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γ-RADIATION PRODUCED SUPPORTED METAL COMPLEX CATALYSTS

II *. COBALT CARBONYL HYDROFORMYLATION CATALYSTS SUPPORTED ON POLYPROPYLENE CONTAINING PYRIDINE SIDE CHAINS

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Summary

The optimum conditions necessary to prepare novel polymer supports for use in catalysis by the γ-radiation grafting of 4-vinylpyridine on to polypropylene are shown to be a total dose of 2 Mrad at a dose rate of 300 Krad h^{-1} using a monomer to polymer ratio of 40 per cent mol/mol. Addition of 0.1 per cent w/v of *p*-tert-butylcatechol increases the grafting yield almost two fold. Comparison of the hydroformylation of 1-hexene in the presence of cobalt carbonyl supported on 4-vinylpyridine grafted on to polypropylene shows an increase in specificity, as determined by the ratio of normal/branched heptanal formed, by a factor of about 2.5 over the corresponding homogeneous catalyst. The supported system is of similar activity to the homogeneous system. The greater specificity of the supported catalyst is ascribed to the total environment surrounding the catalytically active site in which both the pyridine sidechain and the polypropylene backbone are believed to play an important role.

Introduction

Recently, there has been much interest in developing transition metal catalysts supported on inorganic or polymer matrices [2—4]. The original motivation for supporting homogeneous catalysts was to obtain a catalyst which combines the specificity and opportunities for catalyst tailoring that the single active site in a homogeneous catalyst provides with the ease of separation of a

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* Part 1, reference 1.

heterogeneous system. However, it has become increasingly apparent that leaching is often a severe problem; indeed some supported transition metal catalysts have been described as "leaky" [5]. Although there are examples where supported transition metal complex catalysts have greater activity than their homogeneous counterparts [6—10] these are rare and tend to include mainly examples where the active catalytic species is monomeric with a strong tendency to form an inactive dimer. By supporting such monomers on inflexible supports, dimerisation is prevented and the activity of the monomer is retained.

In view of the problems that have been encountered previously we believe that the future of supported catalysts lies in their potentially greater specificity than the corresponding homogeneous catalysts. This greater specificity may arise both from the proximity of the support to the active site and also the possible need for the reactants to diffuse through the support to the active site. Some examples where greater specificity has been obtained by supporting a homogeneous catalyst have been reported previously [11—13] and the present work provides a further example.

It is apparent from previous work in this field that the factors affecting the performance of supported transition metal complex catalysts are very subtle. Thus it would be of interest to prepare a series of closely related supported catalysts in which the local environment around the active sites was systematically varied, for example by varying the loading of the metal complex on the support, the degree of cross-linking of the support and even the chemical nature of the support itself.

Previously the use of organic polymers as supports has been limited by the fact that the polymer must contain active sites at which groups containing donor atoms may be reacted to anchor the metal complex. Thus, much of the previous work has utilised either polystyrene or styrene-divinylbenzene copolymer which can be chloromethylated or brominated [2,4]. The technique of grafting alkene monomers to polymers using γ-radiation offers the possibility of using almost any polymer as a support since this is a general and well documented reaction [14,15].

In choosing the trunk polymer to be used it was important that it should be, (i) stable after γ-irradiation up to 190°C, a typical temperature for the reactions it was hoped to catalyse, (ii) inert to attack by reactants or products and (iii) be insoluble in benzene and other typical solvents. Additionally the polymer should be cross-linked rather than degraded when subjected to γ-radiation [14]. The polymer chosen for this work, as it most closely complies with these requirements, was polypropylene.

The first part of the programme, described here, is the γ-radiation induced grafting of 4-vinylpyridine onto polypropylene powder. Pyridine has been used previously as the complexing group in polymer supported catalytic studies [2,4] and also as the donor group in resins which may remove transition metal ions from solution [16,17]. The aim of this work was to find the optimum grafting conditions for this system and to test the catalytic activity of a supported cobalt carbonyl complex as an olefin hydroformylation catalyst.

Experimental

Benzene and dioxan were purified by distillation over sodium wire using a 20 cm vacuum-sleeved Vigreux column and stored over sodium wire prior to use. 4-Vinylpyridine (Koch-Light) was distilled in vacuo to remove inhibitor using the same Vigreux column and stored at —25° C, the longest storage time for any batch being one month. Polypropylene powder (ICI, propathene) which contained no inhibitors was used as received.

In a typical radiation experiment polypropylene, benzene and 4-vinylpyridine in the required proportions were placed in a Schlenk tube [18] and degassed by freeze-thawing three times under vacuum. The reactants were then sealed under nitrogen by finally releasing the vacuum to nitrogen. The γ-irradiation was carried out using ^{60}Co source (~3000 Ci); dose rate being determined by placing the sample at a given distance from the source and using calibration charts recalibrated ever three months. During irradiation the suspensions were stirred vigorously to ensure thorough mixing of reactants and homogeneity of radiation does received throughout the sample. After irradiation the powder was filtered off immediately to minimise post-irradiation effects and then soxhlet extracted with benzene/chloroform (1/3) for 24 hours then methanol for 24 hours to remove unreacted monomer and homopolymer. After extraction the samples were dried in vacuo (10^{-3} Torr) for 5 hours and then analysed for C, H and N (Dr. F.B. Strauss, Oxford). The grafting yield, the number of 4-vinylpyridine units per hundred units of propylene monomer, was determined from the formula:

$$\text{Grafting yield} = (4200/\{1400/x) - 105\}\%$$

where x = percentage of nitrogen found in the sample.

1-Hexene was hydroformylated in a glass-lined 250 ml stainless steel autoclave under 100 atmosphere pressure of H_2 + CO (1/1) at 180—190° C for 15 minutes. All runs contained benzene (94 ml), 1-hexene (20.9 g; 0.25 mol) and $[Co_2(CO)_8]$ (1.1 g; 3.2 mmol). Run A contained no other compound, run B contained added pyridine (1.58 g; 20.0 mmol), run C contained added polypropylene (7.04 g) and run D contained added grafted copolymer (7.04 g of 17 per cent mol/mol graft). The copolymer used corresponds to 20 mmol of 4-vinylpyridine. The conversion of 1-hexene to heptanal was essentially the same (>70 per cent) in all runs. The reaction mixtures were analysed by gas chromatography. This was carried out with a Pye 104 chromatograph fitted with a glass capillary column (stationary phase OV17, bore 0.3 mm). The injection block and flame ionisation detector were held at 100° C and the oven temperature programmed for a six minute hold at 25° C followed by an increase of 12° C/min up to 100° C. This programme enabled 1-hexene, *cis*-2-hexene, *trans*-2-hexene, hexane, benzene, 2-ethylpentanal, 2-methylhexanal and heptanal to be separated. Cobalt concentrations in solution were determined by atomic absorption spectroscopy using a Varian AA 575 spectrometer at a wavelength of 240.7 nm. Reference standards were prepared from $[Co_2(CO)_8]$ in benzene/heptanal solution. EPR spectra were recorded on a Jeol JES PE X band spectrometer. Mass spectra were measured using a Hitachi-Perkin Elmer RMU-7M mass spectrometer linked to a VG 2035 data system. X-ray diffraction powder photographs were recorded using a Philips PW 1008 diffraction generator with nickel-filtered Cu-K_α radiation. Exposures were for 16 hours at 30 kV and 20 mA. The photographs were analysed using a Joyce-Lobel micro-densitometer. Pulsed NMR relaxation curves were recorded with a Spin-Lock CPS 2.40 MHz pulsing unit using a Jeol JNM-DBT-18H/F probe and a Jeol JNM-PW40 magnet.

Results and discussion

The first requirement in this study was the choice of solvent or diluent. There have been many studies concerning the effect of solvent on grafting; [19—28], and it can be concluded that it is preferable for the solvent and the trunk polymer to have similar solubility factors [23] and dielectric constants. Thus the solvent chosen in this study was benzene having a solubility factor of 9.2 $\mathrm{cal}^{1/2}\ \mathrm{cm}^{-3/2}$ and a dielectric constant of 2.3 [24]. Polypropylene has the values 9.2 $\mathrm{cal}^{1/2}\ \mathrm{cm}^{-3/2}$ [23] and 2.2 [25], respectively. Benzene was chosen also since there is little radical transfer between trunk polymer and solvent [26]. The optimum ratio of 4-vinylpyridine to solvent used (1/2 v/v) was determined previously [1].

In γ-irradiation induced grafting several product types are possible. Block copolymers are one type which can be ruled out in this case as polypropylene is of the cross-linking and not degrading variety of polymer [14]. Attachment of growing side chain is the other main type of grafting and in our work we require these to be short, since they are only required as sites for coordination of metal ions. Again benzene is a suitable solvent for our purposes as the growing attached homopolymer chain is soluble in benzene and will terminate readily due to the chain flexibility [27]. The main by-product will be homopolymer. This together with unreacted 4-vinylpyridine was removed by soxhlet extraction with benzene/chloroform (1/3) for 24 hours followed by methanol for a further 24 hours.

Effect of monomer to polymer ratio

Figure 1 shows the effect of monomer to polymer ratio on the grafting yield. The 4-vinylpyridine used contained 0.1 per cent weight/volume of *p*-tert-butylcatechol inhibitor. The effect of inhibitor is discussed below. It can be seen that as the ratio of monomer to polymer increased, the grafting yield increased to a maximum between 40 and 50 per cent mol/mol after which the grafting yield decreased. The decrease in grafting yield at high monomer concentrations was almost certainly due to increasing formation of homopolymer. Work-up of the soxhlet extracts and subsequent NMR study showed that, at the optimum ratio of monomer to polymer and under the radiation conditions given above, approximately 33 per cent of the ungrafted 4-vinylpyridine was homopolymer and 67 per cent was unreacted monomer.

It must be noted that there is another way of expressing grafting yield, namely grafting efficiency. This represents the amount of monomer grafted compared with the maximum possible graft as shown by the dotted line on Figure 1. The grafting efficiency is plotted in Figure 2 which clearly indicates a maximum at 40 per cent mol/mol.

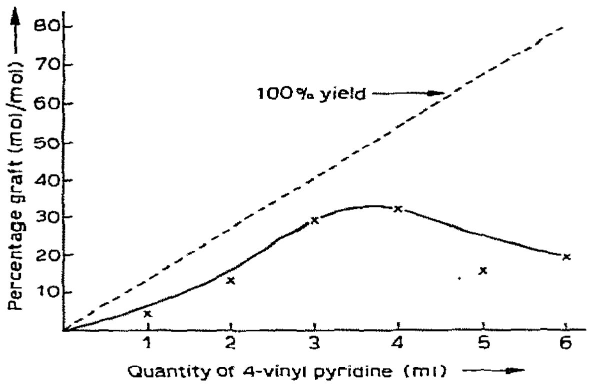


Fig. 1. Effect of the monomer/polymer ratio on grafting yield; obtained by irradiating suspensions of polypropylene (3 g) in solutions of 4-vinylpyridine in benzene (6 ml) with a total of 2 Mrad provided at a rate of 335 Krad h^{-1}.

Effect of inhibitor

Commercial 4-vinylpyridine contains 0.1 per cent w/v *p*-tert-butylcatechol as a stabiliser against polymerisation. In order to determine whether or not the presence of this stabiliser was desirable for γ-radiation grafting, it was all removed by careful fractional distillation. Then the effect of added *p*-tert-butylcatechol on the grafting yield was determined (Figure 3). The optimum concentration of inhibitor was identical to that added commercially as stabiliser to the monomer. With concentration less than 0.1 per cent w/v homopolymerisation is more likely to occur and at relatively high concentrations the inhibitor will inhibit the grafting reaction by "quenching" radical sites formed on the polymer.

Effect of total dose

If the total dose in any experiment is sufficiently large, then all of the monomer will be either grafted or converted to homopolymer. However, large doses will alter the polymer structure and so the optimum total dose will be the

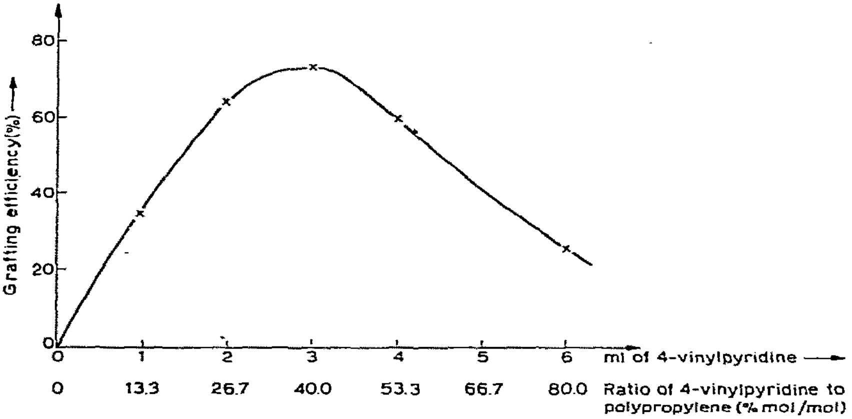
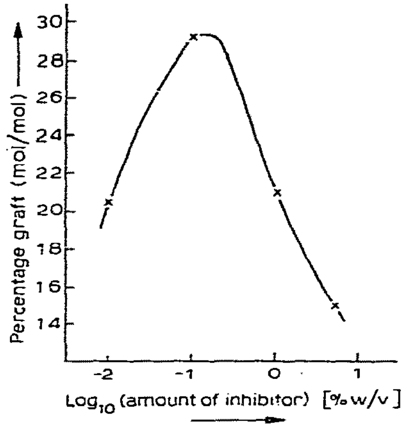


Fig. 2. Effect of monomer: polymer ratio on grafting efficiency (based on the data in Fig. 1).



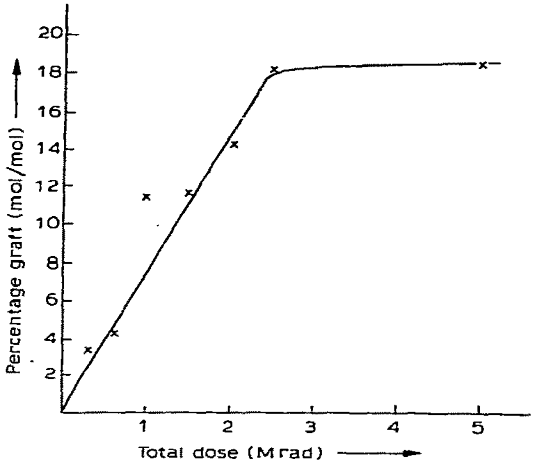


Fig. 3. Influence of inhibitor (*p*-tert-butylcatechol) on grafting yield; obtained by irradiating suspensions of polypropylene (3 g) in solutions of 4-vinylpyridine (3 ml) in benzene (6 ml) with a total dose of 2 Mrad provided at a dose rate of 300 Krad h^{-1}. Since the ratio of 4-vinylpyridine to polypropylene is 40 per cent mol/mol, the theoretical maximum grafting yield is 40 per cent mol/mol.

Fig. 4. The effect of total radiation dose on grafting yield; obtained by irradiating suspensions of polypropylene (3 g) in solutions of 4-vinylpyridine (3 ml) in benzene (6 ml) at dose rates of 300 Krad h^{-1}, (a) in the presence of 0.1 per cent *p*-tert-butylcatechol, (b) in the absence of inhibitor. Since the ratio of 4-vinylpyridine to polypropylene is 40 per cent mol/mol the theoretical maximum grafting yield is 40 per cent mol/mol.

lowest value which gives an acceptable grafting yield. The results of irradiating a 40 per cent mol/mol monomer to polymer mixture at 300 Krad h^{-1} are given in Figure 4. The maximum grafting is with a dose of 2.5 Mrad, but there is only a small increase between 2 and 2.5 Mrad. A total dose of 2 Mrad, which gives a

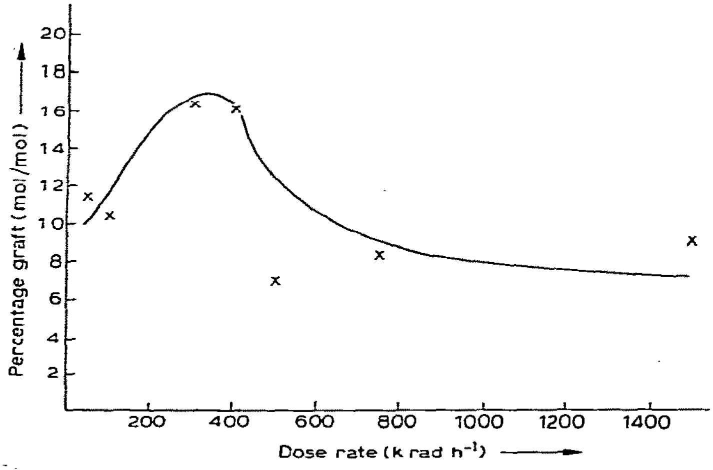


Fig. 5. Effect of dose rate on grafting yield; obtained by irradiating suspensions of polypropylene (3 g) in solutions of 4-vinylpyridine (3 ml) in benzene (6 ml) at total doses of 2 Mrad. Since the ratio of 4-vinylpyridine to polypropylene is 40 per cent mol/mol, the theoretical maximum grafting yield is 40 per cent mol/mol.

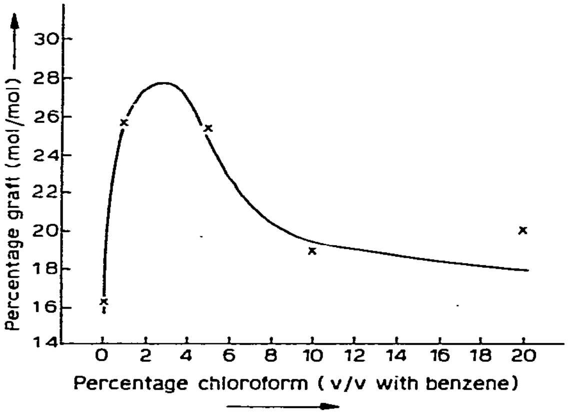


Fig. 6. Effect of chloroform on grafting yield; obtained by irradiating suspensions of polypropylene (3 g) in solutions of 4-vinylpyridine (3 ml) in benzene (6 ml) with added chloroform at a dose rate of 300 Krad h^{-1} to a total dose of 2 Mrad. Since the ratio of 4-vinylpyridine to polypropylene is 40 per cent mol/mol. the theoretical maximum grafting yield is 40 per cent mol/mol.

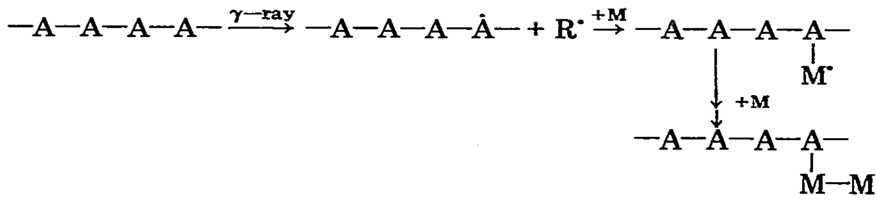
reasonable grafting yield with minimum radiation damage, was therefore used in the rest of this study.

Effect of dose rate

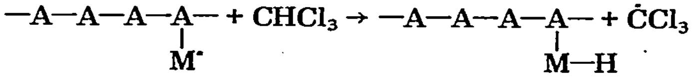
It has previously been shown that higher grafting yields are often associated with lower dose rates [28,29]. Figure 5 shows the effect of dose rate on grafting yield using 40 per cent mol/mol monomer (stabiliser free) to polymer and total dose of 2 Mrad. Above 400 Krad h^{-1} homopolymer is the major product. Below 100 Krad h^{-1} grafting yield is also poor, probably due to insufficient formation of active radical sites on the polymer. Thus our results suggest that 300 Krad h^{-1} is the optimum dose rate.

Effect of chain transfer reagent

γ-Radiation grafting can give rise to poly(4-vinylpyridine) side-chains grafted on to the polymer chain (reaction 1, A = polymer, M = monomer, $R^{\bullet}$ = radical). One possible way to prevent this is to add a chain transfer reagent such as chloroform which terminates the chain through reaction 2. When the effect of the addition of chloroform on the grafting yield was studied (Figure 6), it was apparent that addition of up to 4 per cent by volume of chloroform increased the grafting yield whereas addition of larger amounts had little effect. We find



$$-A-A-A-A- \xrightarrow{\gamma\text{—ray}} -A-A-A-\dot{A}- + R^{\bullet} \xrightarrow{+M} \underset{\textstyle M^{\bullet}}{-A-A-A-A-} \xrightarrow{+M} \underset{\textstyle M-M^{\bullet} \rightarrow \text{etc}}{-A-\dot{A}-A-A-} \qquad (1)$$



$$\underset{\textstyle M^{\bullet}}{-A-A-A-A-} + CHCl_3 \rightarrow \underset{\textstyle M-H}{-A-A-A-A-} + \dot{C}Cl_3 \qquad (2)$$

this hard to explain at the present time. Chloroform has a solubility factor of 9.3 $cal^{1/2}$ $cm^{-3/2}$ [23] and will probably enter the polymer with about the same ease as benzene, although unlike benzene the chloroform may act as either an inhibitor (or chain terminator) or, by radiolysis, as an initiator since chlorine atoms can form which may abstract hydrogen from the trunk polymer [21]. Microanalysis of the samples indicated that there was little incorporation of chlorine into the polymer, <0.2 per cent chlorine by weight.

Electron paramagnetic resonance spectra

γ-Irradiation of polypropylene forms three major radical types. If irradiation is carried out either in vacuo or under nitrogen then both alkyl and allyl radicals are formed. However, when air is present the major radical formed is the peroxy radical [30]. If air is present in the grafting procedure then the monomer will be attached to the trunk polymer by an ether linkage, whereas in the absence of air the linkage will be carbon—carbon. The latter is preferable since it will be the more kinetically stable. Accordingly all γ-irradiations were carried out under oxygen-free nitrogen.

To ensure that the present freeze-degassing procedure was adequate, a sample of polypropylene in benzene was freeze-degassed in an EPR tube and then γ-irradiated under nitrogen. The EPR spectrum was then recorded at room temperature to see if any peroxy radicals were present. The spectrum, Figure 7, was identical to that found in a previous study [30,31], and no peroxy radical signal could be identified. The spectrum is a mixture of the alkyl and allyl radical signals. It has been noted for polyethylene that it is the allyl radicals which promote grafting as the signal due to these radicals disappears on addition of a monomer whereas the signal for the alkyl radicals ramains [32]. It has been suggested that the allyl radicals are produced in the amorphous part of the polymer whereas the alkyl radicals are formed in the crystalline part and are trapped due to restriction by the crystal structure [33]. On exposing the γ-irradiated sample to air and measuring the EPR spectrum (Figure 8) a signal was observed attributable only to peroxy radicals, also agreeing with the previous study [30].

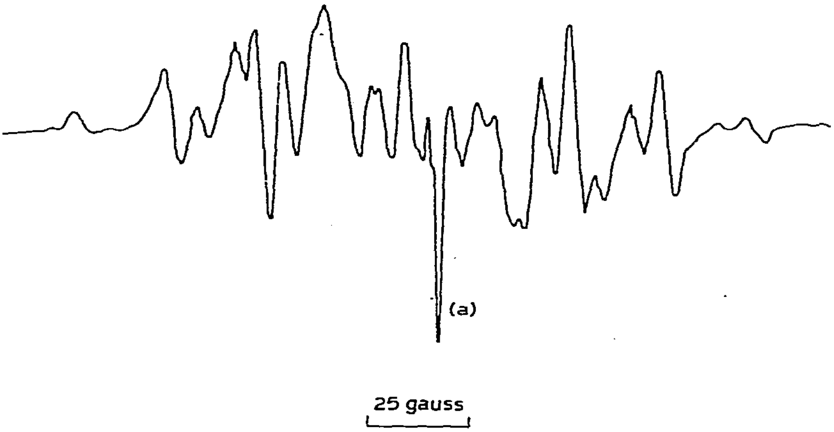


Fig. 7. EPR spectrum at room temperature of polypropylene in benzene after γ-irradiation under N_2 for 6.6 hours at a dose rate of 300 Krad h^{-1} (a) signal from spectrosil tube.

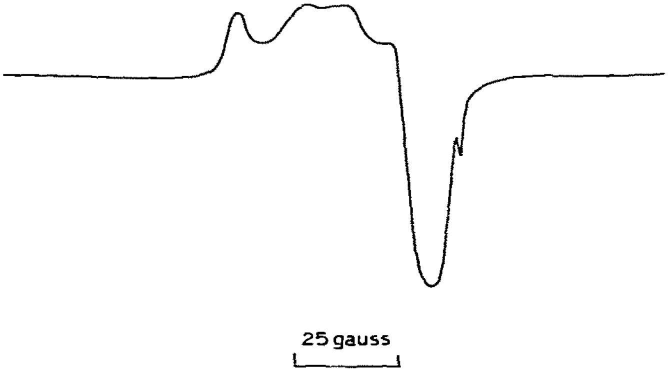


Fig. 8. EPR spectrum of sample in Fig. 7 after exposure to air.

Crystallinity studies

The suggestion (above) that the 4-vinylpyridine is radiation grafted on to allyl radical sites located in the amorphous regions of the polymer implies little change in the overall crystallinity of the polymer following γ-radiation grafting. This was checked by two methods, powder X-ray diffraction [34] and pulsed NMR relaxation studies [35]. Powder X-ray diffraction clearly showed that the degree of crystallinity of the untreated polypropylene (46.5 per cent) was essentially identical to a sample onto which 16.5 per cent mol/mol of 4-vinylpyridine had been radiation grafted. Broad line NMR relaxation studies showed exactly the same and indicated a degree of crystallinity in both samples of approximately 50 per cent. Thus γ-radiation grafting appears to result in grafting of 4-vinylpyridine within the amorphous region of the polypropylene only, since if grafting had occurred in the crystalline region is would have been expected to alter the degree of crystallinity of the polymer.

Mass spectroscopy

The mass spectra of two copolymers (7.3 per cent and 18.1 per cent mol/mol graft) had peaks at m/e = 181, 167, 153, 139, 125, 111, 97, 83, 69, 57, 43 and 27 due to the polypropylene backbone and at m/e = 105, 93, 92, 79 and 78 (monomer), 210, 197, 195, 119, 118 and 117 (dimer) and 315 and 223 (trimer) due to the grafted 4-vinylpyridine. The same peaks as found here, arising from grafted 4-vinylpyridine, are seen also in the mass spectrum of poly-4-vinylpyridine [36]. It should be noted that with poly-4-vinylpyridine the largest fragment recorded was due to a trimer. Thus, our spectra suggest that some, if not all, of the grafted 4-vinylpyridine is present in the form of poly-4-vinylpyridine chains:

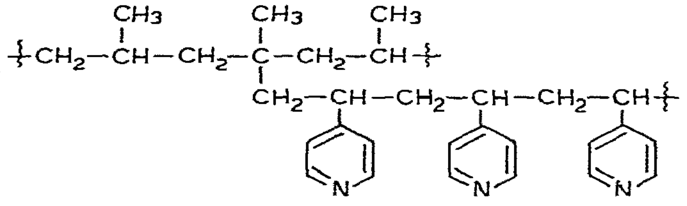


TABLE 1

HYDROFORMYLATION OF 1-HEXENE [a]

Run	Catalyst	Analysis of products (%)						ratio of normal/ branched aldehydes
		1-hexene	n-heptanal	2-methyl hexanal	2-ethyl hexanal	hexane	alcohols and aldehyde condensation products	
A	$[Co_2(CO)_8]$ (1,1 g)	0	30	27	13	10	20	0,75
B	$[Co_2(CO)_8]$ (1.1 g) + pyridine (1.58 g)	8 [b]	36	26	13	12	5	0,92
C	$[Co_2(CO)_8]$ (1.1 g) + polypropylene (7.04 g)	4	37	22	12	8	17	1,09
D	$[Co_2(CO)_8]$ (1,1 g) + grafted copolymer (7.04 g of 17% mol./mol. graft)	0	55	21	9	5	10	1,83

[a] For conditions see Experimental section. [b] Includes 3% *cis*- and *trans*-2-hexene.

Catalytic studies

The poly(2-vinylpyridine)-cobalt carbonyl system has been studied previously as an olefin hydroformylation catalyst [37,38]. It was suggested that the catalysis occurred homogeneously and that the function of the polymer was to bind the cobalt at the end of the reaction to facilitate its removal. The fact that cobalt carbonyl was more easily bound in the presence of hydrogen suggested that the cobalt was present in the form of $[HCo(CO)_4]$. It is apparent from the results obtained in the present work (Table 1) that run D, in which the hydroformylation was catalysed by cobalt carbonyl in the presence of 4-vinylpyridine supported on polypropylene, not only showed 100 per cent conversion of 1-hexene with no hexene isomers present at all, but also more than doubled the normal/branched selectivity of the catalyst compared to cobalt carbonyl alone (run A). This strongly suggests that some catalytically active sites involve cobalt bound to the supported pyridine residues. The greater specificity of the pyridine-supported cobalt carbonyl (run D) as compared to the unsupported catalyst could arise from at least four effects: (i) the presence of pyridine in the coordination sphere of the active cobalt catalyst, (ii) the proximity of the polypropylene groups to the active site, (iii) the need for the reactants to diffuse into the polymer and (iv) the total geometry around the active site in the polymer-supported case creates a more sterically demanding site than in the unsupported catalyst. Run B, where the same amount of pyridine as present in the supported catalyst (run D) is added indicates that the presence of pyridine in the coordination sphere of the active cobalt catalyst gives only a minor enhancement (by a factor of 1.23) to the normal/branched selectivity of the catalyst. Run C indicates that the presence of polypropylene itself does cause a certain enhancement (by a factor of 1.45) even in the absence of specific binding sites on the polymer for cobalt. We ascribe the enhancement observed in run C to a degree of solubility of the catalytically active complex in the benzene-swollen polymer which results in close proximity of the polymer to a significant proportion of the catalytically active species. It is hard to see how point (iii) could be responsible for the greater specificity of the supported catalyst since the same reactants are involved in producing both normal and branched aldehydes. Consequently we ascribe the greater specificity of the supported catalysts to the total environment surrounding the catalytically active site in which both the pyridine side-chain and the polypropylene backbone both play an important role. Thus, although one role of the support is to facilitate separation of the catalyst after the reaction, a more important role is to alter the steric and electronic conditions at the site of catalysis.

Analysis of the solutions after hydroformylation for cobalt by atomic absorption indicated that the copolymer had removed 90 per cent of the total cobalt, in good agreement with earlier studies with poly(2-vinylpyridine) [37].

Conclusions

In this work we have attempted to optimise the grafting conditions for the polypropylene-4-vinylpyridine system. The radiation parameters for this are a total dose of 2 Mrad at a dose of 300 Krad h^{-1}. Addition of 0.1 per cent w/v of *p*-tert-butylcatechol increases the grafting yield almost two-fold. The optimum ratio of monomer to polymer is 40 per cent mol/mol. Preliminary work on hydroformylation by cobalt carbonyl complexes on this type of support indicates that the specificity is higher than with the corresponding homogeneous catalyst, with a negligible reduction in activity.

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References

1 F.R. Hartley and D.J.A. McCaffrey in M. Tsutsui (Ed.), Fundamental Research in Homogeneous Catalysis, Vol. 3, Plenum Press, New York, 1979, p. 95.
2 F.R. Hartley and P.N. Vezey, Adv. Organometal. Chem., 15 (1979) 189.
3 L.L. Murrell, Advanced Materials in Catalysis, Academic Press, New York, 1977, p. 235.
4 Y. Chauvin, D. Commereuc and F. Dawans, Progr. Polym. Sci., 5 (1977) 95.
5 H.W. Altmann, Diss. Abs., 39B (1979) 5463.
6 R.H. Grubbs, C. Gibbons, L.C. Kroll, W.D. Bonds and C.H. Brubaker, J. Amer. Chem. Soc., 95 (1973) 2373.
7 C.U. Pittman, S.E. Jacobson and H. Hiramoto, J. Amer. Chem. Soc., 97 (1975) 4774.
8 S. Jacobson, W. Clements, H. Hiramoto and C.U. Pittman, J. Mol. Cat., 1 (1975) 73.
9 C.U. Pittman, S. Jacobson, L.R. Smith, W. Clements and H. Hiramoto in P.N. Rylander and H. Greenfield (Eds.), Catalyses in Organic Synthesis, 1976, Academic Press, New York, 1976, p. 161.
10 N.L. Holy, J. Org. Chem., 44 (1979) 239.
11 C.U. Pittman, S.E. Jacobson, R.M. Hanes, L.R. Smith and G. Wilemon, Proceedings 7th Int. Conf. Organometal. Chem., Venice, 1975, 187.
12 R.H. Grubbs, E.M. Sweet and S. Phisanbut in P.N. Rylander and H. Greenfield (Eds.), Catalyses in Organic Synthesis 1976, Academic Press, New York, 1976, p. 153.
13 C.U. Pittman and R.M. Hanes, J. Amer. Chem. Soc., 98 (1976) 5402.
14 A. Chapiro, Radiation Chemistry of Polymeric Systems, Wiley-Interscience, New York, 1962.
15 H.A.J. Battaerd and G.W. Tregear, Graft Copolymers, Wiley-Interscience, New York, 1967.
16 N.H. Agnew and M.E. Brown, J. Polym. Sci. A-1, 9 (1971) 2561.
17 H. Nishide, J. Deguchi and E. Tsuchida, J. Polym. Sci., Polym. Chem. Ed., 15 (1977) 3023.
18 D.F. Shriver, The Manipulation of Air-Sensitive Compounds, McGraw-Hill, New York, 1969.
19 H. Barker, J.L. Garnet, R. Levot and M.A. Long, J. Macromol. Sci. Chem., A12 (1978) 261.
20 S. Machi, I. Kamel and J. Silverman, J. Polym. Sci., A-1, 8 (1970) 3329.
21 S. Dilli, J.L. Garnett, E.C. Martin and P.H. Phuoc, J. Polym. Sci.: Part C, 37 (1972) 57.
22 J.L. Garnett and E.C. Martin, Aust. J. Chem., 29 (1976) 2591.
23 J. Brandrup and E.H. Immergut (Eds.), Polymer Handbook, Wiley-Interscience, New York, 1966, IV-341.
24 P.W. Atkins, Physical Chemistry, Oxford University Press, 1978.
25 F. Rodriquez, Principles of Polymer Systems, McGraw-Hill, New York, 1970.
26 T. Yasukawa, T. Takahashi, K. Murakami, K. Araki, T. Sasuga and H. Ohmichi, J. Polym. Sci, A-1, 10 (1972) 259.
27 G. Odian, M. Sobel, A. Rossi and R. Klein, J. Polym. Sci., 55 (1961) 663.
28 P.J. Fydelor, A. Messenger, G. Partridge, J.A. Bant and D. Johnson in D.H. Collins (Eds.), Power Sources 3, Proc. 7th Int. Symposium, Oriel Press, Newcastle-upon-Tyne, 1971, p. 327.
29 L.B. Adams, P.J. Fydelor, G. Partridge and R.H. West in D.H. Collins (Ed.), Power Sources 4, Proc. 8th Int. Symposium, Oriel Press, Newcastle-upon-Tyne, 1973, p. 141.
30 H. Fischer and K.H. Hellwege, J. Polym. Sci., 56 (1962) 33.
31 S.Ya. Pshezhetskii, A.G. Kotov, V.K. Millinchuk, V.A. Roginskii and V.I. Tunikov, EPR of Free Radicals in Radiation Chemistry, Khimiya, Moscow, 1972; translated by P. Shelnitz, John Wiley, New York, 1974.

32 M. Tamura and T. Seguchi, Repts. Progr. Polym. Phys. Japan, 6 (1963) 273.
33 M. Imai and H. Shimizu, J. Polym. Sci. Polym. Chem. Edn., 12 (1974) 2729.
34 A.V. Tobolsky, Properties and Structure of Polymers, Wiley-Interscience, New York, 1960.
35 R. Folland, personal communication.
36 A. Zeman, Angew. Makromol. Chem., 31 (1973) 1.
37 A.J. Moffat, J. Catal., 18 (1970) 193.
38 A.J. Moffat, J. Catal., 19 (1970) 322.