Determination of carbonyl groups in polymers by reaction with 2,4-dinitrophenylhydrazine

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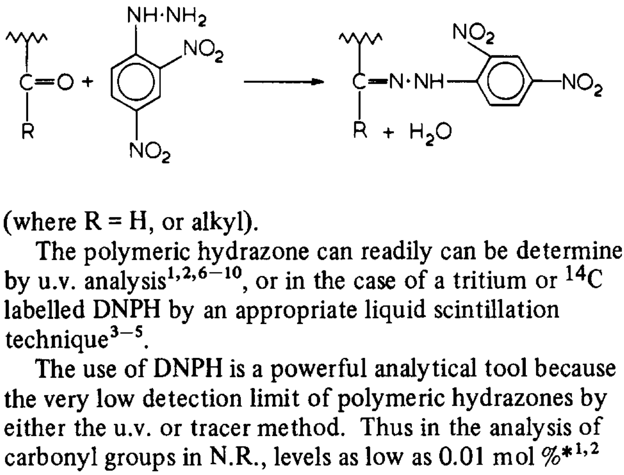
The 2,4-dinitrophenylhydrazine (DNPH) analysis of oxygenated functional groups in model polymers has been investigated. Whereas, aldehydic functional groups can be quantitatively analysed by previously reported methods, ketonic groups are only partially detected. Carboxylic, ester and epoxy groups do not significantly interfere in the conventional analytical methods. The reactivity of polymeric carbonyl groups towards DNPH appears to be markedly affected by steric factors, determined by the polymeric microstructure. The applicability of the DNPH method to the analysis of oxygenated functional groups in natural rubber and oxidized poly(ethylene) is discussed.

INTRODUCTION

The analysis of carbonyl groups in natural rubber (N.R.)[1,2], oxidized N.R.[3,4], and oxidized polyethylene[5–10] has been effected by determination of the 2,4-dinitrophenylhydrazone content after treatment of the oxygenated polymer with 2,4-dinitrophenylhydrazine (DNPH).



(I)

(where R = H, or alkyl).

The polymeric hydrazone can readily can be determined by u.v. analysis[1,2,6–10], or in the case of a tritium or ^{14}C labelled DNPH by an appropriate liquid scintillation technique[3–5].

The use of DNPH is a powerful analytical tool because of the very low detection limit of polymeric hydrazones by either the u.v. or tracer method. Thus in the analysis of carbonyl groups in N.R., levels as low as 0.01 mol %*[1,2] have been detected by u.v. analysis, and lower levels still are possible.

However, a major disadvantage of the method is the apparent lack of specificity of the DNPH reagent. Thus although reactions with aldehydes and ketones are well established and used routinely[11], reactions with epoxides have been reported[12], and the formation of derivatives of carboxylic acids is feasible. Since, such oxygenated groups together with hydroperoxide, esters and lactones have been detected in oxygenated polymers it is clear that the formation of hydrazone derivatives cannot be unambiguously attributed to aldehyde and ketones species alone.

This paper is concerned with an examination of the reactivity of DNPH with polymers containing a variety of functional groups in order to determine the degree of specificity under the reaction conditions normally employed in the DNPH analysis.

EXPERIMENTAL

Materials

Chemicals were mainly reagent grade and were purified where appropriate by distillation and drying over molecular sieves[13,14]. DNPH and the model compounds for i.r. calibration were of at least 99% purity. Solvents for i.r. and u.v. measurements were of spectro-grade quality.

Natural rubber samples were isolated from freshly tapped latex (Clone RRIM 600).

Synthesis of model copolymers

Copolymers containing approximately 10 mol% of aldehyde, ketone, carboxyl and epoxide functional groups were synthesized by the copolymerization of styrene with acrolein, methylvinylketone, acrylic acid and glycidyl methacrylate respectively. In a typical synthesis a mixture containing 10 ml styrene, 1 ml co-monomer, 40 ml benzene and 0.2 g benzoyl peroxide was heated at 60°C, overnight, under nitrogen. The co-polymer was isolated by precipitation into excess methanol and purified by subsequent reprecipitation from dichloromethane.

Synthesis of Model DNPH Derivatives

A DNPH reagent solution was prepared from 5 g DNPH, 4 ml conc. H_2SO_4 and 100 ml methanol according to the method of Vogel[11]. Derivatives of acetaldehyde, crotonaldehyde, isobutyraldehyde, acetone and propylene oxide were prepared by dropwise addition of freshly prepared, filtered DNPH reagent to a stirred methanolic solution of the appropriate compound. Acetyl-2,4-dinitrophenylhydrazide was synthesized by the direct reactions of DNPH with ex-

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* $$\text{mol\%} = \frac{\text{mole carbonyl group}}{\text{mol polymeric repeating unit}} \times 100$$

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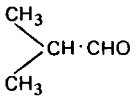
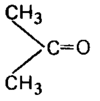
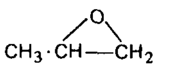
Table 1 Characteristics of model DNPH derivatives

	u.v. absorption characteristics						
	Experimental			Literature			
Precursor	Solvent	λ_{max}(nm)	$\epsilon_{max} \times 10^{-4}$	Solvent	λ_{max}(nm)	$\epsilon_{max} \times 10^{-4}$	Ref
$CH_3 \cdot CHO$	$CHCl_3$	356	2.42 ± 0.03	95% Ethanol	356	2.10	17
				$CHCl_3$	355	2.22	27
					360	2.50	28
$CH_3 \cdot CH{=}CH \cdot CHO$	$CHCl_3$	370	2.37 ± 0.02	95% Ethanol	377	2.66	17
 $(CH_3)_2CH \cdot CHO$	$CHCl_3$	355	2.29 ± 0.10	$CHCl_3$	357	2.18	27
 $(CH_3)_2C{=}O$	$CHCl_3$	360	1.97 ± 0.03	CCl_4	345–350	1.30	18
				95% Ethanol	360	2.11	17
$(CH_3CO)_2O$	THF	335	1.35 ± 0.03				
	$CHCl_3$	325–330	1.36 ± 0.03				
 $CH_3 \cdot CH{-}CH_2$ (epoxide)	THF	340	1.94				
	$CHCl_3$	340	1.94				
2,4-DNPH	THF	355	1.53	95% Ethanol	352	1.53	17

cess acetic anhydride in the absence of solvent and acid catalyst. The precipitated derivatives were filtered off and recrystallized from 95% ethanol.

Melting points of the DNPH derivatives were in accord with literature values[11,17].

Chlorination of poly(styrene-co-acrolein)

Copolymer (0.3 g) was dissolved in 10 ml dichloromethane and stirred with an excess (0.21 g) of phosphorous pentachloride, at room temperature, overnight. The chlorinated copolymer was precipitated into excess methanol and purified by reprecipitation from dichloromethane.

Reaction of DNPH with oxygenated polymers

Two distinct procedures were used. Method I which is essentially the procedure of Barnard *et al.*[4] and Method II which was derived from the work of Subramaniam[1].

Method I Polymer (0.2 g) was dissolved in benzene (50 ml) containing *N,N*-dimethylformamide (5 ml), 1N hydrochloric acid (1 ml) and DNPH) (0.1 g) and was subsequently refluxed for one hour under nitrogen. Excess benzene (c.a. 30 ml) was distilled off, and the reacted polymer isolated by precipitation with 95% ethanol. The polymer was purified by three reprecipitations from chloroform or dichloro methane, and dried under vacuum at 50°C. (In some experiments the polymer and DNPH concentrations were different to the above – these are indicated in text .)

Method II The polymer (0.2 g) was dissolved in 50 ml of a 50:50 solvent mixture of toluene/tetrahydrofuran containing DNPH (0.1 g), and subsequently thermostated at 45°C for 3 h. The polymer was isolated and purified as described above. (Variations in polymer and DNPH concentrations are indicated in text).

Modified method II[2] Rubber (0.2 g) and DNPH (0.05 g) were dissolved in 10 ml of a 50:50 solvent mixture of toluene/tetrahydrofuran. After allowing to stand for 24 h, one drop of conc. hydrochloric acid was added and the mixture heated under nitrogen at 50°C for 3 h. The polymer was isolated and purified as described above.

Epoxide determination

Epoxy content of polymers was determined by direct HBr titration, as previously described[15,16].

U.v. analysis

All measurements were made with a Varian 635 double-beam spectrophotometer. Molar extinction coefficients of the model DNPH derivatives in THF and chloroform were determined from the slope of linear plots of adsorbance versus molar concentration, over the range 0–5 x 10^{-5} mol l^{-1} (*Table 1*).

U.v. spectra of polymer-DNPH derivatives were obtained for chloroform solutions, employing an equivalent unreacted polymer solution as a blank.

I.r. analysis

The i.r. spectra of dilute chloroform solutions of model compounds and copolymers, were scanned between 1500 cm^{-1} and 2000 cm^{-1} using a Beckmann *IR*-4240 spectrophotometer. The maximum absorption in the 1700 cm^{-1} region was calculated using a base line method. Calibration curves of $\log_{10}(I_0/I)$ versus molar concentration were obtained for the model compounds. The composition of the copolymers was deduced from the appropriate calibration curve.

Elemental analysis

Nitrogen, oxygen and chlorine determinations were performed by a professional analyst.

RESULTS

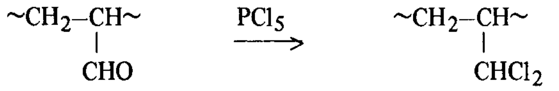
Analysis of aldehyde groups

The aldehyde content of a model copolymer, poly(acrolein-co-styrene), was determined by a variety of methods, for two different samples. The results of these analyses are summarized in *Table 3*. It is evident that, for the DNPH analysis, Method I conditions allow more complete reaction of the polymeric aldehyde groups. This is not surprising in view of the observed kinetics of the reaction. Thus it has been shown[22] that the reaction is essentially third order, i.e.,

$$\text{rate} = [DNPH]\,[C{=}O](k_H + [H^+] + k_{HA}[HA]) \qquad (2)$$

involving catalysis by both hydroxonium ion and weak acid. Method I, employing added acid catalyst and higher reaction temperatures thus permits essentially quantitative conversion within 1 h, whereas, hydrazone formation is still far from complete after 3 h, under Method II conditions. In the case of the high acrolein sample the essential completeness of the Method I DNPH reaction is confirmed by inspection of the i.r. spectrum of the polymeric derivative which reveals only a small residual carbonyl absorption at 1720 cm^{-1} (<3%).

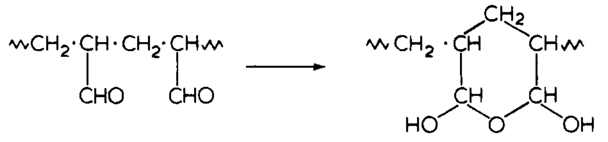
Good correlation is apparent for the determination of the DNPH content of the copolymer by u.v. and nitrogen analysis. This infers that the extinction coefficient of the acetaldehyde and isobutylraldehyde DNPH derivatives approximate reasonably closely to that of the polymeric derivatives. Alternative methods of analysis, however, show extremely large deviations from the DNPH result. The estimation of the carbonyl content by chlorination with PCl_5, is based on the scheme:



$$\sim CH_2-\underset{CHO}{CH}\sim \xrightarrow{PCl_5} \sim CH_2-\underset{CHCl_2}{CH}\sim \qquad (3)$$

Since the accuracy of the chlorine analysis is good, the low value by this method indicates that the above reaction is not quantitative under the conditions employed. This was confirmed from the i.r. spectrum of the chlorinated polymer which showed significant residual carbonyl absorption.

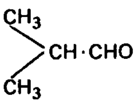
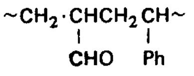
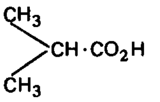
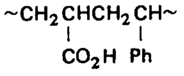
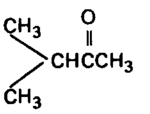
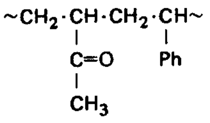
The very low analysis figure by the direct i.r. method may be due to a phenomenon reported earlier by Kern *et al.*[21], who showed that for acrylonitrile/acrolein polymers the carbonyl absorption *decreased* in intensity at high aldehyde contents. This was attributed to hemi-acetal formation through neighbouring group participation (equation 4).



(4)

which becomes important at high carbonyl content. This explanation is consistent with the better correlation at low carbonyl contents and the high values obtained by direct oxygen determination.

Table 2 Position of carbonyl (C = O stretching) frequency in model compounds and copolymers (Run as 5% w/v solutions in chloroform)

Model Compound	Frequency ν cm^{-1}	Copolymer	Frequency ν cm^{-1}
	Doublet 1720, 1735	 $\sim CH_2\cdot\underset{CHO}{CH}CH_2\underset{Ph}{CH}\sim$	1720
	1700	 $\sim CH_2\underset{CO_2H}{CH}CH_2\underset{Ph}{CH}\sim$	1700–1705
	1700	 $\sim CH_2\cdot\underset{\underset{CH_3}{C=O}}{CH}\cdot CH_2\cdot\underset{Ph}{CH}\sim$	1698

Analysis of ketone groups

Comparison of the carbonyl content of poly(methyl vinyl ketone-co-styrene) by DNPH and i.r. analysis* (*Table 4*) reveals that neither DNPH method approaches a realistic analysis figure. Failure to achieve quantitative hydrazone formation, under Method I reaction conditions, appears to be largely governed by thermodynamic rather than kinetic factors. Thus *Figure 1* shows that the reaction reaches equilibrium within two hours reaction time, at which point hydrazone formation is less than 20% of the known ketone content. Furthermore, the actual polymer hydrazone content under equilibrium conditions is seen to be critically dependent on the initial DNPH concentration.

This behaviour may be rationalized by considering the

Table 3 Analysis of the carbonyl content of poly(acrolein-co-styrene)

	Carbonyl content mol g^{-1} x 10^3						
		Method I		Method II			
Polymer sample	DNPH Deriv. λ_{max}(nm)	u.v.	N analysis	u.v.	I.R.	PCl_5 Chlorination	Oxygen Determination
High acrolein content	360–361	1.34[a,d] 1.42[a,e]	1.38[a,f]	–	0.3	0.98[g]	2.4[h]
Low acrolein content	360–361	0.052[b,d] 0.055[b,e]		0.0012[c,d] 0.0012[c,e]	0.076	–	–

Reaction conditions:
[a] – [C=O] 5 x 10^{-3} mol 1^{-1}, [DNPH] = 45 x 10^{-3} mol l^{-1}; [b] –[C=O] 0.6 x 10^{-3}, [DNPH] = 19 x 10^{-3} mol l^{-1}; [c] –[C=O] 0.2 x 10^{-3} mol l^{-1}, [DNPH] = 19 x 10^{-3} mol l^{-1}; [d] –calculated using $\epsilon = 2.42 \times 10^4$; [e] –calculated using $\epsilon = 2.29 \times 10^4$; [f,g,h] –carbonyl content calculated from N, Cl and O analysis respectively.

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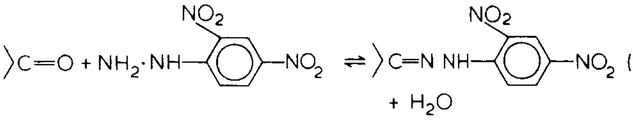
* The value of the carbonyl content as determined by the i.r. analysis agreed closely with the value obtained by an independent radiotracer method[20].

hydrazone formation to be described by the overall equation:



(5)

Table 4 Analysis of the carbonyl content of poly(methylvinylketone-co-styrene)

DNPH Derivative λ_{max} (nm)	Carbonyl content (mol g^{-1}) x 10^4		
	METHOD I	METHOD II	i.r.
365	3.3^a $(3.1)^{a,d}$	0.012^a $0.31^{a,b}$	17.8
368	0.55^c		17.8

Reaction conditions:
[a] –[C=O] = 16 x 10^{-3} mol l^{-1}; [DNPH] = 180 x 10^{-3} mol l^{-1}
[b] –T = 90° C
[c] –[C=O] = 4 x 10^{-3} mol l^{-1}; [DNPH] = 18 x 10^{-3} mol l^{-1}
[d] –Duplicate experiment

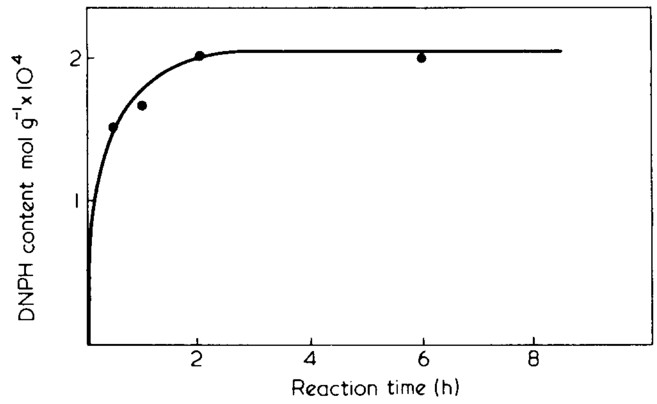


Figure 1 Plot of polymeric hydrazone formation *versus* time, for poly(styrene-co-methylvinyl ketone). Method I analysis. [>C=O] = 16 x 10^{-3} mol l^{-1}; [DNPH] = 180 x 10^{-3} mol l^{-1}

Adopting normal conventions the equilibrium constant (K) for the reaction may be written as:

$$K = \frac{[C{=}NR]_{eq}}{[C{=}O]_{eq}\,[DNPH]_{eq}} \qquad (6)$$

where, $[\;]_{eq}$ refers to equilibrium concentrations. Since the polymeric hydrazone concentration is determined directly by u.v. analysis, and as the equilibrium concentrations of ketonic groups and DNPH can be readily calculated values of K may be derived. (*Table 5*). It can be seen that K remains approximately constant as the reactant concentrations are varied thus confirming the presence of an equilibrium reaction which in turn explains the observed variation of hydrazone content with reactant concentrations. The reversible nature of the polymeric hydrazone formation was further demonstrated by experiments wherein the preformed derivative was refluxed in the acidified reaction mixture in the absence of added DNPH. An approximately 30% reduction in the bound hydrazine content was observed.

Clearly the value of K precludes the quantitative determination of ketone content by DNPH analysis, for this particular system.

Analysis of carboxylic and epoxy functional groups

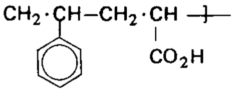
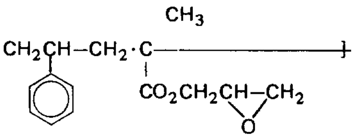
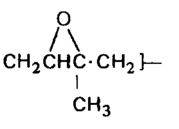
Table 6 reveals that carboxylic acids, and internal and terminal epoxides do not react significantly with DNPH under the reaction conditions employed with either Method I or II. Somewhat higher analysis figures were obtained for

Table 5 Equilibrium constant for hydrazone formation

	[>C=O] (mol l^{-1}) x 10^3	[DNPH] (mol l^{-1}) x 10^3	$[>C{=}NR]_{eq.}$ (mol l^{-1}) x 10^3	K (1 mol^{-1})
Case I	4.1	18	0.12	1.7
Case II	16	180	2.8	1.2
Case III[a]	16	180	2.95	1.3
				Mean = 1.4

[a] –A duplicate determination of case II

Table 6 Analysis of carbonyl and epoxy functional groups

Functional Group	DNPH Derivative λ_{max} (nm)	Functional group analysis (mol g^{-1}) x 10^3			
		METHOD I	METHOD II	I.R.	HBr Titration
	364	5.8 x 10^{-3}	1.8 x 10^{-3}	1.53	–
	353	2.2 x 10^{-3}	2.6 x 10^{-4}	–	1.95
	353	6.6 x 10^{-3} 26 x 10^{-3} a	–	–	0.78

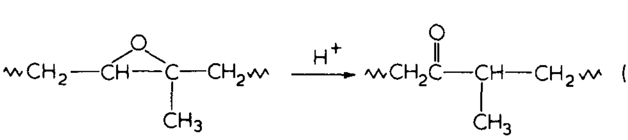
[a] –As for Method I but HCl replaced by 4 ml 85% H_3PO_4

Table 7 DNPH analysis of natural rubber

Sample	DNPH Derivative λ_{max} (nm)	Carbonyl content[b] (mol g^{-1}) x 10^6 METHOD I	METHOD II	Modified METHOD II
A[a]	353–355	4.5 (5.0)[c]	2.9	–
B[a]	353–355	5.1	2.6	4.8 (4.4)[d]
Literature Value[a]	358	–	3.7[e]	4.5[f]

[a] –Fresh natural rubber samples isolated from different batches of rubber latex (clone RRIM 600)
[b] –Calculated using ϵ = 2.42 x 10^4 (acetaldehyde derivative)
[c] –Duplicate sample
[d] –No added HCl catalyst
[e] –From reference 1
[f] –From reference 2

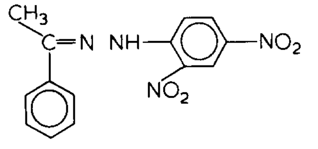
epoxidized N.R. (internal epoxide) by using 85% phosphoric acid as catalyst under Method I conditions. Such incorporation could occur via rearrangement[23] of the epoxide (equation 7).


(7)

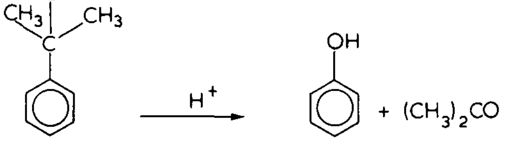
and subsequent determination of the ketone, rather than by direct reaction with the epoxide.

Analysis of hydroperoxide groups

Although no model polymeric hydroperoxide compounds were prepared, it was of interest to see whether DNPH would form derivatives with low molecular weight hydroperoxides. Accordingly, the reaction of cumene hydroperoxide was investigated. Addition of cumene hydroperoxide to the DNPH reagent solution, specified in the experimental, gave rise to an immediate precipitate, which appears to be the acetophenone derivative (I). (M.Pt. 236–238°C, Lit.Val. 1^t250 (237)°C:


(I)

This observation is unusual, since acid catalysed hydrolysis of cumene hydroperoxide normally results in quantitative formation of acetone[24] (equation 8).


(8)

This would suggest that the DNPH reagent reacts directly with the hydroperoxide or with a reactive intermediate rather than with the product ketone.

Whatever the mechanism of this reaction it seems probable that DPNH could react with polymeric hydroperoxide groups.

Analysis of fresh natural rubber

Two separate samples of natural rubber which had been isolated from freshly tapped rubber latex, by acetic acid coagulation and handled with minimum exposure to atmospheric oxygen, were analysed by both DNPH methods (*Table 7*). It is apparent that hydrazone formation occurs, in general agreement with earlier work[1,2], but that Method I as in previous analyses, yields significantly higher hydrazone levels.

DISCUSSION

Specificity of DNPH Reagent

The results obtained in this work clearly demonstrate that, under the reaction conditions employed, the DNPH reagent may be considered a specific[25] reagent for aldehyde and ketonic groups. Thus the presence of carboxylic acid, ester or epoxide groups will not significantly interfere in the determination of the former groups in oxidized polymers.

Quantitative aspects of DNPH reaction

The acid catalysed DNPH analysis (Method I) appears to provide quantitative estimations of polymeric aldehyde groups at high or low concentrations, whereas, the milder DNPH reaction conditions (Method II) are not quantitative particularly at low concentrations, when only a small fraction (~2%) of groups are analysed. The inefficiency of Method II must be attributed to the kinetic features of the reaction, mentioned earlier. The reaction being essentially incomplete under the reaction conditions employed. It should be emphasized that these conclusions only strictly apply to the particular model copolymer investigated since the reactivity of the polymeric aldehyde groups will be markedly dependent on steric factors which are determined by their polymeric environment (*vide infra*).

On the other hand, both DNPH methods prove inadequate for the determination of ketonic groups in the model poly(methylvinyl ketone-co-styrene). In this case, the failure to obtain a quantitative analysis is determined largely by thermodynamic factors, which prohibit complete reaction of ketonic groups. (These could possibly be overcome by concomittant removal of water from the reaction medium thereby forcing the equilibrium (equation 5) to the right).

Quantitative aspects of the u.v. analysis

Although the u.v. absorption of polymeric DNPH derivatives can be determined accurately, calculation of the cor-

Table 8 Comparison of λ_{max} for DNPH derivatives of polymers and low molecular weight compounds

Functional group	λ^a_{max} DNPH Derivative (nm) Model Compound	Polymeric Analogue
R—CHO	356	360–361
–CH=CH–CHO	370	–
$>$C=O	360	365–368
	340	353
Natural rubber	?	353–355

[a] –All u.v. samples run in $CHCl_3$ solution

responding carbonyl concentration in hindered by the necessity of assuming the validity of the extinction coefficient of an appropriate model derivative. In this work differences of about 5% were observed between the extinction coefficients of possible models (*Table 1*). However, an independent nitrogen analysis confirmed that in this case, the extinction coefficients of the model compounds corresponded fairly closely to that of the polymeric derivative (*vide supra*). A further difficulty is the possibility that the extinction coefficient of the polymeric derivative may be concentration dependent, as has been observed[29] for polymeric carbazole derivatives, where the molar extinction coefficient decreases with increasing carbazole content due to interaction between adjacent chromophores.

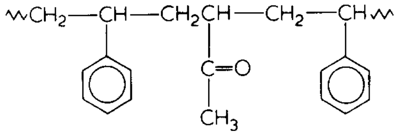
These uncertainties could be obviated by recourse to nitrogen analysis at high DNPH contents or a radiotracer technique for low levels of incorporation.

Analysis of oxygenated groups in natural rubber

In earlier work[1,2], DNPH has been shown to form derivatives with natural rubber, and these have been attributed to the presence of naturally occurring aldehyde groups. These conclusions have been questioned[26] since it appeared likely that DNPH could also react with other oxygenated groups believed to be present in natural rubber. However, the results of this work support[25] the original assignment, since low concentrations of functional groups such as carboxylic acid, ester, or epoxide groups would not give significant incorporation under the reaction conditions employed. Furthermore, the observation (*Table 7*) that the DNPH incorporation into rubber is of the same order of magnitude for the two methods, strongly suggests the presence of aldehydic rather than ketonic groups, since the latter are much less reactive and would be expected to give very low values by Method II. This inference is further corroborated by the recent publication[31] of work which demonstrates that the aldehyde content of fresh rubber may also be specifically determined by reaction with ^{14}C labelled dimedone. The value so obtained for a particular rubber sample (5.4×10^{-6} mol/g) agreed closely with that obtained from the DNPH Method I analysis (5.3×10^{-6} mol/g).

On the other hand it would appear unlikely that the rubber aldehyde groups have been analysed quantitatively in the earlier work[1], where the Method II analysis was employed. This is evident from the comparison of the hydrazone content of N.R. determined by the two methods (*Table 7*). This point appears to have been realized and in more recently published work[2] a modified Method II analysis is employed. The modified method, employing higher rubber and DNPH concentrations and an acid catalyst, gives values approaching the Method I analysis (*Table 7*).

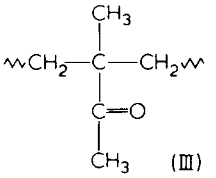
Elsewhere[4], the DNPH Method I analysis has been employed to determine total concentrations of small amounts of aldehyde and ketone groups in oxidized natural rubber samples. A superficial comparison of the results obtained in this work would indicate that the analysis of ketonic groups in natural rubber was non-quantitative. However, the self-consistency of the reported results[4] provides strong internal evidence that an adequate analysis was in fact effected. One must therefore conclude that the effectiveness of the DNPH analysis on both kinetic and thermodynamic grounds is largely governed by the polymeric environment of the bound functional groups. Thus, it is not unreasonable to suppose that reaction of DNPH with ketonic groups in the model copolymer (II) is more sterically hindered and thus less efficient than the analogous reaction with terminal ketonic groups in natural rubber. The effects of polymer microstructure on reactivity of functional groups clearly merit further investigation.



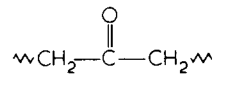
(II)

Analysis of carbonyl groups in oxidized polyethylene

Recently[10] a DNPH analysis method has been used to study carbonyl groups in oxidized polyethylene. In a comparison of the reaction of DNPH with films of oxidized polyethylene and a model copolymer poly(ethylene-co-methylisoprenyl ketone) it was observed that the rate of reaction of the former was very much faster than the latter. This was interpreted as an indication that the reactivity of the surface carbonyl groups in the oxidized polymer, was greater than that of the uniformly distributed carbonyl groups in the model copolymer. However, in accord with the above discussion the differences in reactivity may in fact be attributable to the sensitivity of the DNPH reaction to the steric environment of the reactive functional group. Thus carbonyl groups in the model copolymer (III) would be significantly hindered compared to the probable structure of polyethylene ketonic groups (IV).



(III)



(IV)

Alternatively the greater reactivity of the oxidized poly(ethylene) may reflect the involvement of the more reactive aldehydic groups. This latter interpretation appears less likely since recent i.r. studies[27] indicate that ketonic and acidic groups are the major products in oxidized poly(ethylene).

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