Network Formation III—Influence of Organometallic Initiator on Network Structure

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The nature of the primary radicals arising from the interaction of halides and organometallic derivatives has been investigated with the aid of tracer and gelation techniques. Halides studied include carbon tetrachloride and esters of trichloracetic acid; with $Mo(CO)_6$, $Mn_2(CO)_{10}$ and $Pt(PPh_3)_4$ these yield radicals derived from the halide by removal of chlorine atoms to give 'attached' primary radicals. The nickel derivatives $Ni\{P(OPh)_3\}_4$, $Ni(CO)_4$, $Ni(CO)_2(PPh_3)_2$ produce some radicals which do not contain an organic residue and are therefore 'unattached'; these may be chlorine atoms or an adduct with monomer. Since unattached radicals promote branch formation, the use of the nickel derivatives increases the range of available network structures. Values for the ratio of combination to disproportionation in the termination reaction of methyl methacrylate polymerization are a byproduct of these investigations and are given for three temperatures.

1. INTRODUCTION

THE primary radicals formed by interaction of organometallic compounds and organic halides are frequently those derived by chlorine-atom abstraction from the halogen-containing groups. For example, carbon tetrachloride[1,2] or an organic trichloracetate[2] yield as radical products only $\dot{C}Cl_3$ or $Cl_2\dot{C}COOR$, respectively, on thermal interaction with molybdenum carbonyl at 80°C, or on photochemical reaction with manganese carbonyl ($\lambda = 4\,358$Å) at 25°C. The primary radicals produced from a polymeric halide such as polyvinyl trichloracetate by this type of reaction are attached to the polymer chain, and may be utilized in network syntheses as already described[3]. The previous paper[2] shows that attached radicals are also the sole or predominating products in the presence of benzene, ethyl acetate or dioxan.

The nature of the primary radical depends on the details of the electron-transfer process. If the latter results in scission of a chloride ion an attached radical is formed, but it is at least conceivable that electron-transfer to a halide containing electron-withdrawing groups would lead to a different result with formation of an unattached radical—a chlorine atom—and an organic anion. Since the anion would be associated with the metal, the relative probabilities of the two reaction paths may be determined by the nature of the metal as well as that of the halide.

In the synthesis of networks, the formation of unattached primary radicals would lead to unattached propagating polymer radicals and ultimately to branches (instead of crosslinks) together with some soluble polymer. For a given rate of initiation, the gel-time will clearly be longer if unattached primary radicals are generated. We have now investigated the

character of the primary radicals produced with the aid of derivatives of different metals by the gelation technique and also by the use of tracers and the results are described in the present paper.

2. EXPERIMENTAL

Materials

The organometallic derivatives studied were $Mo(CO)_6$, $Mn_2(CO)_{10}$, $Ni(CO)_4$, $Ni(CO)_2(PPh_3)_2$, $Ni\{P(OPh)_3\}_4$, $Pt(PPh_3)_4$. These materials, with the exception of nickel carbonyl, were purified as described in earlier papers[3-6]. Nickel carbonyl was vaporized from a cylinder and condensed into benzene; the concentration of the benzene solution was determined by estimation of the nickel content with dimethylglyoxime.

The following labelled halides were employed: $^{14}CCl_4$, $^{14}CCl_3COOCH_2CH_3$, $CCl_3^{14}COOCH_2CH_3$, $CCl_3COO^{14}CH_2CH_3$. Labelled carbon tetrachloride was purchased from the Radiochemical Centre, Amersham, and suitably diluted with inactive AR CCl_4. The preparation and purification of $CCl_3^{14}COOCH_2CH_3$ were described in Part II[2]. Pure samples of the other ethyl trichloracetates were obtained by a similar procedure; the appropriate labelled starting materials $^{14}CCl_3COOH$ and $CH_3^{14}CH_2OH$ were purchased from the Radiochemical Centre, Amersham, and diluted with the inactive materials before use.

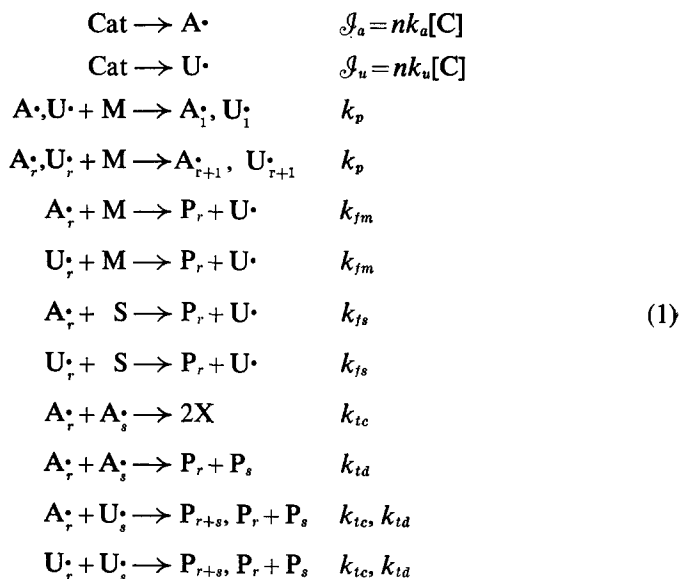Methyl methacrylate and polyvinyl trichloracetate (the prepolymer) were prepared and purified as in earlier work[3].

Techniques

The measurement of gel-times has already been described[3]. Rates of polymerization were determined gravimetrically, and the molecular weights of the resulting polymers were measured viscometrically with the aid of the relation between $[\eta]$ and $\overline{M}_n$ given by Fox, Kinsinger, Mason and Schuele[7], modified[5] to allow for the incidence of combination in the termination reaction. Polymerizations initiated by $Ni(CO)_4$ are strongly inhibited by carbon monoxide, which is a product of the initiation reaction. To minimize changes in reaction rate[8], the polymerizations were carried out in vessels with a dead space equal to 20 times the volume of the reaction mixture.

The activities of the labelled polymers were measured by internal liquid scintillation counting as described in Part II[2].

3. EFFECT OF FORMATION OF UNATTACHED PRIMARY RADICALS ON GEL-TIME

In this section we develop relations between the observed gel-time and the corresponding value of t_g^0, the gel-time corresponding to the same rate of initiation if formation of unattached radicals, consumpton of initiator and chain transfer were all negligible. t_g^0 is given in equation (2) of Part II[2]. The kinetic scheme and nomenclature employed below are similar to those of Part II[2].

$$\text{Cat} \longrightarrow \text{A·} \qquad \mathcal{J}_a = nk_a[\text{C}]$$

$$\text{Cat} \longrightarrow \text{U·} \qquad \mathcal{J}_u = nk_u[\text{C}]$$

$$\text{A·,U·} + \text{M} \longrightarrow \text{A}_1^·, \text{U}_1^· \qquad k_p$$

$$\text{A}_r^·, \text{U}_r^· + \text{M} \longrightarrow \text{A}_{r+1}^·, \text{U}_{r+1}^· \qquad k_p$$

$$\text{A}_r^· + \text{M} \longrightarrow \text{P}_r + \text{U·} \qquad k_{fm}$$

$$\text{U}_r^· + \text{M} \longrightarrow \text{P}_r + \text{U·} \qquad k_{fm}$$

$$\text{A}_r^· + \text{S} \longrightarrow \text{P}_r + \text{U·} \qquad k_{fs} \qquad (1)$$

$$\text{U}_r^· + \text{S} \longrightarrow \text{P}_r + \text{U·} \qquad k_{fs}$$

$$\text{A}_r^· + \text{A}_s^· \longrightarrow 2\text{X} \qquad k_{tc}$$

$$\text{A}_r^· + \text{A}_s^· \longrightarrow \text{P}_r + \text{P}_s \qquad k_{td}$$

$$\text{A}_r^· + \text{U}_s^· \longrightarrow \text{P}_{r+s}, \text{P}_r + \text{P}_s \qquad k_{tc}, k_{td}$$

$$\text{U}_r^· + \text{U}_s^· \longrightarrow \text{P}_{r+s}, \text{P}_r + \text{P}_s \qquad k_{tc}, k_{td}$$

$\mathcal{J}_a$, $\mathcal{J}_u$ represent the rates of formation of attached and unattached radicals, with rate constants k_a, k_u, respectively. As before[2] we use $R_a = \sum_r [\text{A}_r^·]$, $R_u = \sum_r [\text{U}_r^·]$. If R_a, R_u are stationary, we have:

$$dR_a/dt = \mathcal{J}_a - k_{fm}R_a[\text{M}] - k_{fs}R_a[\text{S}] - k_t R_a(R_a + R_u) = 0 \qquad (2)$$

$$dR_u/dt = \mathcal{J}_u + k_{fm}R_a[\text{M}] + k_{fs}R_a[\text{S}] - k_t R_u(R_a + R_u) = 0 \qquad (3)$$

From these equations it follows that

$$R_u/R_a = 1/f + (1 + 1/f)(k_p/\mathcal{J}k_t)^{\frac{1}{2}}(C_m[\text{M}] + C_s[\text{S}]) \qquad (4)$$

where $\mathcal{J} = \mathcal{J}_a + \mathcal{J}_u$ and $f = \mathcal{J}_a/\mathcal{J}_u$. The observed gel-time t_g is given in terms of t_g^0 by

$$t_g^0 = t_g[R_a/(R_a + R_u)]^2 \qquad (5)$$

or, from (4),

$$t_g^0 = [f/(1+f)]^2[t_g/(1+B)^2] \qquad (6)$$

where (cf. Part II[2])

$$B = (k_p/k_t^{\frac{1}{2}})\{C_m[\text{M}] + C_s[\text{S}]\}/\mathcal{J}^{\frac{1}{2}} \qquad (7)$$

We see from (6) that the effects on the gel-time of unattached radical formation and chain transfer are separable. Allowance for initiator con-

sumption may therefore be deduced directly from the results in Part II[2], § 3, the complete relation being.

$$t^0_g = \frac{1}{k}\left(\frac{f}{1+f}\right)^2 \left\{1 - y^2 - 4B_0(1-y) + 6B_0^2\ln\left(\frac{1+B_0}{y+B_0}\right) - \frac{2B_0^3(1-y)}{(1+B_0)(y+B_0)}\right\} \quad (8)$$

in which $y = e^{-kt_g/2}$, k is the first order rate constant for initiator decay and B_0 is the initial value of B, i.e. with $\mathscr{I} = \mathscr{I}_0$.

Note that k_t is assumed constant in the pre-gelation period. This has been justified in Part II.

The quantity $f/(1+f)$ is the fraction of the total primary radicals which are attached to the chains of the polymeric halide.

4. RESULTS AND DISCUSSION

In studies with labelled halides as components of the initiating system we have determined the following quantities: (i) the rates of polymerization ω; (ii) the activities of the polymer n_p, expressed as counts per 100 s per 100 mg of polymer; and (iii) the number of counts per 100 s per mole of the halide, n_h. The mean kinetic chain length is given by

$$\bar{\nu} = 10^{-3}(n_h/n_p)(f/[1+f]) \quad (9)$$

From the data mentioned above we have calculated the rate of formation $\mathscr{I}^\star$ of radicals containing a labelled atom; the required relation is

$$\mathscr{I}^\star = \mathscr{I}f/(1+f) = 10^3\omega(n_p/n_h) \quad (10)$$

It will be seen that $\mathscr{I}^\star$ and $\mathscr{I}_a$ both represent the same quantity; the former symbol issued to indicate values derived from tracer studies. We also tabulate values of $\xi = \mathscr{I}^\star/\omega^2$, which is the rate of formation of attached radicals per unit rate of polymerization. In the general case

$$k_p k_t^{-\frac{1}{2}} = \{1/[M]\xi^{\frac{1}{2}}\}f/(1+f) \quad (11a)$$

If all primary radicals are attached (11a) can be reduced to

$$k_p k_t^{-\frac{1}{2}} = 1/\{[M]\xi^{\frac{1}{2}}\} \quad (11b)$$

Note that equations (9) and (10) are independent of the ratio of combination to disproportionation, and also of the occurrence of chain transfer, except to halide, which is negligible in these experiments.

In some cases the molecular weights of the resulting polymers were measured viscometrically.

4.1 Mo(CO)₆, Mn₂(CO)₁₀ and Pt(PPh₃)₄

4.1.1 Information from tracer studies—Table 1 presents data for molybdenum carbonyl with the halides $^{14}CCl_4$ and $CCl_3^{14}COOEt$, details for each experiment being given to illustrate the reproducibility. Within experimental error ξ has the same value for the two systems. The mean value of $k_p k_t^{-\frac{1}{2}}$ estimated from (11b) for all the experiments in Table 1 is 0·13 mole$^{-\frac{1}{2}}$ l$^{\frac{1}{2}}$ s$^{-\frac{1}{2}}$, which is in the range normally encountered in poly-

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merizations of methyl methacrylate at 80°C initiated by molybdenum carbonyl in conjunction with organic halides. We therefore believe that effectively all the primary radicals in the systems in *Table 1* are of the attached type.

Table 1. Polymerization of methyl methacrylate at 80°C. Initiation by Mo(CO)$_6$ and labelled halides.

(1)   [^{14}CCl$_4$] = 0·03 mole l^{-1}; n_h = 9·65 × 10^9 counts per 100 s per mole

$10^4\omega$, mole l^{-1} s^{-1}	n_p, counts per 100 s per 100 mg	$10^8 \mathcal{J}\star$, mole l^{-1} s^{-1}	$\xi = \mathcal{J}\star/\omega^2$, mole^{-1} l s
1·61	1227	2·05	0·792
1·47	1295	1·97	0·915
1·50	1266	1·97	0·875
1·70	1351	2·38	0·825
1·56	1218	1·97	0·812
1·49	1198	1·86	0·836
		mean:	0·843

(2)   [CCl$_3$^{14}COOEt] = 0·03 mole l^{-1}; n_h = 8·75 × 10^9 counts per 100 s per mole

2·24	1613	4·13	0·825
1·96	1459	3·28	0·854
2·00	1706	3·90	0·975
2·19	1747	4·36	0·910
2·09	1396	3·34	0·765
2·08	1764	4·20	0·970
2·05	1321	3·10	0·739
		mean:	0·863

[Mo(CO)$_6$] = 3·49×10^{-4} mole l^{-1}; [monomer] = 8·7 mole l^{-1} initially; conversions (1) 4 per cent, (2) 5 per cent, approximately.

Similar data for the polymerization reaction at 25°C photosensitized by Mn$_2$(CO)$_{10}$ are presented in *Table 2*. Again we see that there is no significant difference in the values of ξ for the two halides. In each case $k_p k_t^{-\frac{1}{2}}$ calculated from (11b) has the normal value 0·055 mole$^{-\frac{1}{2}}$ l$^{\frac{1}{2}}$ s$^{-\frac{1}{2}}$, so we conclude that in both systems effectively all the primary radicals are attached.

Measurement of the molecular weight of the polymer formed allows calculation of μ, the fraction of the termination which occurs by combination, from the relation

$$\mu = k_{tc}/(k_{tc} + k_{td}) = 2(1 - \bar{\nu}/\bar{P}_n) \tag{12}$$

The mean values of $\bar{P}_n$ were 1 640 and 1 230 for CCl$_4$ and CCl$_3$COOEt, respectively. Substitution into (12), with the values of $\bar{\nu}$ in *Table 2*, gives $\mu = 0·43$ and 0·22, respectively; the discrepancy between the two estimates is attributable to the sensitivity of (12) to errors in $\bar{\nu}$ and $\bar{P}_n$. A mean value of μ at 25°C obtained from all systems considered in this paper which give attached radicals is 0·33, a figure close to that reported by Bevington *et al.*[9] (see *Table 7*).

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Table 2. Photopolymerization of methyl methacrylate at 25°C.
Initiation by $Mn_2(CO)_{10}$ and labelled halides.

(1) $[^{14}CCl_4] = 0.03$ mole l^{-1}; $n_h = 9.65 \times 10^9$ counts per 100 s per mole

$10^4\omega$, mole $l^{-1}s^{-1}$	n_p, counts per 100 s per 100 mg	$10^7 \mathcal{J}\star$, mole $l^{-1} s^{-1}$	$\xi = \mathcal{J}\star/\omega^2$, mole^{-1} l s	$10^{-3} \bar{\nu}$
2·1	7854	1·71	3·89	1·23
2·1	8078	1·76	4·00	1·20
1·8	6351	1·19	3·69	1·53
2·1	8019	1·75	3·97	1·20
1·9	7584	1·49	4·13	1·275
		means:	3·94	1·29

(2) $[CCl_3{}^{14}COOEt] = 0.03$ mole l^{-1}; $n_h = 8.75 \times 10^9$ counts per 100 s per mole

2·30	8037	2·11	3·99	1·09
2·23	8289	2·12	4·26	1·06
2·24	8027	2·05	4·08	1·09
2·08	7515	1·79	4·14	1·16
2·20	8191	2·06	4·26	1·07
		means:	4·15	1·09

$[Mn_2(CO)_{10}] = 5.14 \times 10^{-4}$ mole l^{-1}; [monomer] ≈ 9.3 mole l^{-1} initially; conversions 4 per cent approximately.

A similar conclusion about the nature of the primary radicals may be drawn from the data in *Table 3*, which refer to the polymerization initiated by $Pt(PPh_3)_4$ in the presence of halide. Mean results of four experiments are quoted for each system. $k_p k_t^{-\frac{1}{2}}$ deduced from (11b) has the normal value $(0.11$ mole$^{-\frac{1}{2}}$ l$^{\frac{1}{2}}$ s$^{-\frac{1}{2}})$ at 60°C.

Table 3. Polymerization of methyl methacrylate at 60°C.
Initiation by $Pt(PPh_3)_4$ and labelled halides.

(1) $[^{14}CCl_4] = 0.03$ mole l^{-1}; $n_h = 9.65 \times 10^9$ counts per 100 s per mole

$10^5\omega$, mole $l^{-1} s^{-1}$	n_p, counts per 100 s per 100 mg	$10^9 \mathcal{J}\star$, mole $l^{-1} s^{-1}$	$\xi = \mathcal{J}\star/\omega^2$ mole^{-1} l s
5·57	630	3·65	1·18

(2) $[CCl_3{}^{14}COOEt] = 0.03$ mole l^{-1}; $n_h = 8.75 \times 10^9$ counts per 100 s per mole

10·7	1082	13·3	1·16

$[Pt(PPh_3)_4] = 3.22 \times 10^{-4}$ mole l^{-1}; [monomer] $= 8.96$ mole l^{-1}, initially; conversions (1) 1·5 per cent, (2) 2·5 per cent, approximately.

4.1.2 Gelation studies—t^0_g was calculated with the aid of equation (8) and kinetic parameters given in earlier papers[2, 6, 10, 11]. *Figure 1* shows plots of $1/t^0_g$ against the rate of chain starting for the three organometallic derivatives. Instead of the linear relation predicted for an uncomplicated system, the plots are somewhat curved, indicating radical wastage at the higher rates of initiation. Reasons for this have already been advanced[3], and will not be discussed further here. The interesting feature for present purposes is that the three curves have similar shapes. In fact curve 1 referring to $Mn_2(CO)_{10}$ (25°C) can be made to approximate closely to 2 $[Pt(PPh_3)_4, 60°C]$ and 3 $[Mo(CO)_6, 80°C]$ by multiplication of the ordinates by factors 0·82
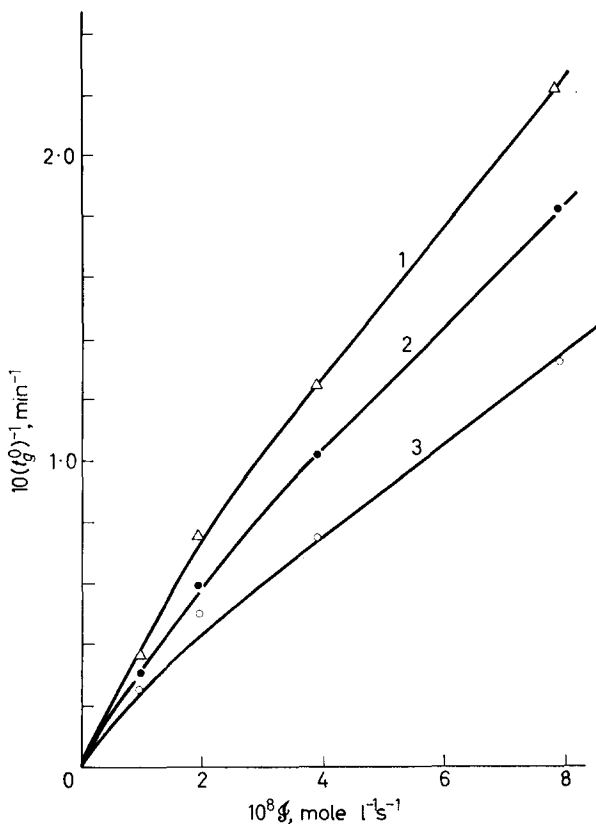
Figure 1—Dependence of gel-time on rate of initiation at three temperatures, for systems in which all primary radicals are attached. [prepolymer]$=2\cdot6\times10^{-2}$ base mole l^{-1}; methyl methacrylate—bulk. 1. 25°C, photoinitiation by $Mn_2(CO)_{10}$, $\lambda=4\,358$Å; 2. 60°C, thermal initiation by $Pt(PPh_3)_4$; 3. 80°C, thermal initiation by $Mo(CO)_6$. Curves 2 and 3 derived from 1 as described in text (§ 4.1.2)

and 0·61 respectively. These results would be expected if the primary radicals were attached in all cases, and if the proportion of combination in the termination reaction decreases with increasing temperature. All observers[9, 12] agree that μ shows a qualitative dependence on temperature of this kind. If we accept the value $\mu=0\cdot33$ at 25°C, we find that at 60°C $\mu=0\cdot27$ and at 80°C $\mu=0\cdot20$.

4.2 $Ni\{P(OPh)_3\}_4$, $Ni(CO)_2(PPh_3)_2$ and $Ni(CO)_4$

4.2.1 Tracer studies—Data for the first of these are presented in *Table 4*. In experiments with CCl_4, the value of $k_p k_t^{-\frac{1}{2}}$ derived from values of ξ with the aid of equation (11b) is reasonably close to the normal figure for methyl methacrylate polymerization at 25°C, and is indeed identical with the estimate made in the conventional way from measurements of ω and $\overline{P}_n$

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[*Table 4* (1)]. Bamford and Hargreaves[5], using the latter procedure, obtained $k_p k_t^{-\frac{1}{2}} = 0.053$ mole$^{-\frac{1}{2}}$ l$^{\frac{1}{2}}$ s$^{-\frac{1}{2}}$. There is therefore no doubt that $\mathscr{J}\star$ represents the total rate of radical formation, and all that the primary radicals are attached, i.e. they are $\dot{C}Cl_3$. A completely different situation is encountered with $CCl_3{}^{14}COOEt$ as halide [*Table 4* (2)]. Here the values of ξ are con-

Table 4. Polymerization of methyl methacrylate at 25°C.
Initiation by Ni{P(OPh)₃}₄ and labelled halides.

(1) [¹⁴CCl₄]=0·03 mole l⁻¹; n_h=9·65×10⁹ counts per 100 s per mole

$10^5\omega$, mole l⁻¹ s⁻¹	n_p, counts per 100 s	$10^8 \star$, mole l⁻¹ s⁻¹	$\xi= \star/\omega^2$, mole⁻¹ l s	$10^{-3}\bar{\nu}$, mean	$10^{-3}\bar{P}_n$, mean	$k_p k_t^{-\frac{1}{2}}$, mean, mole⁻½ l½ s⁻½	
						from (11b)	from $\bar{P}_n$
7·41	2919	2·24	4·08				
7·74	3017	2·41	4·03				
8·00	3049	2·54	3·96				
7·72	3593	2·87	4·81				
7·57	3505	2·75	4·80	2·92	3·55	0·052	0·052
7·45	3611	2·79	5·01				
7·57	3622	2·84	4·95				
			mean: 4·52				

(2) [CCl₃¹⁴COOEt]=0·03 mole l⁻¹; n_h=8·75×10⁹ counts per 100 s per mole

8·02	1652	1·515	2·35				
7·92	1610	1·46	2·32				
7·30	1592	1·33	2·50			0·071	0·052
			mean: 2·39				

[Ni{P(OPh)₃}₄]=1·60×10⁻⁴ mole l⁻¹; [monomer]=9·3 mole l⁻¹ initially; conversions (1) 3 per cent, (2) 3·5 per cent, approximately.

siderably lower than those obtained with CCl_4 and $k_p k_t^{-\frac{1}{2}}$ calculated from ξ as above is unacceptably high (0·071 mole$^{-\frac{1}{2}}$ l$^{\frac{1}{2}}$ s$^{-\frac{1}{2}}$). However, the value estimated from $\bar{P}_n$ is normal. It follows that $\mathscr{J}\star$ corresponds to only a portion of the total rate of initiation, so that a significant fraction of the primary radicals must be unattached, and contain no labelled atom (i.e. $f/(1+f) < 1$).

Tables 5 and *6* present results for Ni(CO)₂(PPh₃)₂ and Ni(CO)₄. The conclusions to be drawn are in each case similar to those for Ni{P(OPh)₃}₄. With CCl_4 as halide, $k_p k_t^{-\frac{1}{2}}$ derived from activity measurements and equation (11b) agrees with that from degrees of polymerization; the values in *Table 5* may be compared with that obtained in the same system (with inactive CCl_4) by Bamford and Hargreaves[4]—0·054 mole$^{-\frac{1}{2}}$ l$^{\frac{1}{2}}$ s$^{-\frac{1}{2}}$. All the primary radicals are therefore of the attached type. On the other hand, with the esters as halides, both nickel derivatives show lower values of ξ and correspondingly higher values of $k_p k_t^{-\frac{1}{2}}$ estimated from (11b). In these systems, a significant part of the initiation reaction must involve unattached radicals.

Table 5. Polymerization of methyl methacrylate at 25°C.
Initiation by $Ni(CO)_2(PPh_3)_2$ and labelled halides.
(1) $[^{14}CCl_4] = 0.03$ mole l^{-1}; $n_h = 9.65 \times 10^9$ counts per 100 s per mole

$10^5\omega$, mole $l^{-1} s^{-1}$	n_p counts per 100 s per 100 mg	$10^8\mathcal{J}\star$, mole $l^{-1} s^{-1}$	$\xi = \mathcal{J}\star/\omega^2$, mole^{-1} l s	$10^{-3}\bar{\nu}$ mean	$10^{-3}\bar{P}_n$ mean	$k_p k_t^{-\frac{1}{2}}$, mean mole$^{-\frac{1}{2}}$ l$^{\frac{1}{2}}$ s$^{-\frac{1}{2}}$	
						from (11b)	from $\bar{P}_n$
7·51	2470	1·92	3·40				
7·65	2881	2·28	3·90				
8·03	2690	2·23	3·47				
6·95	2603	1·875	3·88	3·82	4·52	0·056	0·055
6·70	2395	1·66	3·71				
6·30	2620	1·71	4·30				
6·05	2161	1·355	3·70				
			mean: $\overline{3\cdot77}$				

(2) $[CCl_3^{14}COOEt] = 0.03$ mole l^{-1}; $n_h = 8.75 \times 10^9$ counts per 100 s per mole

8·4	2020	1·94	2·75				
7·4	1842	1·56	2·84	3·61		0·064	0·054
8·2	2171	2·03	3·02				
9·1	2385	2·38	2·99				
			mean: $\overline{2\cdot90}$				

$[Ni(CO)_2(PPh_3)_2] = 3.40 \times 10^{-4}$ mole l^{-1}; [monomer] = 9·3 mole l^{-1} initially; conversions (1) 3 per cent, (2) 2·5 per cent, approximately.

Table 6. Polymerization of methyl methacrylate at 25°C.
Initiation by $Ni(CO)_4$ and labelled halides.
(1) $[^{14}CCl_4] = 0.03$ mole l^{-1}; $n_h = 9.65 \times 10^9$ counts per 100 s per mole

$10^5\omega$, mole $l^{-1} s^{-1}$	n_p counts per 100 s per 100 mg	$10^9\mathcal{J}\star$, mole $l^{-1} s^{-1}$	$\xi = \mathcal{J}\star/\omega^2$, mole^{-1} l s	$10^{-3}\bar{\nu}$ mean	$10^{-3}\bar{P}_n$ mean	$k_p k_t^{-\frac{1}{2}}$, mean, mole$^{-\frac{1}{2}}$ l$^{\frac{1}{2}}$ s$^{-\frac{1}{2}}$	
						from (11b)	from $\bar{P}_n$
9·91	4681	4·80	4·90				
9·83	4663	4·74	4·92				
9·62	3982	3·96	4·30	2·25	2·71	0·051	0·052
9·58	3972	3·95	4·29				
			mean: $\overline{4\cdot60}$				

(2) $[CCl_3^{14}COOEt] = 0.03$ mole l^{-1}; $n_h = 8.75 \times 10^9$ counts per 100 s per mole

9·07	2093	2·17	2·62				
8·29	2089	1·98	2·87	3·46		0·066	0·052
8·22	2170	2·03	3·01				
6·10	1401	0·98	2·64				
			mean: $\overline{2\cdot79}$				

$[Ni(CO)_4] = 8.82 \times 10^{-4}$ mole l^{-1}; [monomer] = 9·3 mole l^{-1}, initially; conversions 3 per cent approximately.

Table 7. Polymerization of methyl methacrylate at 25°C initiated by nickel compounds. (1) Values of $f/(1+f)$ for reactions with trichloracetate esters; (2) Fraction of combination in termination (μ) derived from tracer studies with $^{14}CCl_4$.

Derivative	$f/(1+f)$		μ
	tracers	gelation	
Ni{P(OPh)$_3$}$_4$	0·53	0·525	0·36
Ni(CO)$_2$(PPh$_3$)$_2$	0·77	0·81	0·31
Ni(CO)$_4$	0·60	0·64	0·31

The proportions of attached radicals in these reactions calculated from the above observations are given in *Table 7*, which also shows values of μ at 25°C for the termination reaction estimated with the aid of equation (12) from the data relating to CCl$_4$ in *Tables 4, 5* and *6*.

4.2.2 Gelation studies—Application of the gelation technique leads to conclusions about the nature of the primary radicals produced by the nickel derivatives which are in general agreement with those already described. Observed gel-times have been corrected for transfer to monomer and for initiator consumption with the aid of equation (8) and the kinetic
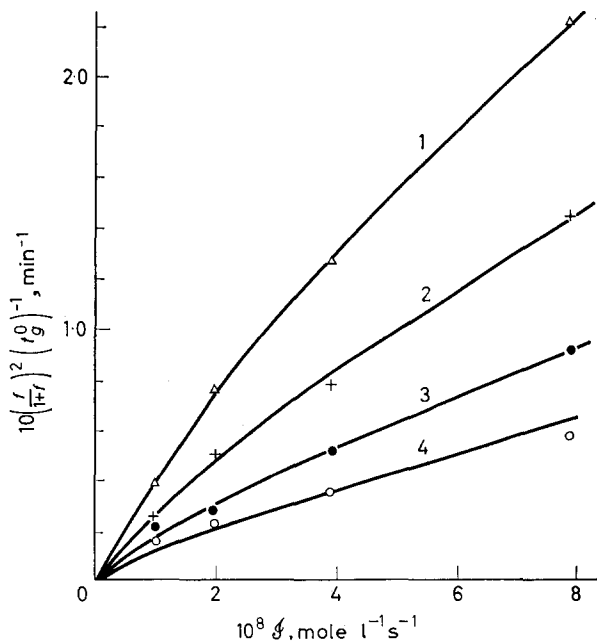

Figure 2—Dependence of gel-times on rate of initiation at 25°C. The Ni derivatives give some unattached primary radicals. [prepolymer]=2·6×10⁻² base mole l⁻¹; methyl methacrylate—bulk. 1. photoinitiation by Mn$_2$(CO)$_{10}$, λ=4 358Å; 2. thermal initiation by Ni(CO)$_2$(PPh$_3$)$_2$; 3. thermal initiation by Ni(CO)$_4$; 4. thermal initiation by Ni{P(OPh)$_3$}$_4$. Curves 2, 3 and 4 derived from 1 as described in text (§ 4.2.2). Experimental points are shown

parameters given in refs. 2, 4, 5 and 8; this equation permits calculation of $[(1+f)/f]^2\,t_g^0$, and the reciprocal of this quantity has been plotted against $\mathscr{J}$ in *Figure 2* for reactions initiated by the three nickel derivatives. Similar data for $Mn_2(CO)_{10}$ are also included for comparison; we have already seen that this initiator produces only attached primary radicals, i.e. $f/(1+f)=1$. The corrected gel-times obtained with the nickel derivatives are considerably longer than those with $Mn_2(CO)_{10}$ initiation. *Tables 4* to *6* indicate that there are no kinetic complications in the polymerizations to which these differences may be attributed, consequently it follows that the long gel-times must arise from the formation of unattached primary radicals. All curves in *Figure 2* have similar shapes, and the curve for $Mn_2(CO)_{10}$ may be brought into close proximity with those for $Ni(CO)_2(PPh_3)_2$, $Ni(CO)_4$, $Ni\{P(OPh)_3\}_4$ by multiplication of the ordinates by factors 0·66, 0·41, 0·275, respectively. We therefore equate each of these factors with $f^2/(1+f)^2$ for the appropriate initiator. The values of $f/(1+f)$ so derived are given in *Table 7*, and agree very satisfactorily with those from tracer studies.

4.3 Nature of primary radicals

To investigate further the nature of the unattached primary radicals we have examined the polymerization initiated by $Ni\{P(OPh)_3\}_4$ and the labelled halides $^{14}CCl_3COOEt$, $CCl_3COO^{14}CH_2CH_3$. The results, given in *Table 8*, are very similar to those in *Table 4* (2) referring to $CCl_3^{14}COOEt$. It therefore appears that no carbon atom of the ester is incorporated in

Table 8. Initiation of polymerization of methyl methacrylate at 25°C by $Ni\{P(OPh)_3\}_4$ with $^{14}CCl_3COOEt$ and $CCl_3COO^{14}CH_2CH_3$
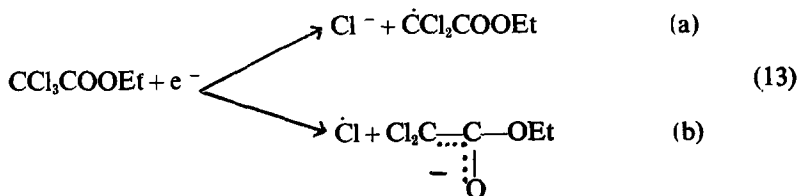
(1) $[^{14}CCl_3COOEt]=0.03$ mole l^{-1}; $n_h=3.47\times10^9$ counts per 100 s per mole

$10^4\omega$ mole l^{-1} s^{-1}	n_p, counts per 100 s per 100 mg	$10^8\,\mathscr{J}\star$, mole l^{-1} s^{-1}	$\xi=\mathscr{J}\star/\omega^2$, mole^{-1} l s	$10^{-3}\bar{P}_n$ mean	$k_p k_t^{-\frac{1}{2}}$, mean, mole$^{-\frac{1}{2}}$ $l^{\frac{1}{2}}$ $s^{-\frac{1}{2}}$	
					from (11b)	from $\bar{P}_n$
1·22	1109	3·90	2·62			
1·23	1150	4·08	2·69	2·53	0·067	0·053
1·07	1001	3·09	2·69			
		mean:	2·67			

(2) $[CCl_3COO^{14}CH_2CH_3]=0.03$ mole l^{-1}; $n_h=1.13\times10^9$ counts per 100 s per mole

1·15	317	3·22	2·43			
1·12	285	2·82	2·25	2·65	0·073	0·053
1·15	284	2·89	2·19			
		mean:	2·29			

$[Ni\{P(OPh)_4\}_4]=3.20\times10^{-4}$ mole l^{-1}; [monomer]$=9.3$ mole l^{-1} initially; conversions 4 per cent approximately.
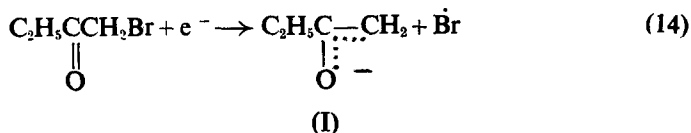
an unattached radical. We propose that an unattached primary radical is either a chlorine atom or an adduct of such an atom with a monomer

molecule—$ClCH_2\dot{C}(Me)COOMe$. The two types of primary radical may arise from an electron transfer as follows:

$$CCl_3COOEt + e^- \nearrow \quad Cl^- + \dot{C}Cl_2COOEt \qquad (a)$$

$$\searrow \quad \dot{C}l + Cl_2C \cdots C{-}OEt \qquad (b) \qquad (13)$$
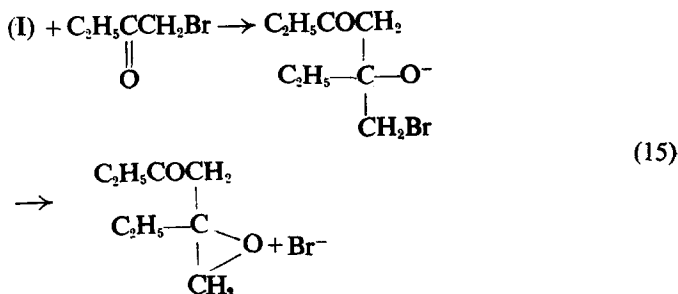$$\overset{-}{\underset{\overset{:}{\underset{O}{|}}}{}}$$

Reaction (13a) gives attached primary radicals; (13b), leading to unattached primary radicals, is able to compete with (13a) if the halide contains an additional group with a sufficiently high electron affinity. The anion formed in (13b) is probably associated with the metal, for example chelated to give a five-membered ring. The relative importance of (13b) would therefore be expected to depend on the nature of the metal atom and, of the metals we have studied in detail, nickel alone enters into this type of reaction to a significant extent. *Table 7* shows that the probability of this reaction depends on the nature of the ligands attached to nickel.

We may note that the findings of Yoshisato and Tsutsumi[13] may be interpreted in terms of a reaction similar to (13b). These workers showed that β-epoxy ketones are formed in good yield (50 to 80 per cent) by reaction of nickel carbonyl with α-bromo ketones at 30°C in N,N-dimethyl-formamide solution. From analogy with (13b) we write for the first step in a typical case

$$C_2H_5\overset{\|}{\underset{O}{C}}CH_2Br + e^- \longrightarrow C_2H_5\overset{\cdots}{\underset{\overset{:}{\underset{O}{|}}}{C}}CH_2 + \dot{B}r \qquad (14)$$
$$\text{(I)}$$

This is followed by addition of the anion (I) to the carbonyl group of a second molecule of α-bromo ketone, and cyclization—

$$\text{(I)} + C_2H_5\overset{\|}{\underset{O}{C}}CH_2Br \longrightarrow C_2H_5COCH_2$$
$$\underset{\overset{|}{\underset{CH_2Br}{C_2H_5-C-O^-}}}{|}$$

$$\longrightarrow \quad \underset{\overset{|}{\underset{CH_3}{C_2H_5-C}}}{\overset{C_2H_5COCH_2}{\underset{|}{|}}} \!\!> O + Br^- \qquad (15)$$

Dr Go Hata has shown in these laboratories that α-bromoacetone in the presence of $Ni\{P(OPh)_3\}_4$ is a good initiator for the polymerization of

methyl methacrylate at 25°C, the limiting rate being the same as that obtained with carbon tetrachloride. The reaction sequence shown is clearly able to explain the formation of a β-epoxy ketone and the concurrent initiation of free radical polymerization (by bromine atoms).

5. CONCLUSIONS

The structure of the final network depends on the termination reaction and on the nature of the primary radicals. The combination : disproportionation ratio is a function of the monomer and the temperature, and it is not affected by the presence of the organometallic derivatives used in this work, since estimates of $f/(1+f)$ by tracer and gel techniques are in agreement (*Table 7*). If all the primary radicals are attached to the prepolymer chain the ratio of crosslinks to branches is determined by termination and transfer processes. It is now possible to vary this ratio by the use of initiating systems which give rise to unattached radicals, since the presence of these radicals increases the proportion of branches in the network. At present it seems that nickel derivatives are most active in producing unattached radicals so that their use extends the range of network structures available.

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