP-CN repeat unit was added in six equal portions at intervals of 10 min. The resulting mixture was heated with stirring at 70° for 1 hr under nitrogen, and the hydrogenated polymer was isolated by precipitation into methanol. After washing with methanol, distilled water, and methanol again, the product was dried at room temperature *in vacuo* for 24 hr. The hydrogenation of the residual double bonds (about 10 to 20 mol % based on repeat units) in the polymer was carried out with excess TSH in *p*-xylene at 135° for 1 to 2 hr under nitrogen in the presence of a small amount of pyridine to obtain completely hydrogenated PP-CN. The product was isolated, washed with methanol and distilled water, and dried.

When hydrogenation is carried to completion with TSH in this manner, a small amount of a side reaction occurs which causes the reversion of the nitrile groups to the formyl groups. This may be schematically represented by eq 3. Therefore, the small quantity of

Table II
Characterization Data

Sample	T_g or (T_m),[a] °C	Calcd,[b] % C	Calcd,[b] % H	Calcd,[b] % N	Found, % C	Found, % H	Found, % N
PP	−98	88.24	11.76		88.47	11.53	
PP—CH=N—OH (10)	−82	85.40	11.53	1.45	84.89	11.28	1.44
PP—CH=N—OH (20)	*c*	81.04	11.17	3.12	80.01	10.73	3.09
PP-CN (10)	−83	86.98	11.53	1.48	86.51	11.25	1.23
PP-CN (20)	−66	85.01	11.17	3.82	83.75	10.68	3.29
Hy-PP-CN (10)	(122)	84.66	13.90	1.44	83.84	13.91	1.43
Hy-PP-CN (20)	(98)	82.98	13.30	3.72	83.63	13.56	3.74

[a] Determined by DSC. [b] Calculated values are based upon pendant group contents for the (10) and (20) series of 7.4 and 20.0 mol %, respectively. [c] Undetectable.

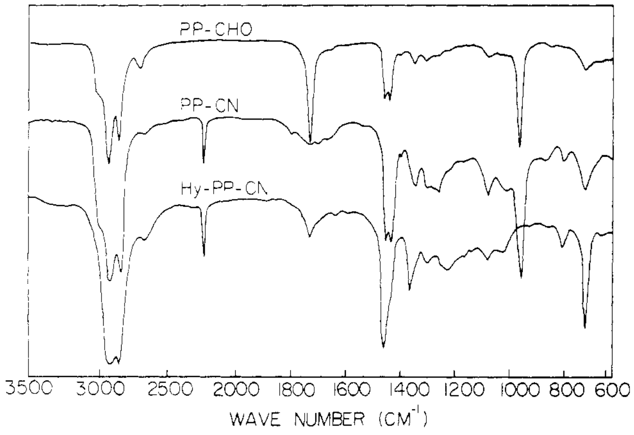


Figure 1. Infrared spectra for PP-CHO (20), PP-CN (20), and Hy-PP-CN (20).

formyl groups present at the completion of the hydrogenation were reconverted to the nitrile as follows.

$$\mathrm{PP{-}CN} \xrightarrow{H_2} \mathrm{Hy{-}PP{-}CN} + \mathrm{Hy{-}PP{-}CH{=}NH}$$

$$\mathrm{Hy{-}PP{-}CH{=}NH} \xrightarrow[+\,H_2O]{-\,NH_3} \mathrm{Hy{-}PP{-}CHO} \qquad (3)$$

The hydrogenated polymer (8 g) was dissolved in a mixture of *p*-xylene (500 ml) and pyridine (100 ml) at 80° under nitrogen, and hydroxylamine hydrochloride (1 g) was added. Acetic anhydride (100 g) was added to this hot mixture in portions. After the resulting mixture was heated at 110° for 1 hr with stirring, the product was isolated, purified, and dried in the usual manner. The polymer was purified by reprecipitation from *p*-xylene–pyridine solution into methanol and then dried at 40° *in vacuo* for 15 hr.

Polymer characterizations were carried out on the basis of elemental analysis, Gel Permeation Chromatography (gpc), and infrared spectroscopy (ir). The results are shown in Tables II and III and Figure 1, respectively. Table II shows good agreement between calculated and observed values of carbon, hydrogen, and nitrogen for all the derivatives.

Table III indicates a slight broadening in molecular weight distribution in going from the original PP to the most highly substituted derivative PP-CN (20). The effect is very small, however, and indicates that no significant backbone degradation has occurred as a result of the reaction sequences described above. Gpc measurements were also carried out on the Hy-PP-CN derivatives at 135° using dichlorobenzene as solvent. The resolution was too poor under these conditions to permit meaningful comparisons to be made. This poor resolution may stem from association of the polymer in solution or interaction of the polymer with the column due to the presence of the polar nitrile groups.

Figure 1 presents a comparison of the ir spectra of the PP-CHO, PP-CN, and Hy-PP-CN derivatives. There is some evidence for the presence of a small amount of acylated oxime groups ($CH{=}N{-}OCOCH_3$) in PP-CN and Hy-PP-CN (band at around 1740 cm^{-1}). This is presumably an intermediate in the dehydration of the oxime with acetic anhydride. In addition, the carbonyl stretching band at 1740 cm^{-1} is more prominent in Hy-PP-CN than in PP-CN. This could be due to the acylation of small amounts of hydroxyl side groups formed during hydrogenation by acetic anhydride. A suggested sequence is presented in eq 4.

$$\mathrm{PP{-}CN} \xrightarrow{H_2} \mathrm{Hy{-}PP{-}CN} + \mathrm{Hy{-}PP{-}CH{=}NH} \xrightarrow[+\,H_2O]{-NH_3} \mathrm{Hy{-}PP{-}CHO}$$

$$\mathrm{Hy{-}PP{-}CHO} \xrightarrow{H_2} \mathrm{Hy{-}PP{-}CH_2OH} \xrightarrow{AC_2O} \mathrm{Hy{-}PP{-}CH_2OCOCH_3} \qquad (4)$$

It may be concluded that the methods outlined in this note lead to CN derivatives of the starting PP which are linear and of approximately the same mojecular weight and distribution as the PP itself. The PP-CN derivatives contain small quantities of acylated oxime side groups and acetate side groups as a result of side reactions. In addition, similar experiments with anionically polymerized polybutadiene lead to essentially the same results as the PP, no gelation occurs in contrast to the earlier study cited in the introduction. Also, infrared measurements indicate the absence of hydroxyl groups in the PP-CHO prepared by the present technique. The hydroformylation reaction with the cobalt catalyst leads to appreciable quantities of hydroxyl groups in the product.

Table III
Gpc Data

Sample	Solvent[a]	$\bar{A}_n$, Å	$\bar{A}_w$, Å	$\bar{A}_w/\bar{A}_n$
PP	THF	4700	9,000	1.9
PP-CN (10)	THF	4300	8,400	2.0
PP-CN (15)[b]	THF	5000	8,700	1.7
PP-CN (20)	THF	3300	8,200	2.5
Hy-PP	TCB	6100	10,800	2.8

[a] For THF as solvent: room temp; column pore sizes of 10^6, 10^5, 10^4, 10^3 Å. For TCB as solvent: 135°; column pore sizes of 10^6, 10^5, 10^4, 10^3 Å. [b] PP-CN (15) means PP having about 12.5 mol % of pendant nitrile group.

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The Far-Infrared Spectrum of Collagen

While the near and middle infrared absorption spectra of collagen have been assiduously studied (see ref 1 for a review), the far infrared region, *i.e.*, the region below *ca.* 400 cm^{-1}, has not received much attention. We report here the spectra of native, partially denatured and fully denatured collagen in the range 400–240 cm^{-1} and comment on their use toward the determination of the relative amount of denatured collagen in the solid state.

Collagen was extracted from rat tail tendon with 0.05 *M* acetic acid, using a method similar to that of Piez, Lewis, Martin, and Gross.[2] A specimen of collagen extracted from bovine hide by H. I. Sinnamon and coworkers (United States Department of Agriculture, Philadelphia) and purified in our laboratory was also used as a control. (Spectra obtained with the two collagen specimens were identical.) A solution of denatured collagen was prepared from the