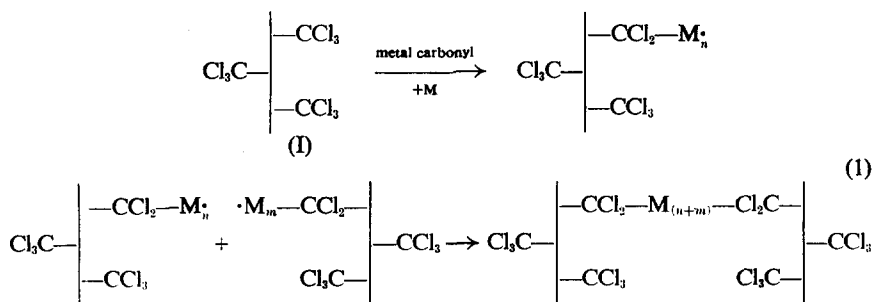# Network Formation II—The Radical-forming Process in the Presence of Solvents

C. H. BAMFORD, R. W. DYSON, G. C. EASTMOND and D. WHITTLE

The formation in solution of networks consisting of polyvinyl trichloracetate crosslinked by methyl methacrylate chains has been studied. Benzene, ethyl acetate and dioxan have been used as diluents, with molybdenum carbonyl as thermal initiator at 80°C and manganese carbonyl as photoinitiator at 25°C. Relations have been developed which allow corrections to be made to the observed gel-times to take account of chain transfer and initiator consumption. With molybdenum carbonyl the corrected gel-times agree with those calculated from the prevailing rates of initiation, showing that all the initiating radicals are attached to the prepolymer (polyvinyl trichloracetate) chains. In ethyl acetate and dioxan solutions the majority (and probably all) of the radicals are similarly attached. Gelation experiments with photoinitiation by manganese carbonyl provide no evidence for the formation of any unattached radicals in solutions containing up to 70% v/v benzene. With ethyl acetate as diluent abnormally long gel-times were observed. Tracer investigations with $CCl_3{}^{14}COOEt$ as the halide component of the initiating system indicate that only attached radicals are formed, consequently the long gel-times indicate an unexpectedly low rate of photoinitiation under these conditions. This conclusion has been confirmed by direct measurement of the rates of initiation in the presence of ethyl acetate. Deviations from the inverse relation between gel-time and initiator concentration predicted by simple gelation theory are encountered when the carbonyl concentration is relatively high and are discussed briefly.

1. INTRODUCTION

WE HAVE already shown that when the free-radical polymerization of a vinyl monomer is initiated by a polymeric halide in association with a metal carbonyl, a molecular network may be formed[1,2]. The mechanism of crosslinking is shown in (1).

$$
Cl_3C{-}\!\!\begin{vmatrix} -CCl_3 \\[4pt] -CCl_3 \end{vmatrix} \quad\xrightarrow[+M]{\text{metal carbonyl}}\quad Cl_3C{-}\!\!\begin{vmatrix} -CCl_2{-}M_n^{\cdot} \\[4pt] -CCl_3 \end{vmatrix}
$$

$$\text{(I)}$$

$$
Cl_3C{-}\!\!\begin{vmatrix} -CCl_2{-}M_n^{\cdot} \\[4pt] -CCl_3 \end{vmatrix} \;+\; \begin{vmatrix} \cdot M_m{-}CCl_2{-} \\[4pt] Cl_3C{-} \end{vmatrix} \quad\begin{array}{c} -CCl_3 \to Cl_3C{-} \end{array}\quad \begin{vmatrix} -CCl_2{-}M_{(n+m)}{-}Cl_2C{-} \\[4pt] -CCl_3 \qquad\qquad Cl_3C{-} \end{vmatrix}\!\!{-}CCl_3
$$

$$\text{(1)}$$

Here (I) represents a portion of the chain of the polymeric halide, and M the vinyl monomer. Clearly crosslinks can only be formed if part of the termination reaction occurs by radical combination, and indeed gel-

formation is one of the most sensitive methods of detecting combination. In an earlier paper[2] we discussed the conditions which must hold in order that gelation should occur without radical wastage. Under these conditions the gel-time t_g^0 is given by

$$t_g^0 = c(k_{tc} + k_{td})/(\overline{P}_w \mathcal{I}_0 k_{tc}) \tag{2}$$

where c, $\overline{P}_w$ are the base-molar concentration and weight-average molecular weight of the prepolymer, $\mathcal{I}_0$ the (constant) rate of chain-starting and k_{tc}, k_{td} the velocity coefficients for chain termination by combination and disproportionation, respectively[2]. The general conditions which minimize radical wastage are[2]: (i) the prepolymer should be readily soluble and homogeneous with respect to molecular weight which must not be too high, (ii) the concentration of prepolymer should not be very low, (iii) the rate of chain-starting must be low and (iv) chain-transfer to monomer or diluent must be insignificant. Conditions (i) and (iii) are connected since the acceptable range of molecular weights of the prepolymer depends on the rate of initiation. Radical wastage naturally gives rise to gel-times longer than those predicted from (2).

In order to study the properties of these networks it is desirable to prepare them under conditions as diverse as possible, particularly in the presence of solvents. We have previously established that for initiation by molybdenum carbonyl and photoinitiation by manganese carbonyl, in bulk methyl methacrylate and styrene, all the initiating radicals are attached to the prepolymer chains[1,3] but it does not follow that the same is true in dilute monomer solutions. The formation of unattached radicals would not be surprising in systems in which the solvent participates in initiation[4], e.g. molybdenum carbonyl + ethyl acetate + methyl methacrylate. In this paper we report gelation studies with benzene, ethyl acetate and dioxan as solvents and methyl methacrylate as monomer; photoinitiation by manganese carbonyl and thermal initiation by molybdenum carbonyl have been employed. In some cases the results are supplemented by tracer studies. Conditions (iii) and (iv) above do not always hold in these systems; further, since the observed gel-times are frequently long the rate of initiation is not constant. Consequently the observed gel-times must be corrected if they are to be used in equation (2). The method of correction is developed below and is general for this type of system.

2. EXPERIMENTAL

Materials

The methods adopted for purifying molybdenum and manganese carbonyls, methyl methacrylate, ethyl acetate and dioxan have already been described[4-6]. The prepolymer, polyvinyl trichloracetate, was prepared and purified as in earlier work[2].

In some cases labelled ethyl trichloracetate ($CCl_3^{14}COOEt$) was used as the halide component to determine the nature of the initiating process. This compound was prepared by esterifying $CCl_3^{14}COOH$, obtained from the Radiochemical Centre, Amersham, with ethanol[7]. A solution of 0·2 mcurie of the acid in 10 ml methylene chloride was added to 8g sublimed inactive

trichloracetic acid dissolved in 10 ml methylene chloride. The solvent was removed in a vacuum and 8 ml 'super dry' ethanol distilled on to the acid. Hydrogen chloride was bubbled into the stirred mixture for 5 min and stirring continued for 1 h. The liquid was then refluxed for 5 to 10 min. After cooling, excess distilled water was run in and the lower layer (ester) removed, washed with water until free from hydrogen chloride, dried over magnesium sulphate, filtered and distilled. The fraction boiling at 167° to 168°C was collected. No impurities in the ester so obtained could be detected by gas chromatography.

Apparatus and technique

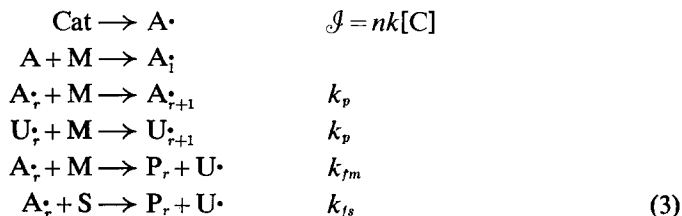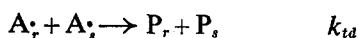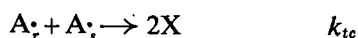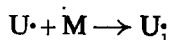All experiments were performed in a laboratory lighted by inactive (sodium) light.

Gel-times were measured in vacuum viscometers as described by Bamford, Dyson and Eastmond[2]. Rates of polymerization were determined by conventional dilatometric and gravimetric techniques. The relation of Fox, Kinsinger, Mason and Schuele[6] was used in deducing number-average degrees of polymerization from the intrinsic viscosities of polymers.

The activities of polymers prepared with the aid of labelled ethyl trichloracetate were determined by internal liquid scintillation counting using a Packard Model 3003 Tricarb scintillation spectrometer. The procedure described in ref. 1 was followed.

3. THE INFLUENCE OF CHAIN TRANSFER AND CATALYST CONSUMPTION ON MEASURED GEL-TIMES

The reaction scheme, which includes transfer to monomer and solvent S, is given below. The initiating system, composed of prepolymer and carbonyl C, is designated Cat and is considered to produce primary radicals A· which are all attached to prepolymer chains; the latter may or may not have reacted previously, but we shall assume that only very few of the reactive sites on a prepolymer chain are utilized. Unattached radicals U· are formed by transfer. $A_r^\cdot$, $U_r^\cdot$ represent attached and unattached radicals, formed from A· or U·, respectively, by addition of r monomer units. A crosslink is formed by combination of two $A_r^\cdot$-type radicals and X represents a unit of a prepolymer chain forming one end of such a crosslink. Dead polymer, in the form of branches or unattached molecules, is designated P. Transfer by unattached radicals to monomer or solvent regenerates unattached radicals, and so does not affect the gel-time; this process is not included in (3). Transfer to polymer or prepolymer has been neglected since it is insignificant in these experiments.

$$\text{Cat} \twoheadrightarrow \text{A·} \qquad \mathscr{I} = nk[\text{C}]$$
$$\text{A} + \text{M} \twoheadrightarrow \text{A}_1^\cdot$$
$$\text{A}_r^\cdot + \text{M} \twoheadrightarrow \text{A}_{r+1}^\cdot \qquad k_p$$
$$\text{U}_r^\cdot + \text{M} \twoheadrightarrow \text{U}_{r+1}^\cdot \qquad k_p$$
$$\text{A}_r^\cdot + \text{M} \twoheadrightarrow \text{P}_r + \text{U·} \qquad k_{fm}$$
$$\text{A}_r^\cdot + \text{S} \twoheadrightarrow \text{P}_r + \text{U·} \qquad k_{fs} \qquad (3)$$

$$U\cdot + \dot{M} \longrightarrow U_1^{\cdot}$$

$$A_r^{\cdot} + A_s^{\cdot} \longrightarrow 2X \qquad\qquad k_{tc}$$

$$A_r^{\cdot} + A_s^{\cdot} \longrightarrow P_r + P_s \qquad\quad k_{td}$$

$$A_r^{\cdot} + U_s^{\cdot} \longrightarrow P_{r+s}, P_r + P_s, \quad k_{tc}, k_{td}$$

$$U_r^{\cdot} + U_s^{\cdot} \longrightarrow P_{r+s}, P_r + P_s, \quad k_{tc}, k_{td}$$

If $R_a = \sum_r [A_r^{\cdot}]$ and $R_u = \sum_r [U_r^{\cdot}]$ are stationary we find that

$$R_a + R_u = (\mathscr{J}/k_t)^{\frac{1}{2}} \tag{4}$$

and

$$\frac{R_u}{R_a} = \frac{k_{fm}[M] + k_{fs}[S]}{k_t(R_a + R_u)} \tag{5}$$

where $k_t = k_{tc} + k_{td}$. Hence

$$\frac{R_a}{R_a + R_u} = \frac{1}{1 + \dfrac{k_p}{(\mathscr{J}k_t)^{\frac{1}{2}}}\{C_m[M] + C_s[S]\}} \tag{6}$$

where C_m, C_s are the transfer constants of monomer and solvent, respectively. The rate of formation of crosslinked units is given by

$$\frac{d[X]}{dt} = k_{tc}R_a^2 = \frac{k_{tc}}{k_t} \cdot \frac{\mathscr{J}}{1 + \dfrac{k_p}{(\mathscr{J}k_t)^{\frac{1}{2}}}\{C_m[M] + C_s[S]\}} \tag{7}$$

in which the rate of initiation $\mathscr{J}$ is a function of time. If the decomposition of one molecule of carbonyl starts n chains, we have

$$\mathscr{J} = nk[C] = nk[C]_0 e^{-kt} \tag{8}$$

k being the first order constant for the decomposition and $[C]_0$ the initial concentration of the carbonyl. Substitution of $\mathscr{J}$ from (8) into (7) followed by integration leads to the expression (9) for the number of crosslinked units formed after a reaction-time t, assuming that $[X] = 0$ when $t = 0$.

$$[X] = \frac{k_{tc}\mathscr{J}_0}{kk_t}\left\{1 - y^2 - 4B_0(1-y) + 6B_0^2 \ln\left(\frac{1+B_0}{y+B_0}\right) - \frac{2B_0^3(1-y)}{(1+B_0)(y+B_0)}\right\} \tag{9}$$

In this equation

$$y = e^{-kt/2}$$

and

$$B_0 = \frac{k_p(C_m[M] + C_s[S])}{(k_t nk[C]_0)^{\frac{1}{2}}} = \frac{k_p}{k_t^{\frac{1}{2}}}\frac{C_m[M] + C_s[S]}{\mathscr{J}_0^{\frac{1}{2}}} \tag{10}$$

According to the simple gel theory, at the gel point

$$[X] = \mathscr{J}_0 t_g^0 k_{tc}/k_t \tag{11}$$

where, as in (2), t_g^0 is the gel-time corresponding to a constant rate of chain-starting $\mathcal{J}_0$ in the absence of transfer and radical wastage. Hence if t_g is the observed gel-time we see from (9), (10) and (11) that the corrected gel-time is

$$t_g^0 = \frac{1}{k}\left\{1 - y^2 - 4B_0(1-y) + 6B_0^2 \ln\left(\frac{1+B_0}{y+B_0}\right) - \frac{2B_0^3(1-y)}{(1+B_0)(y+B_0)}\right\} \qquad (12)$$

in which $$y = \exp\left(-kt_g/2\right) \qquad (13)$$

If $k_p k_t^{-\frac{1}{2}}$, C_m, C_s and $\mathcal{J}_0$ are known, t_g^0 may be calculated from the observed gel-time with the aid of (12) together with (10) and (13). This value can then be compared with that estimated from (2), or values of t_g^0 for various systems may be compared to deduce k_{tc}/k_t or to obtain information about the nature of the initiation process. This paper is only concerned with the latter aspect. In deriving (12) we have assumed that the termination coefficient k_t is constant during the pre-gelation period. This is justifiable because conversions at the gel-point are usually small; further, none of the systems examined shows an increase in rate of polymerization before the gel-point, and the rates are equal to those observed with non-polymeric halide components. We note two special cases in which particularly simple forms of (12) are obtained.

(i) For negligible consumption of carbonyl (12) can be reduced to

$$t_g^0 = t_g/(1 + B_0)^2 \qquad (14)$$

In this case only transfer need be considered.

(ii) If $B_0 = 0$,

$$t_g^0 = (1/k)(1 - e^{-k}t_g) \qquad (15)$$

Here transfer is absent, and only initiator decay is significant.

4. RESULTS AND DISCUSSION

4.1 Molybdenum carbonyl

Figures 1, 2 and *3* show the variation in gel-time with solvent concentration for benzene, ethyl acetate and dioxan, respectively, at 80°C. The gel-times observed (curves *a*) in the presence of solvents are considerably longer than with bulk monomer. This may arise from three possible causes: (i) variation in rate of initiation with solvent concentration, (ii) the production of unattached radicals by transfer to solvent and (iii) the formation of unattached radicals during initiation in the presence of solvents. The kinetic parameters for initiation in these systems are known from earlier work[4,5], so that the rates of initiation may be calculated. Benzene is an inert diluent, while the other solvents play an active part in initiation[4,5]. The transfer corrections may be computed as described in § 3. Knowledge of the transfer constants to monomer and solvents is necessary and although values are
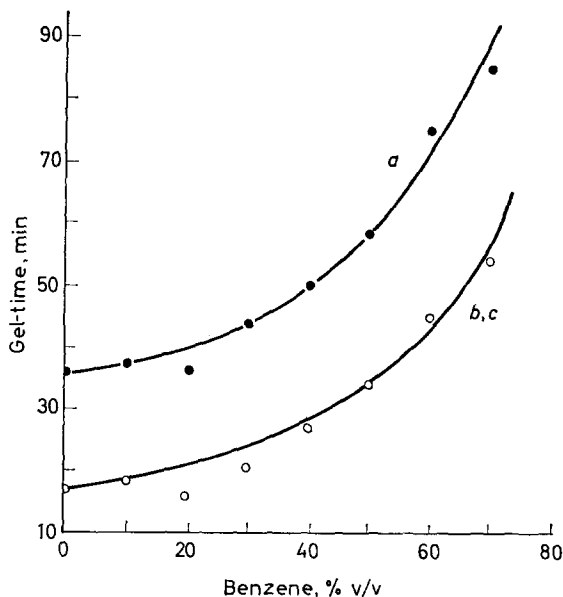
Figure 1—Gelation in methyl methacrylate–benzene mixtures at 80°C. $[Mo(CO)_6] = 8 \cdot 7 \times 10^{-5}$ mole 1^{-1}; [prepolymer] = $2 \cdot 6 \times 10^{-2}$ base mole 1^{-1}. *a* Observed gel-times; *b* (points) gel-times corrected for transfer and initiator consumption; *c* (curve) gel-times calculated from corrected value in bulk monomer
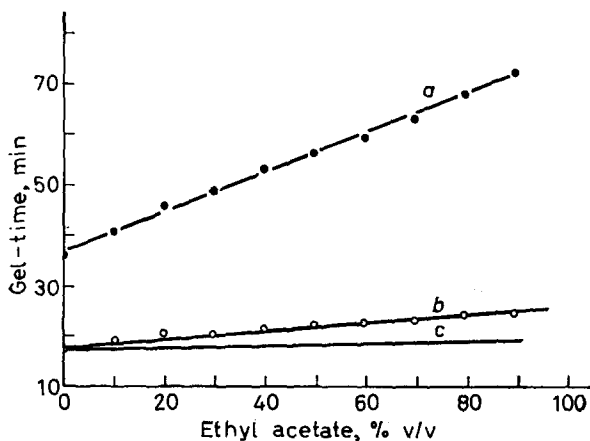

Figure 2—Gelation in methyl methacrylate–ethyl acetate mixtures at 80°C. $[Mo(CO)_6] = 8 \cdot 7 \times 10^{-5}$ mole 1^{-1}. [prepolymer] = $2 \cdot 6 \times 10^{-2}$ base mole 1^{-1}. *a* Observed gel-times; *b* observed gel-times corrected for transfer and initiator consumption; *c* gel-times calculated from corrected value in bulk monomer

764

reported in the literature[9], they show considerable scatter. Consequently we have redetermined the transfer constants using conventional techniques; the mean values at 80°C are given below:

$$
\begin{array}{lll}
\text{Monomer} & 2\cdot8 \ \times 10^{-5} & \\
\text{Ethyl acetate} & 3\cdot65 \times 10^{-5} & \quad\quad (16) \\
\text{Dioxan} & 1\cdot85 \times 10^{-5} &
\end{array}
$$

Transfer to benzene is assumed to be negligible.

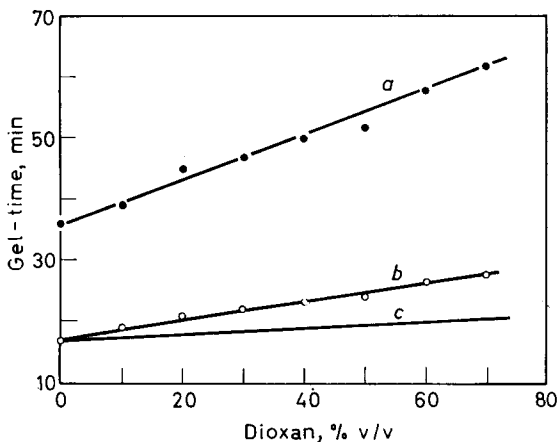Figure 3—Gelation in methyl methacrylate–dioxan mixtures at 80°C. $[Mo(CO)_6] = 8\cdot7 \times 10^{-5}$ mole 1^{-1}. [prepolymer] $= 2\cdot6 \times 10^{-2}$ base mole 1^{-1}. *a* Observed gel-times; *b* observed gel-times corrected for transfer and initiator consumption; *c* gel-times calculated from corrected value in bulk monomer

Values of t_g^0 for the rates of initiation holding in the presence of solvents have been computed from the observed gel-times with the aid of equations (10), (12) and (13), and are shown in curves *b* of *Figures 1, 2* and *3*. Curves *c* in these figures are derived from t_g^0 in bulk monomer by making allowance for the modified rates of initiation in solution. If there were no unattached radicals formed in the initiation process in solvents, curves *b* and *c* would be identical. This is so, within experimental error, for the results in benzene solution shown in *Figure 1*; no meaningful distinction is possible between the values t_g^0 derived from observations in solution and those calculated from rates of initiation. The discrepancy between curves *b* and *c* in *Figures 2* and *3* is not large and may also be within experimental error. Clearly, in benzene the whole, and in ethyl acetate and dioxan the majority, of the initial radicals are attached to the prepolymer chains. It may easily be shown from equation (8) in Part III of this series that the maximum values for the fraction of unattached radicals in mixtures rich in solvents are: ethyl acetate (90% v/v) 0·12, dioxan (70% v/v) 0·14.

When higher carbonyl concentrations are used, the conditions for efficient utilization of radicals mentioned in § 1 do not hold; the gel-times may then be protracted and may not obey the expected simple kinetic relations.

Examples of this behaviour are shown in *Figure 4*. Curves *a*, *b* and *c* show the variation of t_g^0 calculated from experimental gel-times in benzene, ethyl acetate and dioxan solutions, respectively; *d*, *e* and *f* are calculated from t_g^0 in bulk monomer to allow for changes in the rate of initiation in solutions. In benzene solution again no distinction can be drawn between the two sets of data, and only one curve is shown. Even in bulk monomer the gel-times are longer than would be expected from the values obtained at lower carbonyl concentrations (cf. *Figures 1, 2* and *3*); with ethyl acetate, and particularly dioxan solutions, the discrepancy increases as the monomer is diluted. These solvents produce a comparatively large increase in gel-time in relatively low concentrations (up to 20% v/v) and a very marked increase occurs with dioxan at higher concentrations. We think these effects are connected with conformational changes in the polymer molecules which give rise to greater radical wastage at the higher rates of initiation. Apparently benzene solutions do not show this behaviour. It is interesting to note that, even at the lower carbonyl concentrations, unexpectedly long gel-times are found when the monomer concentration falls below those shown in *Figures 2* and *3*.
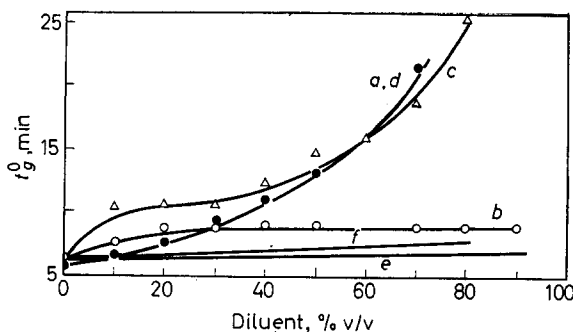

Figure 4—Gelation in methyl methacrylate solutions at 80°C with high [Mo(CO)$_6$]. [prepolymer] $= 2\cdot6 \times 10^{-2}$ base mole l^{-1}. Observed gel-times corrected for transfer and consumption (t_g^0): *a* (points) benzene solution, [Mo(CO)$_6$] $= 6\cdot98 \times 10^{-4}$ mole l^{-1}; *b* ethyl acetate solution, [Mo(CO)$_6$] $= 3\cdot49 \times 10^{-4}$ mole l^{-1}; *c* dioxan solution, [Mo(CO)$_6$] $= 3\cdot49 \times 10^{-4}$ mole l^{-1}. Gel-times (t_g^0) calculated from corrected values in bulk monomer: *d* benzene solution, [Mo(CO)$_6$] $= 6\cdot98 \times 10^{-4}$ mole l^{-1}; *e* ethyl acetate solution, [Mo(CO)$_6$] $= 3\cdot49 \times 10^{-4}$ mole l^{-1}; *f* dioxan solution, [Mo(CO)$_6$] $= 3\cdot49 \times 10^{-4}$ mole l^{-1}

4.2 Manganese carbonyl

We have previously published observations on gelation at 25°C in systems containing methyl methacrylate and polyvinyl trichloracetate, with manganese carbonyl as photoinitiator[2]. Bulk monomer and benzene solutions were studied, but no corrections for chain transfer were applied. *Figure 5* presents essentially the same data obtained with a prepolymer concentration of $4\cdot8 \times 10^{-3}$ b mole l^{-1}, corrected for transfer to monomer with the transfer constant $C_m = 2 \times 10^{-5}$. The rates of initiation in this figure are cal-
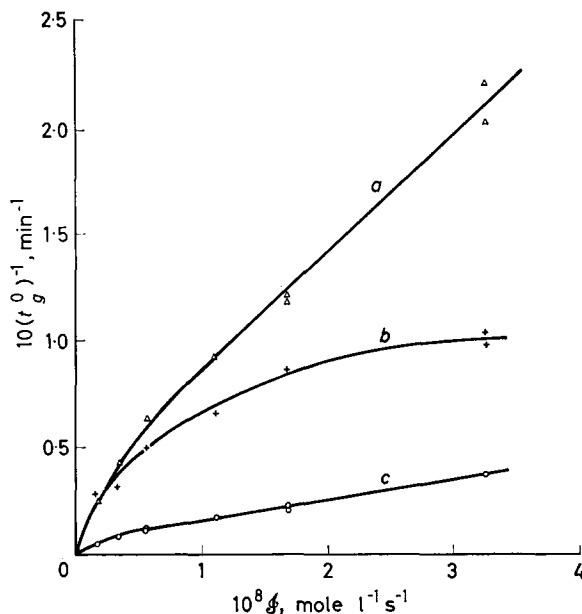
Figure 5—Photogelation in bulk methyl methacrylate, and in benzene and ethyl acetate solutions at 25°C. $[Mn_2(CO)_{10}] = 2.57 \times 10^{-4}$ mole l^{-1}; [prepolymer] = 4.8×10^{-3} base mole l^{-1}. Curve a bulk methyl methacrylate; b methyl methacrylate (20% v/v) + benzene; c methyl methacrylate (20% v/v) + ethyl acetate. t_g^0 is the observed gel-time corrected for transfer (initiator consumption was negligible) and $\mathscr{I}$ is the rate of initiation calculated on the assumption that it is the same in solution as in bulk monomer (see text)

culated on the assumption that they are independent of the monomer concentration, as established for benzene solutions[6]. It will appear subsequently that this does not hold for ethyl acetate solutions. Carbonyl consumption was not important in these experiments. According to equation (2), a plot of $1/t_g^0$ against $\mathscr{I}$ should be linear; the curvature in plots a and b of *Figure 5* indicates wastage of radicals at the higher rates of initiation; clearly this is more pronounced in benzene solution, as would be anticipated in view of the fact that benzene is a poor solvent for the prepolymer at 25°C. At low rates of initiation the two curves coincide; hence we conclude that the initial radicals are all attached to the prepolymer chains.

In ethyl acetate solution (curve c, *Figure 5*) the gel-times are relatively long; the explanation of this behaviour must differ from that advanced for the benzene system since ethyl acetate is a better solvent for the prepolymer than either benzene or monomer. In § 4.1 we have enumerated three general reasons for the existence of unexpectedly long gel-times in the presence of diluents. Of these, (ii) may be allowed for on the assumption that the rate of photoinitiation is independent of the monomer concentration, as it is in benzene solution. Using a value of the transfer constant to

767

ethyl acetate of 2×10^{-5} we thus obtain curve c of *Figure 5*. Evidently transfer is not the prime cause of the long gel-times observed in ethyl acetate solution.

The formation of unattached initial radicals [*(iii)* in § 4.1] was investigated by a tracer technique using $CCl_3{}^{14}COOEt$ (i.e. the monomeric equivalent of the prepolymer) as halide in place of the prepolymer. Results are given in *Table 1*; they may be compared with the following mean values obtained with bulk monomer—$k_p k_t^{-\frac{1}{2}} = 0.055$ mole$^{-\frac{1}{2}}$ l$^{\frac{1}{2}}$ s$^{-\frac{1}{2}}$; initiator fragments per polymer molecule 1.19.

Table 1. Photopolymerization in ethyl acetate solution; 25°C

Reaction time, min	$10^5\omega$, mole $l^{-1} s^{-1}$	$10^{-4}\bar{M}_n^0$	$k_p k_t^{-\frac{1}{2}}$* mole$^{-\frac{1}{2}}$ $l^{\frac{1}{2}} s^{-\frac{1}{2}}$	Initiator fragments per polymer molecule
90	1.59	5.37		1.19
51	1.47	7.27	0.053	1.20

$[Mn_2(CO)_{10}] = 7.71 \times 10^{-4}$ mole l^{-1}; $[M] = 1.87$ mole l^{-1}; $[CH_3COOEt] = 8.2$ mole l^{-1}; $[CCl_3COOEt] = 0.04$ mole l^{-1}. $\bar{M}_n^0$ is the number-average molecular weight of the polymer obtained after (a small) correction for transfer, and ω the rate of polymerization.
*Calculated as in ref. 10; the mean of six determinations is given.

The data for $k_p k_t^{-\frac{1}{2}}$ show that there is no abnormality in the polymerization in ethyl acetate solution, while the incorporation of initiator fragments indicates conclusively that all the initiating radicals are attached to the labelled halide residues. In the gelation experiments there are therefore no unattached primary radicals. The long gel-times in ethyl acetate solution are thus attributable to unusually low rates of initiation. This was confirmed by direct measurement of rates of photopolymerization in the system methyl methacrylate + ethyl acetate + ethyl trichloracetate + manganese carbonyl (*Table 2*).

Table 2. Rates of initiation in ethyl acetate solution; 25°C

$[M]$, mole l^{-1}	Reaction time, min	$10^5 \bar{\omega}$, mole $l^{-1} s^{-1}$	$10^8 \mathcal{I}$, mole $l^{-1} s^{-1}$
9.30	30	9.98	3.8
6.51	38	5.96	2.8
4.65	43	4.00	2.4
1.85	56	1.09	1.2

$[Mn_2(CO)_{10}] = 2.57 \times 10^{-4}$ mole l^{-1}; $[CCl_3COOEt] = 0.04$ mole l^{-1}; $k_p k_t^{-\frac{1}{2}} = 0.055$ mole$^{-\frac{1}{2}}$ l$^{\frac{1}{2}}$ s$^{-\frac{1}{2}}$.

The rates of initiation are evidently significantly lower in the presence of ethyl acetate. Further, preliminary results on the dependence of gel-time on prepolymer concentration suggest that the variation of rate of initiation with halide concentration is also affected by ethyl acetate in this system. In the absence of a complete kinetic investigation it is not possible to carry out a detailed correction of the gel-times given in curve c, *Figure 5*.

A similar situation is encountered with dioxan as solvent. Gel-times, corrected for transfer, are given in *Table 3*, assuming that the rate of

consumption of carbonyl is the same as that in bulk monomer ($3 \cdot 8 \times 10^{-8}$ mole $l^{-1} s^{-1}$ in these experiments).

Table 3. Gel-times in dioxan solution; $25\,^{\circ}C$

[M] mole l^{-1}	[dioxan], mole l^{-1}	10^2 prepolymer concentration, base mole l^{-1}	t_g, min corrected for transfer
9·3	0	2·6	23·0
1·86	9·4	2·6	34·0
9·3	0	0·52	6·5
1·86	9·4	0·52	14·0

[$Mn_2(CO)_{10}$] $=2 \cdot 57 \times 10^{-4}$ mole l^{-1}; transfer constant for dioxan 10^{-3} at $25\,^{\circ}C$.

As with ethyl acetate, measurements of the rates and degrees of polymerization made with ethyl trichloracetate as halide show that the value of $k_p k_t^{-\frac{1}{2}}$ is normal and hence that there is no retardation; further, the calculated values of the rates of initiation are lower than those in the absence of solvent (Table 4). However, the effect is much less marked than with ethyl acetate as solvent.

Table 4. Photopolymerization in dioxan solution; $25\,^{\circ}C$

[M], mole l^{-1}	[dioxan], mole l^{-1}	$10^5 \omega$ mole $l^{-1} s^{-1}$	$10^{-5} \overline{M}_n^0$	$k_p k_t^{-\frac{1}{2}}$, mole$^{-\frac{1}{2}}$ $l^{\frac{1}{2}} s^{-\frac{1}{2}}$	$10^8 \mathcal{J}$, mole $l^{-1} s^{-1}$
9·30	0	9·00	3·08	0·052	3·1
6·51	3·51	6·10	2·76	0·055	2·9
4·65	5·85	4·31	2·21	0·057	2·8
1·86	9·36	1·58	1·00	0·053	2·4

[$Mn_2(CO)_{10}$] $=2 \cdot 57 \times 10^{-4}$ mole l^{-1}; [CCl_3COOEt] $=0 \cdot 04$ mole l^{-1}; $\overline{M}_n^0$ is the molecular weight corrected for transfer to dioxan. The value of $k_p k_t^{-\frac{1}{2}}$ was calculated as in ref. 10 after correcting the rates of polymerization for changes in solvent viscosity.

4.3 Conclusion

The work described in this paper shows that in photoinitiating systems based on manganese carbonyl in association with a trichloracetate each radical formed is attached to the organic residue resulting from scission of a chlorine atom from the halide molecule. When molybdenum carbonyl is used as thermal initiator at $80\,^{\circ}C$ the majority of the radicals are similarly attached, the proportion of unattached radicals observed in gelation experiments being less than 15 per cent, approximately. This figure is sensitive to the value adopted for the transfer constant of the solvent; tracer studies are not sufficiently accurate to allow it to be determined precisely.

The rate of photoinitiation by manganese carbonyl under the conditions employed has been shown to decrease when the monomer is diluted with ethyl acetate or dioxan particularly in the former case. This is surprising. Earlier work showed that the rate of initiation is not affected by dilution of the monomer with benzene[6], and this is consistent with the determinations of the gel-time in the presence of benzene described in this paper.

Neither set of observations thus provides any reasons for believing that monomer is involved in the radical-forming process. However, the present observations on initiation in ethyl acetate solution suggest that the monomer must participate in this way, in a process in which ethyl acetate may compete so as to reduce the rate of initiation. Further investigation of these systems is in progress.

Department of Inorganic, Physical and Industrial Chemistry,
  Donnan Laboratories,
    University of Liverpool

REFERENCES

[1] BAMFORD, C. H., EASTMOND, G. C. and ROBINSON, V. J. *Trans. Faraday Soc.* 1964, **60,** 751

[2] BAMFORD, C. H., DYSON, R. W. and EASTMOND, G. C. *J. Polym. Sci. (C),* 1967, **16,** 2425. (To be regarded as Part I of this series)

[3] Unpublished results

[4] BAMFORD, C. H., DENYER, R. and EASTMOND, G. C. *Trans. Faraday Soc.* 1965, **61,** 1459

[5] BAMFORD, C. H., DENYER, R. and EASTMOND, G. C. *Trans. Faraday Soc.* 1966, **62,** 688

[6] BAMFORD, C. H., CROWE, P. A. and WAYNE, R. P. *Proc. Roy. Soc. A,* 1965, **284,** 455

[7] SPIEGEL, L. and SPIEGEL, P. *Ber. dtsch. Chem. Ges.* 1907, **40,** 1734
   TOOLE, S. GERALDINE and SOWA, F. J. *J. Amer. chem. Soc.* 1937 **59,** 1972

[8] FOX, T. G., KINSINGER, J. B., MASON, H. F. and SCHUELE, E. M. *Polymer, Lond.* 1962, **3,** 71

[9] *Polymer Handbook,* ed. J. BRANDRUP and E. H. IMMERGUT. Interscience: New York, 1965

[10] BAMFORD, C. H. and HARGREAVES, K. *Proc. Roy. Soc. A,* 1967, **297,** 425