Network Formation IV. The Nature of the Termination Reaction in Free-radical Polymerization

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The gelation technique has been applied to the following monomers to determine the nature of the termination reactions in the free-radical polymerizations at 25°C: methyl, ethyl and n-*butyl methacrylates; methyl and ethyl acrylates; acrylonitrile and methacrylonitrile; vinyl acetate. The photo-initiating system used was manganese carbonyl+polyvinyl trichloracetate and the efficiencies of initiation were found to be similar for all monomers studied. The ratios of combination to disproportionation in the termination reactions were deduced from a comparison of the gel-times for the various monomers with those for styrene (which correspond to 100% combination), under conditions of known rates of initiation. Exclusive combination was found with the acrylates, acrylonitrile and vinyl acetate; with the other monomers both combination and disproportionation occur. Factors influencing the nature of the termination reaction are discussed.*

INTRODUCTION

THE use of initiating systems based on polyfunctional halides and organometallic derivatives in the synthesis of block copolymers and networks has been described in Parts I–III of this series[1-3]. The structures of the polymers formed depend on the character of the initiation and termination reactions; the former determines the fraction of the total initiating radicals which are attached to the polyfunctional halide molecules and which can therefore partake in block formation or crosslinking, while the relative importance of combination and disproportionation in the termination reaction influences the ratio of crosslinks to branches in the network.

In Parts II[2] and III[3] we studied initiation by the following metal derivatives: $Mo(CO)_6$, $Mn_2(CO)_{10}$, $Pt(PPh_3)_4$, $Ni(CO)_4$, $Ni(CO)_2(PPh_3)_2$, $Ni\{P(OPh)_3\}_4$ with carbon tetrachloride or a trichloracetate ester as the halide components of the initiating systems. Only the nickel derivatives in association with the trichloracetate esters produced a significant proportion of unattached radicals[3]. Further, in the systems examined, dilution with benzene, ethyl acetate, or dioxan did not lead to the formation of unattached radicals[2].

We have already pointed out[1] that the proportion of combination in the termination reaction can be estimated from gelation observations in suitable systems. For this purpose relation (1), based on simple gelation theory, is used.

$$\frac{k_{tc}}{k_{tc}+k_{td}}=\frac{c}{\overline{P}_w t_g^0 \mathcal{J}} \tag{1}$$

Here c, $\overline{P}_w$ are the base-molar concentration and weight-average degree of

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polymerization of the prepolymer (i.e. the polyfunctional halide), respectively; t_g^0 is the observed gel-time, with appropriate corrections for chain transfer and consumption of initiator (described in detail in Part II[2]); and the other symbols have their conventional significance. In the present paper we report investigations of this type on nine monomers; for the majority of these there are few reliable data in the literature. The information is required for a programme of work on network polymers which is being started, and it also provides some insight into the factors which influence the termination reaction. Manganese carbonyl was employed as photosensitiser [$\lambda = 435{\cdot}8$ nm (4358 Å)][4] in this work, which was carried out at 25°C. The polyfunctional halide was essentially poly(vinyl trichloracetate) (see below).

Several limitations in the use of equation (1) must be considered. The prepolymer was prepared by trichloracetylation of poly(vinyl alcohol); this reaction is incomplete, so that the final product is a copolymer. $\bar{P}_w$ in (1) refers to the trichloracetate groups and cannot easily be determined precisely. For this reason we have 'calibrated' the values of $\bar{P}_w$ for the various prepolymers from experiments with styrene. There is considerable evidence that termination in the polymerization of this monomer occurs exclusively by combination[5-8]. Secondly, (1) applies only in the absence of radical wastage such as the formation of loops on the prepolymer chains[1]. The extent to which wastage occurs increases with increasing rate of initiation, and increasing degree of polymerization, and decreasing concentration of the prepolymer[1]. It also depends on the molecular weight distribution in the prepolymer. We have endeavoured to minimise wastage by working at low rates of initiation and relatively high concentrations of prepolymer. However, as the rate of initiation is decreased, chain transfer becomes increasingly important, and the observed gel-time is very sensitive to this. Under these conditions an accurate knowledge of the relevant transfer constants is necessary to allow calculation of t_g^0 from observed gel-times. Unfortunately these data are not available for some of our systems. In such cases the results allow a minimum value for the fraction of combination to be estimated with certainty, and the effect of assuming likely values of the transfer constants have been considered. Unless stated otherwise values of transfer constants are based on data in the Polymer Handbook[9].

In order to apply (1), a knowledge of the rate of chain-starting $\mathcal{J}$ is required. There is some evidence that the rate of thermal initiation by azo-*bis*-isobutyronitrile (AZO) is independent of the nature of the monomer (provided the concentration of the latter is not too low[10]) and we have assumed that this also holds for photo-initiation by AZO. Rates of photo-initiation by AZO were calibrated from rates of polymerization of bulk methyl methacrylate, with the aid of the known value[4] of $k_p k_t^{-\frac{1}{2}}$ (0·055 mole$^{-\frac{1}{2}}$ l$^{\frac{1}{2}}$ s$^{-\frac{1}{2}}$). Values of $\mathcal{J}$ for photo-initiation of the polymerization of various monomers by $Mn_2(CO)_{10}$ were then obtained from a comparison of rates of polymerizations initiated by $Mn_2(CO)_{10}$ and AZO under standard conditions. This technique does not require a knowledge of $k_p k_t^{-\frac{1}{2}}$ for the individual monomers and it can be used to evaluate this parameter. Values of $\mathcal{J}$ obtained for the various monomers, with photo-initiation by $Mn_2(CO)_{10}$

under standard conditions are given in *Table 1* and do not vary from the mean by more than 15%. We believe this finding supports the original assumption that the rate of photo-initiation by AZO is the same for all the monomers studied.

Ethyl acetate solutions, in which rates of initiation are known to be low[2], were not used in this work.

Table 1. Rates of photo-initiation by $Mn_2(CO)_{10} + CCl_3COOEt$ under standard conditions

Monomer	$10^8 \mathscr{I}$ [$mole\ l^{-1}\ s^{-1}$]
styrene	6·06
methyl methacrylate	5·44
ethyl methacrylate	5·21
n-butyl methacrylate	5·35
methyl acrylate	5·40
ethyl acrylate	4·70
acrylonitrile (in DMF)	5·06
acrylonitrile (in DMSO)	5·25
methacrylonitrile	5·20
vinyl acetate	5·30
mean	5·30

EXPERIMENTAL

Materials

Manganese carbonyl (obtained from the Ethyl Corporation, Detroit) was purified by vacuum sublimation and stored in the dark. AZO was purified by recrystallizations from methanol and chloroform. Ethyl trichloracetate was prepared from ethanol and trichloracetyl chloride and purified by fractionation. The preparation and purification of poly(vinyl trichloracetate) have been described previously[1]. AR benzene was dried by azeotropic distillation; it was stored over sodium. N,N-Dimethylformamide was allowed to stand for three days over phosphorus pentoxide which was renewed daily, distilled under reduced pressure and stored in vacuum. Dimethylsulphoxide was dried by molecular sieve and distilled under reduced pressure, stored in vacuum over barium oxide and vacuum-distilled before use.

Inhibitors were removed from the monomers by washing with aqueous sodium hydroxide (5–10% w/v). In addition, acrylonitrile was washed with dilute sulphuric acid. After several washings with distilled water and drying with calcium chloride, the monomers, other than vinyl acetate, were distilled under reduced pressure. Vinyl acetate was fractionated through a 3 foot column at atmospheric pressure. The monomers were partly prepolymerized by ultraviolet irradiation or heating at 100°C, stored under nitrogen at 0°C and vacuum-distilled before use. Vinyl acetate was stored over sodium metabisulphite to ensure absence of acetaldehyde.

Techniques

All experiments were performed in inactive (sodium) light.

Rates of polymerization were measured dilatometrically by conventional techniques.

The optical system employed and the measurement of gel-times have been described in an earlier paper[1].

RESULTS AND DISCUSSION

1 *Styrene*

Values of t_g^0, calculated from the experimental observations by applying corrections for carbonyl consumption and chain transfer to monomer ($C_M = 3 \times 10^{-5}$), for a constant rate of initiation are plotted against the concentration of prepolymer (sample A) in *Figure 1*. At the higher concentrations t_g^0 is proportional to c as required by equation (1), but as the concentration falls below about 6×10^{-2} b mole l^{-1} t_g^0 becomes progressively larger than expected from simple proportionality. We believe this is the result of radical wastage of the type discussed earlier[1], namely that attributable to the simultaneous growth of two chains from the same prepolymer molecule. Such chains have an unusually high probability of mutual termination which destroys radicals without producing cross-links. Application of (1) to the straight line in *Figure 1*, with $\mathscr{I} = 5{\cdot}45 \times 10^{-8}$ mole l^{-1} s^{-1} and $k_{td} = 0$ gives

$$\bar{P}_w(A) = 2420 \qquad (2)$$

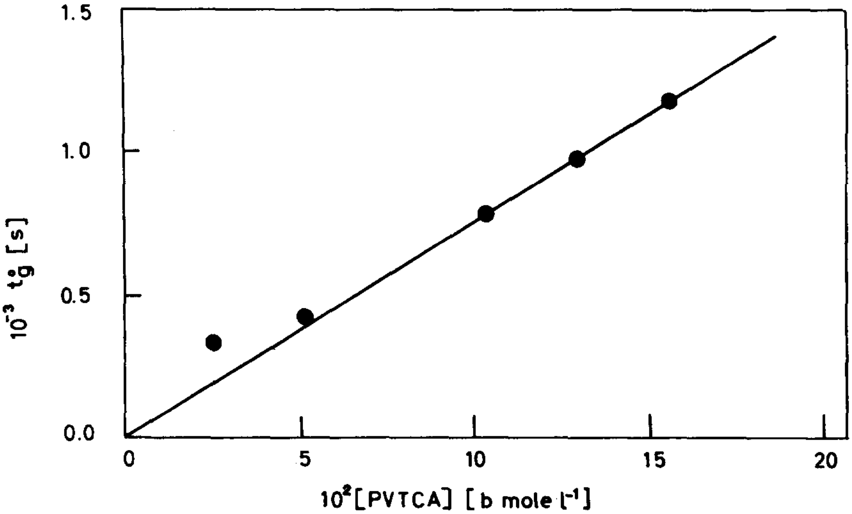


Figure 1—Gelation in bulk styrene ([M]=8·66 mole l^{-1}) at 25°C. [$Mn_2(CO)_{10}$]= $2{\cdot}57 \times 10^{-4}$ mole l^{-1}; $\mathscr{I} = 5{\cdot}45 \times 10^{-8}$ mole l^{-1} s^{-1}; prepolymer specimen A

2 *Methyl methacrylate*

Figure 2 presents a similar plot for methyl methacrylate; the same prepolymer (A) was used in these experiments, with $\mathscr{I} = 6{\cdot}10 \times 10^{-8}$ mole l^{-1} s^{-1}. In deriving t_g^0 from the observed gel-time a value of the transfer constant to monomer of 2×10^{-5} was used. The deviation from linearity in *Figure 2* is less marked than in the case of styrene, although there is a suggestion that radical wastage is occurring at the lowest values of c studied. With the aid of equations (1) and (2) we find that for methyl methacrylate at 25°C

$$k_{tc}/(k_{tc} + k_{td}) = 0{\cdot}342. \qquad (3)$$

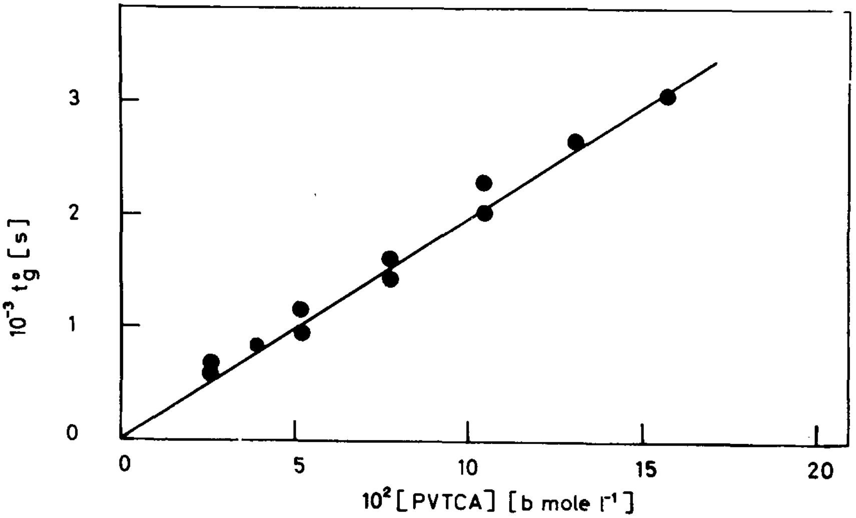


Figure 2—Gelation in bulk methyl methacrylate ([M]=9·38 mole l^{-1}) at 25°C. [$Mn_2(CO)_{10}$]=5·14×10^{-4} mole l^{-1}; $\mathcal{J}$=6·10×10^{-8} mole l^{-1} s^{-1}; prepolymer specimen A

This value is satisfactorily close to that reported in Part III[3] determined by the tracer technique (0·33) and also to that obtained by Bevington *et al*[6].

Two other specimens of prepolymer were used throughout the course of the work reported in this paper. The values of $\bar{P}_w$, obtained by experiments with methyl methacrylate similar to those described above, and applications of (1), (2), (3) are given in (4).

$$\bar{P}_w(C) = 4220 \qquad \bar{P}_w(D) = 4390 \tag{4}$$

In these experiments it was noticed that deviations from (1) occurred at lower values of $\mathcal{J}$ with polymers C, D than with A; this is consistent with the mechanism of radical wastage outlined.

3 *Ethyl methacrylate*

Rates of polymerization, photo-initiated by $Mn_2(CO)_{10}+CCl_3COOEt$, were found to be proportional to the square root of the intensity and led to a value $k_p k_t^{-\frac{1}{2}} = 0{\cdot}072$ mole$^{-\frac{1}{2}}$ l$^{\frac{1}{2}}$ s$^{-\frac{1}{2}}$. Gelation observations were carried out with prepolymer C, the gel-times being determined for a series of values of $\mathcal{J}$ at constant c. In deriving t^0_g, the monomer transfer constant was taken as 1·8×10^{-5}. The plot of $1/t^0_g$ against $\mathcal{J}$ (*Figure 3*), which according to (1) should be a straight line, is in fact somewhat curved over the whole range. Evidently radical wastage is significant even at the lowest intensities used. We have estimated $k_{tc}/(k_{tc}+k_{td})$ from the slope of the curve at the origin, since in this region wastage should be minimal. The result is

$$k_{tc}/(k_{tc}+k_{td}) = 0{\cdot}323 \text{ at } 25°\text{C} \tag{5}$$

The value of the ratio calculated from the point at lowest $\mathcal{J}$ is 0·352.

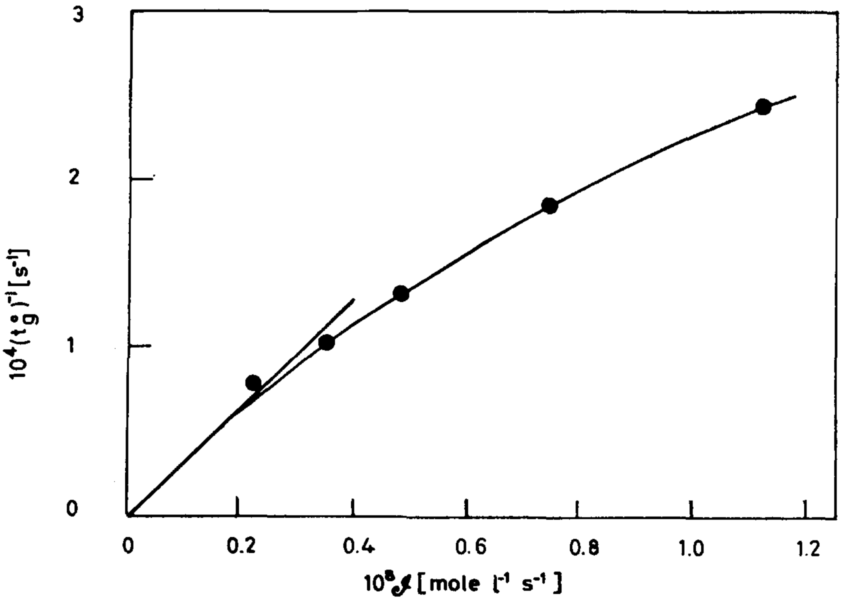


Figure 3—Gelation in bulk ethyl methacrylate ([M] = 7·96 mole l^{-1}) at 25°C. [$Mn_2(CO)_{10}$] = 2·57 × 10^{-4} mole l^{-1}; [prepolymer C] = 0·0424 b mole l^{-1}. (The straight line represents the slope at the origin)

4 n-*Butyl methacrylate*

This monomer gave results generally similar to those of ethyl methacrylate with $k_p k_t^{-\frac{1}{2}} = 0{\cdot}099$ mole$^{-\frac{1}{2}}$ $l^{\frac{1}{2}}$ $s^{-\frac{1}{2}}$. The monomer transfer constant was taken as $1{\cdot}2 \times 10^{-5}$, and a plot of $1/t_g^0$ against $\mathcal{I}$ is presented in *Figure 4* (pre-

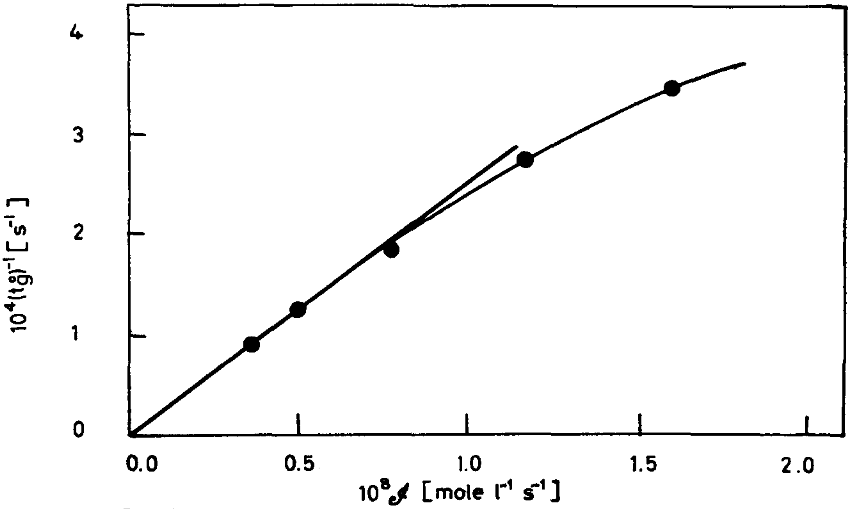


Figure 4—Gelation in bulk *n*-butyl methacrylate ([M] = 6·275 mole l^{-1}) at 25°C. [$Mn_2(CO)_{10}$] = 2·57 × 10^{-4} mole l^{-1}; [prepolymer C] = 0·0424 b mole l^{-1}. (The straight line represents the slope at the origin)

polymer C). From the slope of the curve near the origin we find that at 25°C

$$k_{tc}/(k_{tc}+k_{td})=0{\cdot}255 \tag{6}$$

Essentially the same value of the ratio may be estimated from the point at lowest $\mathcal{I}$.

The experiments described in §§ 2, 3 4 show that the termination reactions in the three methacrylate esters examined are rather similar in character and contain both combination and disproportionation components. The former constitutes from 25 to 35% of the overall process.

5 *Methyl acrylate*

The bulk polymerization of methyl acrylate shows a very pronounced gel-effect, starting virtually from the beginning of the reaction at low rates of initiation[11]. Partly as a consequence of this, the reaction mixtures become highly viscous at low conversion, and observation of gel-times by the techniques described for styrene and the methacrylates are almost impossible. The gel-effect is greatly reduced or eliminated in dilute monomer solutions, and it was decided to investigate gelation under these conditions. Benzene was found to be a suitable diluent. Preliminary experiments showed that at the maximum value of $\mathcal{I}$ the gel-time was independent of monomer concentration, provided the latter did not fall appreciably below 20% bulk. (Similar behaviour has been reported for methyl methacrylate[1]). In experiments at high monomer concentration, gel-formation was also checked by examination of the solubility in chloroform of the polymer resulting from a known period of irradiation.

The polymerization of methyl acrylate (2·19 mole (l^{-1}) in benzene solution at 25°C, photo-initiated by manganese carbonyl in the presence of ethyl trichloracetate, was investigated; the rate of polymerization shows the normal linear dependence on $\mathcal{I}^{\frac{1}{2}}$ and the reaction is first order in monomer concentration up to 40% monomer, indicating the absence of auto-acceleration under these conditions. The value of $k_p k_t^{-\frac{1}{2}}$ deduced from these measurements is 0·69 mole$^{-\frac{1}{2}}$ l$^{\frac{1}{2}}$ s$^{-\frac{1}{2}}$, which is higher than the values recorded in the literature[9] (the mean of which is approximately 0·25 mole$^{-\frac{1}{2}}$ l$^{\frac{1}{2}}$ s$^{-\frac{1}{2}}$, although the values vary over an eightfold range). Reasons for the discrepancy are not clear. It is unlikely that errors in the estimation of $\mathcal{I}$ are responsible; the relative rates of initiation by standard initiating systems based on AZO and $Mn_2(CO)_{10}$ are virtually the same for methyl acrylate and other monomers (*Table 1*). Bamford, Jenkins and Johnston[10] have referred to the caution which is necessary in accepting any given value of $k_p k_t^{-\frac{1}{2}}$ for the polymerization of methyl acrylate, and a more detailed investigation of this polymerization is desirable.

No data are available which allow useful estimates of the transfer constant in the present system; consequently we first present data in which the observed gel-times have been corrected only for initiator consumption. In these circumstances the precise value of $k_p k_t^{-\frac{1}{2}}$ is irrelevant. The dependence of $1/t_g^0$ on $\mathcal{I}$ is shown in *Figure 5* for two different monomer concentrations (prepolymer C). There is no indication that the monomer concentration

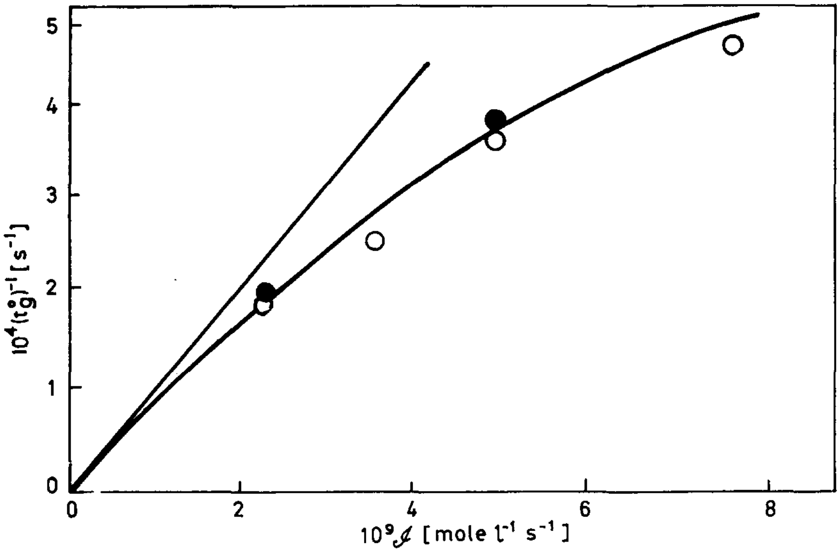


Figure 5—Gelation in methyl acrylate–benzene solution at 25°C. ○, $[M]=3{\cdot}276$ mole l^{-1}; ●, $[M]=2{\cdot}185$ mole l^{-1}; $[Mn_2(CO)_{10}]=2{\cdot}57\times10^{-4}$ mole l^{-1}; [prepolymer C]= 0·0424 b mole l^{-1}. (The straight line corresponds to 100% combination)

has any significant effect on the gel-time in these results. The ratio $k_{tc}/(k_{tc}+k_{td})$ has been estimated (a) from the mean gel-time at the lowest value of $\mathscr{I}$, and (b) from the slope of the curve in *Figure 5* near the origin, and the resulting values are given in (7a), (7b) below.

$$k_{tc}/(k_{tc}+k_{td})=0{\cdot}805 \tag{7a}$$

$$k_{tc}/(k_{tc}+k_{td})=0{\cdot}866 \tag{7b}$$

It will be clear that combination plays an important part in the termination reaction in methyl acrylate polymerization, particularly when it is recalled that no allowance for transfer has been made in deriving these figures. We believe that termination occurs completely by combination. The $1/t_g^0$—$\mathscr{I}$ line for this case is shown in *Figure 5*. The points at the lowest rate of initiation would be brought on to this line if the transfer constant to monomer had a value $3{\cdot}4\times10^{-6}$, approximately, assuming no transfer to benzene.

6 *Ethyl acrylate*

We observed that polymerizations of ethyl acrylate in bulk show a marked auto-acceleration in the earliest stages of reaction, similar to that of methyl acrylate. Consequently rates of polymerization and gel-times were measured in benzene solution using a monomer concentration of 1·83 mole l^{-1}. Under these conditions the rates of polymerization at 25°C, using $Mn_2(CO)_{10}$ in the presence of ethyl trichloracetate as photo-initiator, were accurately proportional to $\mathscr{I}^{\frac{1}{2}}$, and a comparison of these rates with those obtained using AZO as photo-initiator gave a value of $\mathscr{I}$ with $Mn_2(CO)_{10}$, under standard conditions, similar to those obtained with other monomers (*Table 1*). These data led to a value of $k_p/k_t^{\frac{1}{2}}$ of 0·72 mole$^{-\frac{1}{2}}$ l$^{\frac{1}{2}}$ s$^{-\frac{1}{2}}$, which is comparable with the value we found for methyl acrylate.

The results of the gelation experiments, with prepolymer C, are given in *Figure 6*. There do not appear to be any reliable data for transfer for the polymerizations of ethyl acrylate in benzene solution and the values of t_g^0 were obtained from experimental gel-times by correction for initiator consumption alone. The plot of $1/t_g^0$ versus $\mathcal{I}$ appears to be curved over the whole range of rates of initiation employed. A value of the ratio $k_{tc}/(k_{tc}+k_{td})$, obtained by drawing a straight line through the origin and the values of $1/t_g^0$ at the lowest two rates of initiation, is given in equation (8)

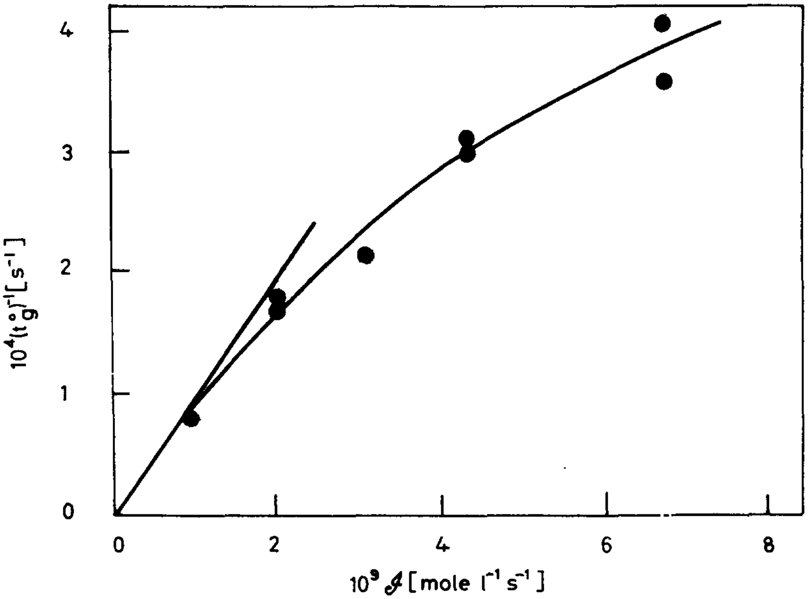


Figure 6—Gelation in ethyl acrylate–benzene solutions at 25°C. $[M]=1{\cdot}83$ mole l^{-1}; $[Mn_2(CO)_{10}]=2{\cdot}57\times10^{-4}$ mole l^{-1}; [prepolymer C]=0·0424 b mole l^{-1}. (The straight line corresponds to 100% combination)

$$k_{tc}/(k_{tc}+k_{td})=0{\cdot}836 \qquad (8)$$

and in the absence of any correction for transfer, this represents a minimum estimate for the fraction of combination. The initial slope of the curve in *Figure 6* corresponds to 100% combination and we conclude that in the polymerizations of ethyl acrylate, as with methyl acrylate, termination occurs almost completely, if not exclusively, by radical combination.

7 *Acrylonitrile*

The relative insolubility of polyacrylonitrile necessitates the use of solvents which are not well-suited to the gelation technique, or about which the transfer data in the literature are sparse and unusually conflicting. We have used N,N-dimethylformamide (DMF) and dimethylsulphoxide

(DMSO). The termination reaction in the polymerization of acrylonitrile has been studied by different techniques, and there are good reasons for believing that it is predominantly a combination process[12, 13]. We shall show that observations on gelation are consistent with this view.

Polymerization in DMF, photosensitized by manganese carbonyl and ethyl trichloracetate, proceeded normally, the rate being proportional to $\mathscr{I}^{\frac{1}{2}}$. Further, comparison of the rates with those arising from photosensitization by AZO showed that the rate of initiation by $Mn_2(CO)_{10} + CCl_3COOEt$ is comparable to those found for other monomers (*Table 1*). However, it was difficult to obtain reproducible gel-times with this solvent. Observed gel-times increased as experiments were repeated, probably on account of decomposition of DMF with formation of amines which are active transfer agents. In view of this, work with DMF was abandoned.

Dimethylsulphoxide does not show this behaviour, and gave satisfactorily reproducible gel-times. In DMSO the rates of polymerization photosensitized by $Mn_2(CO)_{10} + CCl_3COOEt$ are proportional to $\mathscr{I}^{\frac{1}{2}}$, and the rate of initiation is close to that found for other monomers under corresponding conditions (*Table 1*).

A careful study of the polymerization of acrylonitrile in DMSO has been made by White and Zissell[14]. These workers have reported measurements of absolute rate coefficients for propagation and termination in monomer–DMSO mixtures containing 2·51 mole l^{-1} of acrylonitrile, and we shall accept their values, which lead to $k_p k_t^{-\frac{1}{2}} = 0{\cdot}11$ mole$^{-\frac{1}{2}}$ l$^{\frac{1}{2}}$ s$^{-\frac{1}{2}}$ at 25°C.

White and Zissell[14] showed that transfer to DMSO is very much slower than to DMF. They report a transfer constant $1{\cdot}1 \times 10^{-5}$ at 50°C, calculated on the assumption that $C_M = 0\{[M] = 3 \text{ mole } l^{-1}\}$. Since transfer to monomer is not negligible, the true transfer constant to DMSO is less than the value mentioned; if $C_M = 2 \times 10^{-5}$ then it is easy to show that $C_S = 0{\cdot}6 \times 10^{-5}$, approximately. (The value $C_S = 1{\cdot}1 \times 10^{-5}$ given in reference 9 is in error, since transfer to monomer and solvent are both included in this figure.)

Our gelation results are presented in *Figure 7*. On curve (a) the observed gel-times have been corrected for transfer to monomer only ($C_M = 10^{-5}$, $C_S = 0$), while curves (b), (c) show the effects of introducing $C_S = 0{\cdot}2 \times 10^{-5}$ and $C_S = 0{\cdot}5 \times 10^{-5}$, respectively. (Carbonyl consumption is not important in these experiments). The straight line corresponds to 100% combination. It will be clear that, even with $C_S = 0$, the slope of the curve near the origin is not very different from that of the straight line. The best coincidence near the origin is probably obtained with curve (b); in the case of curve (c) the transfer constant used appears too large, and would give fractions of combination exceeding unity. The small transfer constant used in deriving (b) seems likely to be consistent with White and Zissell's measurements at 50°C.

Thus there appears to be little doubt that radical coupling accounts for a very large proportion of the termination reaction; it is probably the sole process, although this cannot be established from the present results.

8 *Methacrylonitrile*

This monomer was studied in DMSO solution. As with acrylonitrile, photo-initiation by $Mn_2(CO)_{10} + CCl_3COOEt$ appeared normal. Grassie and

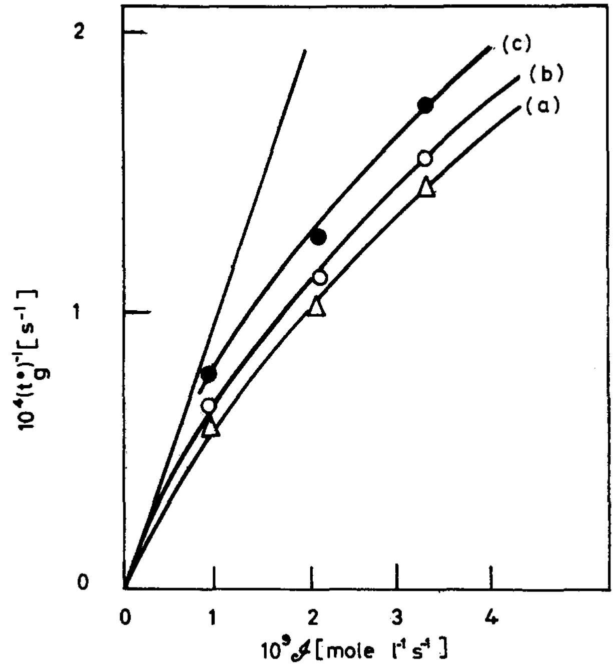


Figure 7—Gelation in acrylonitrile–DMSO solutions at 25°C. $[M]=4{\cdot}56$ mole l^{-1}; $[Mn_2(CO)_{10}]=2{\cdot}57\times10^{-4}$ mole l^{-1}; [prepolymer D]$=0{\cdot}0456$ b mole l^{-1};
(a) transfer to monomer only, $C_M=10^{-5}$;
(b) transfer to monomer and DMSO, $C_S=0{\cdot}2\times10^{-5}$;
(c) transfer to monomer and DMSO, $C_S=0{\cdot}5\times10^{-5}$.
(The straight line corresponds to 100% combination)

Vance[15] have determined absolute rate coefficients in the bulk polymerization of methacrylonitrile over a range of temperatures, and from their results we obtain $k_p k_t^{-\frac{1}{2}}=5{\cdot}7\times10^{-3}$ mole$^{-\frac{1}{2}}$ l$^{\frac{1}{2}}$ s$^{-\frac{1}{2}}$ at 25°C. It is possible that some error is introduced by using this value for calculating corrections to observed gel-times, since our reaction mixtures contain 70% v/v DMSO, but we do not think that this will be significant. Transfer to monomer is comparatively large with methacrylonitrile, the (extrapolated) value of the transfer constant[15] at 25°C being $1{\cdot}6\times10^{-4}$. On the other hand, transfer to DMSO is likely to be negligible; the methacrylonitrile radical has a much lower general reactivity[16] than the acrylonitrile radical, and we have already seen that the latter transfers relatively slowly to DMSO. In correcting observed gel-times for transfer it is therefore justifiable to assume $C_S=0$, especially in view of the greater extent of transfer to monomer.

The corrected gel-times are shown as a function of $\mathcal{J}$ in *Figure 8*. From the initial slope we find that combination constitutes only 35% of the total combination. Methacrylonitrile resembles the methacrylate esters in this respect, and differs from acrylonitrile and the acrylates.

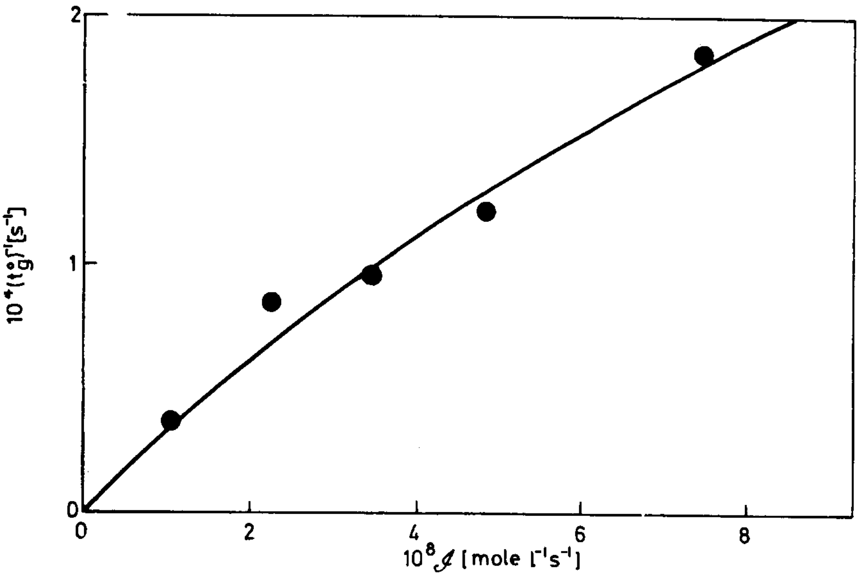


Figure 8—Gelation in methacrylonitrile–DMSO solutions at 25°C. $[M]=3{\cdot}57$ mole l^{-1}; $[Mn_2(CO)_{10}]=2{\cdot}57\times10^{-4}$; [prepolymer D]$=0{\cdot}0456$ b mole l^{-1}

9 *Vinyl acetate*

The extensive chain transfer to monomer which occurs during the polymerization of vinyl acetate hampers the determination of the nature of the termination reaction by all techniques, including gelation. In the latter case the transfer corrections to the gel-times are very large, so that a precise knowledge of the transfer constant is required. Further, as will become apparent, additional complications can arise in systems in which relatively high concentrations of unattached radicals are present.

The polymerization photo-initiated by $Mn_2(CO)_{10}+CCl_3COOEt$ proceeded normally, with rates of initiation similar to those found for other monomers. A value of $k_pk_t^{-\frac{1}{2}}=0{\cdot}115$ mole$^{-\frac{1}{2}}$ $l^{\frac{1}{2}}$ $s^{-\frac{1}{2}}$ was deduced, and is consistent with figures reported in the literature[9].

C_M at 25°C for vinyl acetate is not known accurately. Values reported in the literature[9] (including figures obtained by extrapolation from other temperatures) suggest that it is near $1{\cdot}3\times10^{-4}$, and we have adopted this. The extensive transfer delays gelation so that carbonyl consumption becomes significant; hence the full equation (12) of Part II[2] must be used in calculating the corrections to the observed gel-times.

Table 2 shows observed and corrected gel-times at three rates of initiation, and also the calculated gel-times on the basis of 100% combination. Note the large corrections which must be applied to the observed gel-times. The results at the highest two values of $\mathcal{I}$ apparently favour effectively exclusive combination in the termination reaction. At the lowest rate of initiation, the corrected gel-time is much shorter than that calculated. This situation could arise in at least two ways. Transfer to monomer pro-

Table 2. Gelation in vinyl acetate
$[Mn_2(CO)_{10}] = 2{\cdot}57 \times 10^{-4}$ mole l^{-1}: [prepolymer (C)]$=0{\cdot}0424$ b mole l^{-1}

$10^9\,\mathcal{I}$ mole l^{-1} s^{-1}	3·55	4·93	7·58
$10^{-3}t_g$ s obs	38·4	27·6	12·6
$10^{-3}t_g^0$ s	1·41	1·85	1·21
$10^{-3}t_g^0$ s calc. from (1) with $k_{td}=0$	2·83	2·03	1·32

duces unattached propagating radicals which, having a high general reactivity[16], can enter into transfer reactions with the prepolymer and/or any poly(vinyl acetate) already grafted on to the prepolymer chains. The conversion at the gel point in the experiment at low $\mathcal{I}$ was considerable (2·8 mole l^{-1}, approximately) so that the latter process is by no means unlikely. Both types of transfer reaction convert unattached radicals into attached radicals, and thus lead to an overestimate of the transfer correction, hence to a value of t_g^0 which is too small.

The possible occurrence of these reactions even at the higher rates of initiation clearly throws doubt on the exact value of t_g^0. Nevertheless, in opposition to current views[8], it seems certain that there must be a large proportion of combination in the termination reaction; radical combination is the only process which can produce gelation in systems of this type in which the polymers are readily soluble.

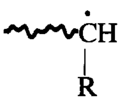
10 *General*

Conclusions reached in this paper about the termination reactions studied in §§ 1–9 are summarised in *Table 3*, together with the results of some earlier investigations on the same monomers. No information about the nature of the termination process is available for monomers other than those shown in *Table 3*.

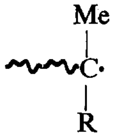
Table 3. Incidence of combination in termination (% of total reaction)

Monomer	*This work* (25 °C)	*Bevington et al*	*Schulz et. al*[17]	*Ayrey and Moore*[7]	*Bamford et al*
Styrene	(100)	100 (25 °C)[6]		95 (60 °C)	~100 (100 °C)[8]
		100 (60 °C)[6]			
Methyl methacrylate	34	40 (0 °C)[6]	69 (40 °C)	39 (60 °C)	33 (25 °C)[3]
		32 (25 °C)[6]	57 (60 °C)		27 (60 °C)[3]
		15 (60 °C)[6]	43 (80 °C)		20 (80 °C)[3]
					~0 (90 °C)[8]
Ethyl methacrylate	32				
n-Butyl methacrylate	25				
Methyl acrylate	~100				~0 (90 °C)[8]
Ethyl acrylate	~100				
Acrylonitrile	~100	~100 (60 °C)[12]			~100 (40–90 °C)[13]
Methacrylonitrile	35				
Vinyl acetate	~100				~0 (90 °C)[8]

The only striking discrepancies between the present and earlier results are found in the cases of methyl acrylate and vinyl acetate, the radicals of which are now seen to combine rather than disproportionate. (Although the two sets of observations were made at different temperatures we do not think this would account for the disagreement.) According to the present results, the polymer radicals examined fall into two classes—those in which the terminal carbon atom C_1 carrying the unpaired spin has only one substituent R (I) and those in which C_1 has both R and methyl substituents (II).


$\sim\!\sim\!\sim\dot{\mathrm{C}}\mathrm{H}(\mathrm{R})$

(I)


$\sim\!\sim\!\sim\mathrm{C}^{\bullet}(\mathrm{Me})(\mathrm{R})$

(II)

At 25°C, radicals of type (I) combine exclusively, while those of type (II) undergo both combination and disproportionation to comparable extents. We also have evidence, which we hope to publish later, that termination in vinyl chloride polymerization occurs by combination. These findings are consistent with the following simple views of the reaction mechanism.

A study of models shows that the transition state in the combination of radicals of type (I) is free from steric hindrance while that for the corresponding reaction of type (II) radicals is often strained (compressed).

Disproportionation, involving the transfer of a hydrogen atom, is likely to require a higher activation energy than combination, which may proceed with virtually zero activation. (In some instances physical effects such as diffusion control or radical occlusion may confer an additional activation energy on the termination process but we are not concerned here with these phenomena.) In view of the steric difficulties encountered in the combination of type (II) radicals, disproportionation may be expected to play a significant part in termination in these systems. In all cases investigated, polymer radicals which disproportionate carry a methyl substituent in addition to the other substituent on C_1. Although the occurrence of disproportionation can be accounted for in the above terms it is possible that the presence of the methyl group offers an easy route to disproportionation which as a consequence may increase in probability to a greater extent than implied in the statistical ratio 5/2. Data currently available do not permit a decision to be made as to whether a methyl or a methylene hydrogen is transferred during disproportionation. It could be argued that if methylene hydrogens were involved, species such as polyvinyl acetate radicals with a high general reactivity, judged by hydrogen abstraction from toluene[16], would be expected to undergo disproportionation. Similarly, the activity of terminal double bonds in poly(methyl methacrylate) in copolymerization with acrylonitrile observed by Bamford and White[18] may be taken as evidence for the transfer of a methyl hydrogen, giving an unsaturated residue with a reactive unsubstituted methylene group. However, no closely analogous systems of known structure have been studied.

Only one example of the interaction of unlike polymer radicals has been studied; Bevington *et al*[6b] showed that poly(methyl methacrylate) and polystyryl radicals combine. This result can be accounted for by the comparative lack of steric hindrance. However, hydrogen abstraction from the methyl group would not be expected to be important in this case since the polystyryl radical has a low general reactivity.

We are at present endeavouring to distinguish between steric control and a possible specific influence of methyl substituents by investigating the behaviour of radicals of high reactivity with two unreactive substituents.

We have assumed that combination and disproportionation involve different transition states. Indeed this must be so, since the ratio k_{tc}/k_{td} for methyl methacrylate has a (negative) temperature coefficient; all published data are consistent in this respect, although absolute values differ.

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ERRATUM

Equation (7) on page 762 (September 1969) of the article by C. H. Bamford, R. W. Dyson, G. C. Eastmond and D. Whittle ('Network formation II') should read as follows.

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