

NEW STUDIES OF THE MECHANISMS OF SOME TRANSFER AND PROPAGATION REACTIONS

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Abstract - Application of the technique of moderated copolymerization to the determination of the transfer constants of very active transfer agents is described. Reactions studied include $\sim\text{St}\cdot + \text{CBr}_4$ and $\sim\text{St}\cdot + 1\text{-BuSH}$ (St = styrene), with methyl methacrylate (MMA) and methyl acrylate (MA) as moderating comonomers. The technique has revealed the existence of a penultimate-unit effect in chain-transfer; thus, the transfer constants of carbon tetrabromide towards the radicals $\sim\text{St}\text{-St}\cdot$, $\sim\text{MMA}\text{-St}\cdot$, $\sim\text{MA}\text{-St}\cdot$ are found to be 337, 60, 302, respectively, at 60°C. These results are interpreted in terms of local steric hindrance between the α -methyl group of the penultimate MMA unit and an incoming bromine atom. All three radicals have similar transfer constants towards 1-BuSH; in these systems no steric hindrance is encountered. The possibility of penultimate-unit effects in homopolymerization is mentioned.

A study has been made of the alternating copolymerization of styrene and methyl acrylate in the presence of the Lewis acid ethyl-aluminium sesquichloride ($\text{Al}_2\text{Et}_3\text{Cl}_3$), with initiation by transition-metal-derivative/organic halide combinations. Photo-initiation ($\lambda=435.8\text{nm}$) by $\text{Mn}_2(\text{CO})_{10}/\text{CCl}_4$ and thermal initiation by $\text{Ni}(\text{CO})_2\{\text{P}(\text{OPh})_3\}_2/\text{CCl}_4$ at 25°C have been used. Kinetic data indicate the existence of a predominant second-order termination reaction between styryl-type radicals, and reveal the very large increase in rate of copolymerization brought about by $\text{Al}_2\text{Et}_3\text{Cl}_3$. The chain-transfer activity of carbon tetrabromide has been examined. Rate and transfer data allow evaluation of relevant kinetic parameters and enable the influence of complexation on reactivities to be assessed. It is considered that all the data for the system are compatible with a scheme in which cross-propagation is the predominant propagation reaction.

INTRODUCTION

This paper is concerned with the reactivities of polymer radicals in chain-transfer and propagation processes. Although the general influence of structural features on the rate coefficients of transfer reactions are appreciated, recent studies have revealed new phenomena; these form the subject of the first part of this paper. The second part describes investigations of the alternating copolymerization of two vinyl monomers in the presence of a Lewis acid, a type of reaction of wide applicability which was recognized mainly through the pioneering work of Hirooka and his colleagues (Ref. 1-5). Reports in the literature (Ref. 3 & 4) that these reactions are insensitive to conventional transfer agents or retarders have naturally led to speculations about the nature of the propagating species. We have found, however, that chain-transfer occurs with active transfer agents such as carbon tetrabromide and that transfer and rate data allow us to construct a relatively simple mechanism for the copolymerization and to draw conclusions about the influence of complexing on reactivities.

PENULTIMATE-UNIT EFFECTS IN CHAIN-TRANSFER

The technique of moderated copolymerization was devised (Ref. 6) to overcome the well-known experimental difficulties associated with determination of the transfer constants of highly active species (S). In this procedure, the monomer under examination (B) is diluted with a large excess of a "moderating" comonomer (A) of much lower transfer activity towards S, so that the incidence of $\sim B\cdot$ radicals in the kinetic chains, determined by the appropriate reactivity ratios and monomer concentrations, is relatively small. Thus the overall transfer constant is not unduly high and may be determined by conventional procedures, without serious complications arising from excessive conversion of S or formation of low polymers. From this, the transfer constant of S for $\sim B\cdot$ radicals may be deduced. Clearly, moderated copolymerization may be a useful technique for studying fast reactions of polymer radicals other than chain-transfer, e.g. reactions with cationic complexes of transition metals.

Under ideal conditions (infinitesimal conversions of all reactants) the appropriate theoretical relations are simple (Ref. 7). In copolymerization, $1/\bar{P}_n$ shows a linear dependence on [S] according to the Mayo-type expression (1),

$$\frac{1}{\bar{P}_n} = \frac{1}{\bar{P}_n^0} + [S] \frac{r_A C_A [A] + r_B C_B [B]}{r_A [A]^2 + 2[A][B] + r_B [B]^2} \quad (1)$$

in which r_A and r_B are reactivity ratios and C_A and C_B are transfer constants. If σ is the slope of the $1/\bar{P}_n$ versus [S] plot, we see from (1) that the required transfer constant C_B is given by

$$C_B = \frac{1}{r_B [B]} \{ \sigma (r_A [A]^2 + 2[A][B] + r_B [B]^2) - r_A C_A [A] \}. \quad (2)$$

Although use of moderated copolymerization greatly reduces the conversion of S, in some systems significant conversion may be unavoidable. Likewise, the conversion of monomer B, normally present in low concentrations, may not be negligible. General equations have been developed which enable accurate transfer constants to be derived from experiments with finite conversions (Ref. 8); this matter will not be further discussed here and for details reference should be made to the original paper (Ref. 8).

Moderated copolymerization was first employed (Ref. 6) in the measurement of the transfer constant of styryl radicals towards carbon tetrabromide at 60°C. Methyl methacrylate (MMA) was the moderating comonomer and with $[MMA] \equiv [A] = 8.85 \text{ mol dm}^{-3}$ and $[St] (St = \text{styrene}) \equiv [B] = 0.091 \text{ mol dm}^{-3}$ it was found that

$$C_B = 51, \text{ approximately.} \quad (3)$$

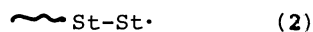
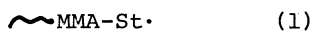
In this work values of the appropriate parameters shown in Table 1 were used.

TABLE 1. Reaction parameters at 60°C

System	r_A	r_B	C_A
MMA/St/CBr ₄	0.470 (Ref. 9)	0.500 (Ref. 9)	0.27 (Ref. 10)
MMA/St/l-BuSH	0.470 (Ref. 9)	0.500 (Ref. 9)	0.66 (Ref. 11)
MA/St/CBr ₄	0.18 (Ref. 12)	0.75 (Ref. 12)	0.41 (Ref. 10)
MA/St/l-BuSH	0.18 (Ref. 12)	0.75 (Ref. 12)	1.69 (Ref. 13)

The values of C_B given in (3) is so much lower than the (necessarily approximate) figure determined by direct measurement by Thomson and Walters (Ref. 14), viz 420 ± 60 , and seems so far outside possible limits of error in both determinations that further consideration was required. Most of the "styryl" radicals in the moderated copolymerization would have structure (1), with

methyl methacrylate as penultimate unit, but in Thomson and Walters' work the radicals would contain only styrene units (2).



A penultimate-unit effect on the reactivity of the radical (hitherto not reported in transfer) would manifest itself in a dependence of the observed transfer constant $C_{B,obs}$ on the ratio $[B]/[A]$ in moderated copolymerization.

Assuming that the influence of non-terminal units is confined to penultimate units, and that there are no penultimate-unit effects in propagation (as demonstrated experimentally for the methyl methacrylate/styrene system) we may show (Ref. 6) that the observed transfer constant is given by

$$C_{B,obs} = \frac{1}{1 + r_B([B]/[A])} \left\{ C_{BA} + C_{BB}r_B \frac{[B]}{[A]} \right\} \quad (4)$$

Here C_{BA} and C_{BB} are the transfer constants for styryl radicals having penultimate units of A and B, respectively.

Determinations over a range of values of $[\text{styrene}]/[\text{methyl methacrylate}]$ indicated not only that $C_{B,obs}$ increases with this ratio, but also that the results are quantitatively in agreement with (4). This is illustrated by the plot in Fig. 1, from which we may deduce that $C_{BA} = 57$ and $C_{BB} = 368$. Thus there is a rather large penultimate-unit effect.

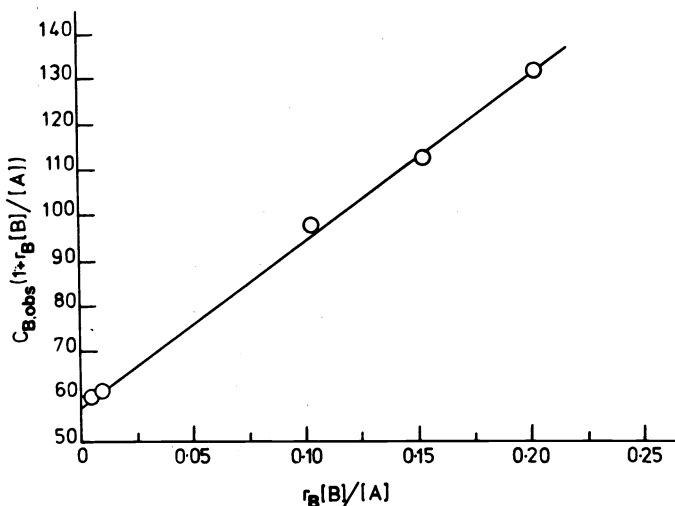
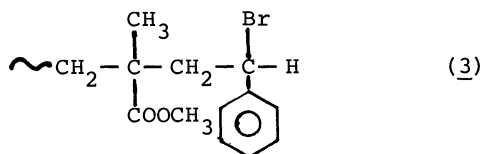


Fig. 1. Dependence of $C_{B,obs}$ on ratio $[\text{styrene}]/[\text{methyl methacrylate}]$. 60°C, plot according to (4). After Bamford and Basahel (Ref. 17).

The presence of a penultimate MMA unit would reduce the electron-density at the terminal carbon atom of the radical to a small extent, and so reduce the transfer activity of the radical towards carbon tetrabromide (Ref. 15). However, such an effect should not be large since it would have to be relayed from the $-\text{COOCH}_3$ group through two saturated carbon atoms. We have not been able to explain our results in terms of the ideas of Russo and Munari (Ref. 16) used to account for the relatively high rate coefficients for cross-termination in the methyl methacrylate/styrene system, which would indeed seem to predict a penultimate-unit influence on transfer opposite to that observed.

It appeared to us (Ref. 17) that the most probable origin of the observed effect lies in local steric hindrance. Models of the polymeric product of the transfer reaction with MMA as penultimate unit reveal that the end portion (3) derived from radical (1) is very congested, mainly on account of unfavourable contacts between the bromine atom and the α -methyl group of the MMA unit. With styrene as penultimate unit there is considerably more



freedom in the model owing to the presence of the hydrogen on C3, in spite of the bulky phenyl group. If these considerations apply to the transition states in reactions of the radicals with carbon tetrabromide we can see at once why radical (1) is much less reactive than radical (2).

The hypothesis of local steric hindrance may be tested in two ways. First, steric hindrance would not arise when the labile atom of the transfer agent is small, so that in these circumstances there should be no penultimate-unit effect. Secondly, a similar result would follow if the moderating comonomer were such that no unfavourable contacts arise with carbon tetrabromide. Accordingly, we have studied three further systems: (i) methyl methacrylate/styrene/1-butane thiol, (ii) methyl acrylate (MA)/styrene/carbon tetrabromide, and (iii) methyl acrylate/styrene/1-butane thiol. In (i) and (iii) the atom transferred is hydrogen, while in (ii) the bromine atom is transferred, but there is no α -methyl in the penultimate unit. The electronic properties of MMA and MA are not very different, so that these systems allow us to assess the influence of electronic effects arising from the penultimate residues in the absence of steric effects.

Results are presented in Table 2. In these experiments corrections were applied for changes in concentration of all reactants (Ref. 8) and we believe the data are the most precise currently available.

TABLE 2. Transfer constants at 60°C

Transfer agent Radical	CBr ₄	1-BuSH
\sim MMA-St. (1)	60	22
\sim St-St. (2)	337	22
\sim MA-St. (4)	302	20

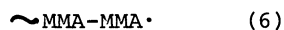
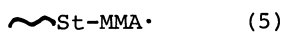
The reaction parameters used for these calculations are given in Table 1.

The value of $C_{B,obs}$ in the system MMA/St/1-BuSH showed only about 10% variation over a range of [MMA]/[St] from 97 - 4.9 so that there is no marked penultimate-unit effect in this case. If differences in the electronic properties of radicals (1) and (2) were responsible for the large differences in the transfer constants of CBr₄ they would show up similarly for 1-BuSH, since the polarities of the transition states are qualitatively similar for the two transfer agents (Ref. 15). Further, the values of C_B in Table 2 for transfer to 1-BuSH lie within the range reported in the literature for the transfer constant of this compound in the homopolymerization of styrene (Ref. 18a), viz. 21-25. Comparison of C_B for reactions between radicals (1) and (4) and CBr₄ reveals the large influence exerted by the α -methyl substituent in the penultimate unit of (1). Any electronic effect arising from this methyl must be small and would, in any case, tend to increase the transfer constant (Ref. 15). On the other hand, for transfer to 1-BuSH, the presence of the α -methyl group has little effect. The results, therefore, strongly reinforce our view that steric congestion involving the α -methyl in (1) is mainly responsible for the relatively low reactivity of this radical towards carbon tetrabromide.

Very recently, Thomson and his colleagues (Ref. 19) examined transfer to trichlorobromomethane by determining relative rates of consumption of monomer and transfer agent. In the copolymerization of methyl methacrylate and styrene they find evidence of a penultimate-unit effect, radical (2) reacting with CCl₃Br about twice as rapidly as radical (1). This difference does not

appear in the corresponding methyl acrylate/styrene/ CCl_3Br system. These results are, therefore, in line with our own for CBr_4 ,³ although the influence of the penultimate unit is less marked with CCl_3Br .

We conclude by mentioning briefly two further topics. (i) The methods described for evaluating C_B require a knowledge of the transfer constant C_A of comonomer A (cf. (1) and (2)). Although we have assumed that this quantity is constant, our results suggest that $\sim\text{A}\cdot$ radicals may exhibit penultimate-unit influences so that $C_{AA} \neq C_{AB}$. For example, it seems likely that radical (5) is more reactive to carbon tetrabromide than radical (6).



In the system MMA/St/CBr_3 errors introduced into determinations of C_B by neglect of this factor are not significant, since the terms in C_A are relatively small. In other cases, however, a more complete treatment, allowing for penultimate-unit effects on both $\sim\text{A}\cdot$ and $\sim\text{B}\cdot$ radicals may be necessary. This has been developed (Ref. 20), and will be published in due course. (ii) There is no reason why penultimate-unit effects of the type described should be confined to copolymerizations; on the contrary, our data imply that they should also exist in some homopolymerizations. For example, in the homopolymerization of methyl methacrylate, the rate of transfer with carbon tetrabromide may not be determined solely by the properties of the terminal residue, but is probably reduced by the presence of the α -methyl in the penultimate unit. Evidently this possibility must be borne in mind when assessing reactivities of propagating radicals from chain-transfer data (Ref. 15).

NEW EXPERIMENTS ON ALTERNATING COPOLYMERIZATION

Initiating systems and general features

The pioneering work of Hirooka (Ref. 1-5) established the dramatic influence of Lewis acids on the copolymerization of vinyl monomers. In 1967 Hirooka and his colleagues (Ref. 1) reported that, in the presence of ethylaluminium dichloride, propylene and acrylonitrile yield alternating copolymers and subsequently they recorded similar behaviour for many other pairs of vinyl monomers (Ref. 2-4). These findings are clearly of great theoretical interest and potential practical importance, and have naturally led to a great deal of discussion. The mechanism of alternating copolymerization in the presence of Lewis acids has been interpreted in terms of changes in reactivity of monomers and/or radicals by complexation with Lewis acids: such monomer complexes have been isolated (Ref. 4), while the idea of radical-Lewis acid complexes was first proposed (Ref. 21) in 1957. Copolymerization of styrene and methyl acrylate in the presence of ethylaluminium sesquichloride ($\text{Al}_2\text{Et}_3\text{Cl}_3$) has been investigated in detail by Hirooka and his colleagues, who suggested that regulation results from the formation of a radical complex containing both monomers at the ends of growing chains (Ref. 2,3,22). In several systems, evidence for the existence of ternary complexes between two monomers and Lewis acid has been presented and the intervention of such species in alternating copolymerization is clearly a possibility which must be considered (Ref. 4).

We selected the system styrene/methyl acrylate/ethylaluminium sesquichloride (EASC) for further study since it appeared to possess several advantages: (i) Hirooka has demonstrated that EASC is particularly effective in producing alternating copolymers, (ii) he also established the formation of complexes between methyl acrylate and the Lewis acid and (iii) there is no evidence for the existence of significant concentrations of ternary complexes. Moreover, (iv) the general kinetic behaviour is documented in Hirooka's work (Ref. 2-4).

Hirooka considered EASC to behave both as an initiator and a regulator. He reported (Ref. 22) that both oxygen and organic peroxides (dicumyl-, benzoyl- and lauroyl-peroxides and cumene hydroperoxide) promote the reaction at 25°C and considered that these compounds undergo initiating redox reactions with alkylaluminium halides. With oxygen as promoter, initiation was thought to proceed through ethyl radicals (formed by interaction of oxygen and the ethyl aluminium halide) which, on addition to complexed methyl acrylate, yield primary initiating radicals.

It seemed to us important, for mechanistic studies, to devise a system in which initiation and regulation occur independently, i.e. in which the regulator is not involved in initiation. We decided to explore the suitability of transition metal derivative/organic halide combinations, which have been studied intensively in our laboratories (Ref. 23). Much of Hirooka's work was carried out with relatively low monomer concentrations (0.4 mol dm^{-3}) in toluene solution; under these conditions, which we decided to retain, initiating systems with S_N1 processes as the rate-determining steps (i.e. those not involving monomer intervention) seemed most likely to be effective. Photoinitiation by manganese carbonyl/ CCl_4 and thermal initiation at 25°C by a suitable nickel derivative in association with CCl_4 were obvious possibilities. Ready availability suggested use of $\text{Ni}(\text{CO})_2\{\text{P}(\text{O}Ph)_3\}_2$; although this has not been studied in detail, earlier investigations with $\text{Ni}[\text{P}(\text{O}Ph)_3]_4$ indicated that it might function in the required S_N1 manner (Ref. 23). In the present work both the $\text{Mn}_2(\text{CO})_{10}$ and $\text{Ni}(\text{CO})_2\{\text{P}(\text{O}Ph)_3\}_2$ systems have been found to be very effective initiators.

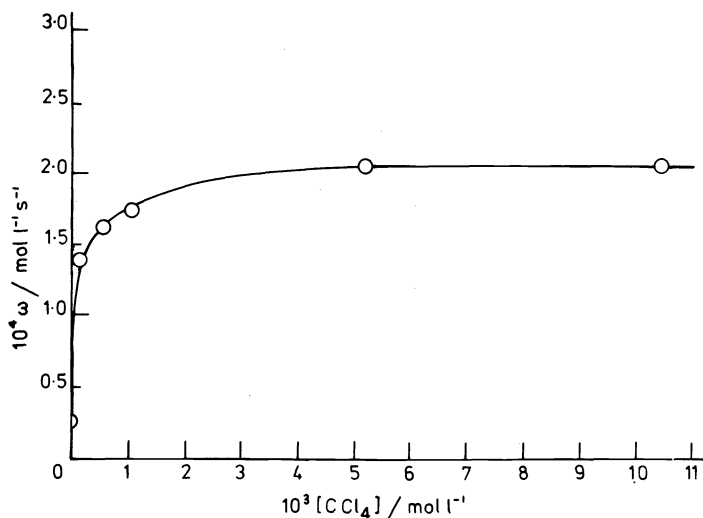


Fig. 2. Copolymerization of styrene (0.4 mol dm^{-3}) and methyl acrylate (0.4 mol dm^{-3}) in the presence of $\text{Al}_2\text{Et}_3\text{Cl}_3$ (0.05 mol dm^{-3}). Photoinitiation ($\lambda = 435.8 \text{ nm}$) by $\text{Mn}_2(\text{CO})_{10} + \text{CCl}_4$, $[\text{Mn}_2(\text{CO})_{10}] = 2.8 \times 10^{-4} \text{ mol dm}^{-3}$. Toluene solution, 25°C . Dependence of rate of copolymerization on $[\text{CCl}_4]$.

Figure 2 shows the dependence on $[\text{CCl}_4]$ of the rate of copolymerization (ω) of styrene + methyl acrylate in the presence of $\text{Al}_2\text{Et}_3\text{Cl}_3$ with photoinitiation ($\lambda = 435.8 \text{ nm}$) by $\text{Mn}_2(\text{CO})_{10}/\text{CCl}_4$ at 25°C . It is closely similar to that found for homopolymerizations photoinitiated by the same system (compare Fig. 2 of Ref. 24). These observations suggest that photoinitiation by $\text{Mn}_2(\text{CO})_{10}/\text{CCl}_4$ proceeds "normally" in the St/MA/EASC system, the aluminium derivative being without significant influence on initiation. No thermal initiation by $\text{Ni}(\text{CO})_2\{\text{P}(\text{O}Ph)_3\}_2$ was observed in the absence of CCl_4 , so that this remark is probably also valid in this case. Rates of initiation (\mathcal{J}) quoted below are based on those derived from calibration experiments in which the homopolymerization of methyl methacrylate was photoinitiated by $\text{Mn}_2(\text{CO})_{10}/\text{CCl}_4$ with similar light intensities and concentrations of $\text{Mn}_2(\text{CO})_{10}$ and CCl_4 . We believe this is justifiable since in homopolymerizations studied the rate of photoinitiation by $\text{Mn}_2(\text{CO})_{10}/\text{CCl}_4$ does not depend significantly on the nature of the monomer (Ref. 23). The concentration of CCl_4 normally used was 0.1 mol dm^{-3} ; this is in the "plateau" range over which the rate of initiation is effectively independent of $[\text{CCl}_4]$ (cf. Fig. 2).

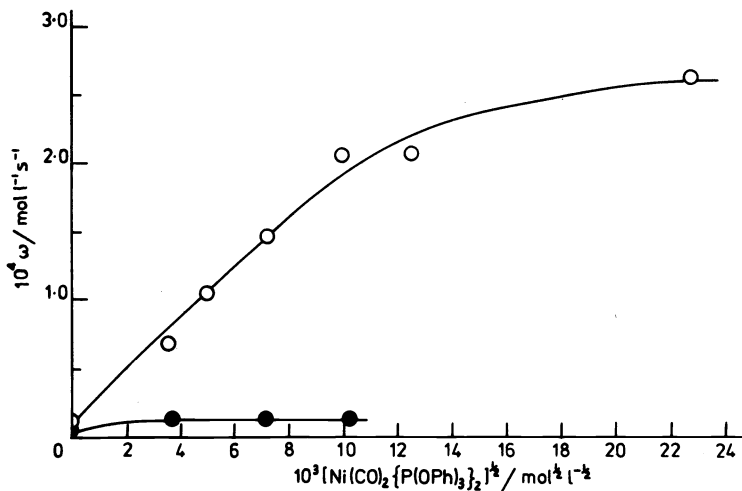


Fig. 3. Copolymerization of styrene (0.4 mol dm^{-3}) and methyl acrylate (0.4 mol dm^{-3}) in the presence of $\text{Al}_2\text{Et}_3\text{Cl}_3$: toluene solution, 25°C . Initiation by $\text{Ni}(\text{CO})_2\{\text{P}(\text{OPh})_3\}_2 + \text{CCl}_4$ (0.1 mol dm^{-3}). Dependence of rate of copolymerization on $[\text{Ni}(\text{CO})_2\{\text{P}(\text{OPh})_3\}_2]^{1/2}$, $[\text{Al}_2\text{Et}_3\text{Cl}_3]$ (mol dm^{-3}): O, 0.05, ●, 0.015.

With thermal initiation by $\text{Ni}(\text{CO})_2\{\text{P}(\text{OPh})_3\}_2/\text{CCl}_4$ the results presented in Fig. 3 were obtained. For $[\text{Al}_2\text{Et}_3\text{Cl}_3] = 0.05 \text{ mol dm}^{-3}$ the plot of ω versus $[\text{Ni}(\text{CO})_2\{\text{P}(\text{OPh})_3\}_2]^{1/2}$ is linear up to $[\text{Ni}(\text{CO})_2\{\text{P}(\text{OPh})_3\}_2] = 8 \times 10^{-5} \text{ mol dm}^{-3}$, approximately ($\omega = 1.8 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$). For higher concentrations, the rate falls progressively below the linear relation, probably indicating retardation or primary termination (see below). The proportionality between ω and $[\text{Ni}(\text{CO})_2\{\text{P}(\text{OPh})_3\}_2]^{1/2}$ is clearly consistent with bimolecular radical termination under the prevailing conditions.

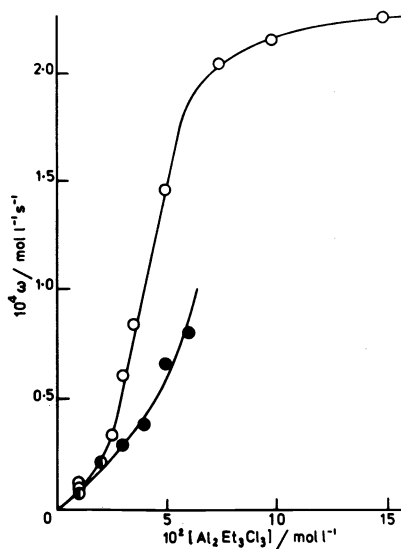


Fig. 4. Copolymerization of styrene (0.4 mol dm^{-3}) and methyl acrylate (0.4 mol dm^{-3}) in the presence of $\text{Al}_2\text{Et}_3\text{Cl}_3$: toluene solution, 25°C . Initiation by $\text{Ni}(\text{CO})_2\{\text{P}(\text{OPh})_3\}_2 + \text{CCl}_4$ (0.1 mol dm^{-3}). Dependence of rate of copolymerization on $[\text{Al}_2\text{Et}_3\text{Cl}_3]$. $[\text{Ni}(\text{CO})_2\{\text{P}(\text{OPh})_3\}_2]$ (mol dm^{-3}): O, 5.2×10^{-5} ; ●, 1.3×10^{-5} .

Figure 4 shows the manner in which the rate of polymerization is influenced by EASC for values of $[\text{Ni}(\text{CO})_2\{\text{P}(\text{OPh})_3\}_2]$ of 5.2×10^{-5} and 1.3×10^{-5} mol dm⁻³. The presence of ethylaluminium sesquichloride leads to greatly enhanced rates; indeed in its absence rates of copolymerization were too small to be measured conveniently. A dependence of ω on $[\text{Al}_2\text{Et}_3\text{Cl}_3]$ similar to that shown in Fig. 4 was also obtained with photoinitiation by $\text{Mn}_2(\text{CO})_{10}/\text{CCl}_4$. We interpret these data to imply increase in the propagation coefficients or decrease in termination coefficients, or both, brought about by EASC. The two curves in Fig. 4 become almost coincident for low values of $[\text{Al}_2\text{Et}_3\text{Cl}_3]$, implying an approximately zero-order dependence on $[\text{Ni}(\text{CO})_2\{\text{P}(\text{OPh})_3\}_2]$ under these conditions. This could arise from primary radical termination; when this process is important the order of the rate of polymerization in initiator concentration falls below 0.5 and approaches zero. To examine this possibility further we carried out the experiments at low $[\text{Al}_2\text{Et}_3\text{Cl}_3]$ shown in Fig. 3. Under these conditions ω becomes effectively independent of $[\text{Ni}(\text{CO})_2\{\text{P}(\text{OPh})_3\}_2]$ at relatively low values of the latter (1.5×10^{-5} mol dm⁻³, approximately) as would be expected if primary radical termination were potentially important.

The low total monomer concentration employed in this work increases the probability of primary radical termination (Ref. 25). Since occurrence of this process would invalidate our calculation of \mathcal{J} it was necessary to ascertain its importance under conditions holding in the kinetic work to be described, for which a knowledge of \mathcal{J} was necessary. Accordingly, rates of copolymerization were measured for monomer mixtures containing three and four times the standard concentration of styrene, with $[\text{Al}_2\text{Et}_3\text{Cl}_3] = 0.075$ mol dm⁻³ and $[\text{Ni}(\text{CO})_2\{\text{P}(\text{OPh})_3\}_2] = 5.2 \times 10^{-5}$ mol dm⁻³. Rates obtained were 2.07×10^{-4} and 2.16×10^{-4} mol dm⁻³s⁻¹, in close agreement with that in Fig. 4 for the normal styrene concentration (0.4 mol dm⁻³). Thus there is no evidence of primary termination under these conditions. Further, the observations support Hirooka's conclusion (Ref. 2) that the rate of copolymerization is independent of styrene concentration (compare eqn.(9)).

Determinations of the number-average molecular weights of polymers prepared at constant $[\text{Al}_2\text{Et}_3\text{Cl}_3]$ (0.05 and 0.03 mol dm⁻³) over a range of $[\text{Ni}(\text{CO})_2\{\text{P}(\text{OPh})_3\}_2]$ have revealed that \bar{M}_n does not vary significantly with initiator concentration. Thus, for example, all the polymers resulting from the reactions referred to in Fig. 3 with $[\text{Al}_2\text{Et}_3\text{Cl}_3] = 0.05$ mol dm⁻³ have similar molecular weights. Under the present conditions, therefore, \bar{M}_n is determined effectively by chain-transfer. The initiating system in these experiments included carbon tetrachloride at a concentration of 0.1 mol dm⁻³, but, as mentioned later, CCl_4 is not an effective transfer agent. Consequently other components of the reaction mixture are responsible for chain-transfer. Hirooka (Ref. 22) has suggested that transfer involves a complexed methyl acrylate radical. We have found that, with a constant rate of initiation, \bar{M}_n is larger at lower $[\text{Al}_2\text{Et}_3\text{Cl}_3]$, consistent with the view that EASC is involved in chain-transfer.

The structures of the copolymers were examined by elemental analysis and by nmr observations. Hirooka (Ref. 22) has described features in the nmr spectrum characteristic of alternating MA/St copolymers. We have concluded that the copolymers are essentially alternating for concentrations of $\text{Al}_2\text{Et}_3\text{Cl}_3$ as low as 0.01 mol dm⁻³ - the lowest value studied. The present systems therefore provide a practical means of synthesizing alternating copolymers with relatively low concentrations of EASC. For example, with the latter equal to 0.01 mol dm⁻³ and $[\text{St}] = [\text{MA}] = 0.4$ mol dm⁻³ conversions of approximately 10%/h are readily obtained with the aid of the thermal- or photo-initiators under consideration.

Chain-transfer

Experiments in which carbon tetrachloride was added to the reaction mixture (in excess of the standard concentration 0.1 mol dm⁻³ in the initiating system)

confirmed the negligible transfer activity of this compound (see also Ref. 2-4). Additional concentrations up to 0.4 mol dm^{-3} were used with $[\text{Al}_2\text{Et}_3\text{Cl}_3] = 0.075$ and 0.03 mol dm^{-3} .

The remarkably high reactivity of carbon tetrabromide towards styryl radicals, discussed earlier (cf. Table 2) encouraged us to examine the transfer activity of CBr_4 in the copolymerization. Results of two series of experiments with different $[\text{Al}_2\text{Et}_3\text{Cl}_3]$ are presented in Table 3.

TABLE 3. Chain-transfer to carbon tetrabromide at 25°C . Styrene and methyl acrylate concentrations each 0.4 mol dm^{-3} in toluene. Initiating system: $\text{Ni}(\text{CO})_2\{\text{P}(\text{OPh})_3\}_2$ ($5.2 \times 10^{-5} \text{ mol dm}^{-3}$) + CCl_4 (0.1 mol dm^{-3}).

$[\text{Al}_2\text{Et}_3\text{Cl}_3]$ mol dm^{-3}	$10^4 [\text{CBr}_4]$ mol dm^{-3}	$10^4 \bar{w}$ $\text{mol dm}^{-3} \text{ s}^{-1}$	\bar{P}_n
0.075	0	2.03	3627
0.075	2	1.97	3087
0.075	4	1.96	2726
0.075	7	1.97	2165
0.075	10	1.88	1875
0.075	20	1.93	1350
0.030	0	0.49	4147
0.030	4	0.37	1941
0.030	20	0.32	626

Table 3 shows that the presence of carbon tetrabromide leads to copolymers of lower molecular weight, as anticipated. Plots of $1/\bar{P}_n$ versus $[\text{CBr}_4]$ presented in Figs. 5 and 6 are both satisfactorily linear and have slopes of

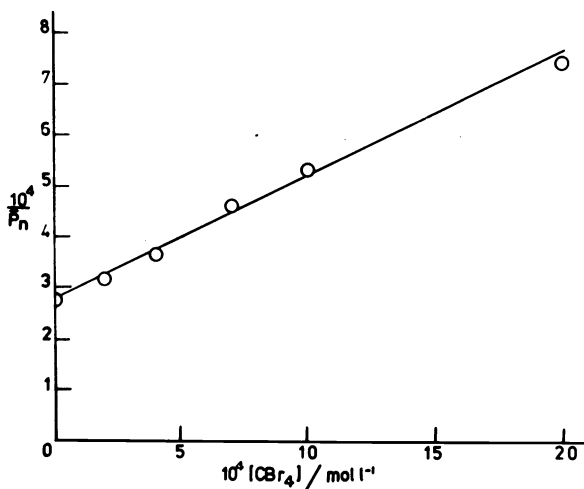


Fig. 5. Dependence of \bar{P}_n on $[\text{CBr}_4]$: plot according to equation (7). $[\text{styrene}] = [\text{methyl acrylate}] = 0.4 \text{ mol dm}^{-3}$; toluene solution, 25°C . Initiator: $\text{Ni}(\text{CO})_2\{\text{P}(\text{OPh})_3\}_2$ ($5.2 \times 10^{-5} \text{ mol dm}^{-3}$) + CCl_4 (0.1 mol dm^{-3}). $[\text{Al}_2\text{Et}_3\text{Cl}_3] = 0.075 \text{ mol dm}^{-3}$.

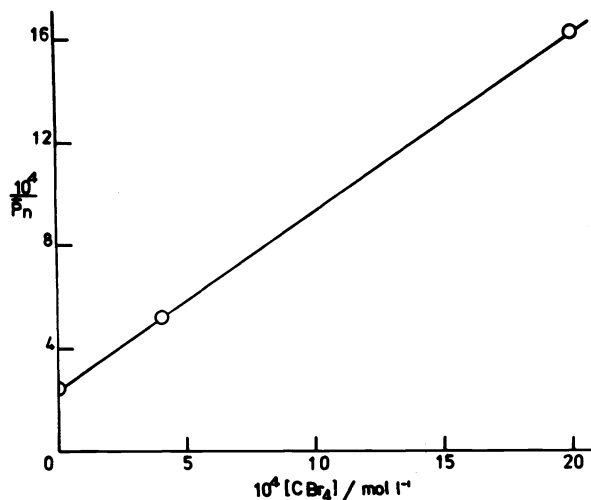


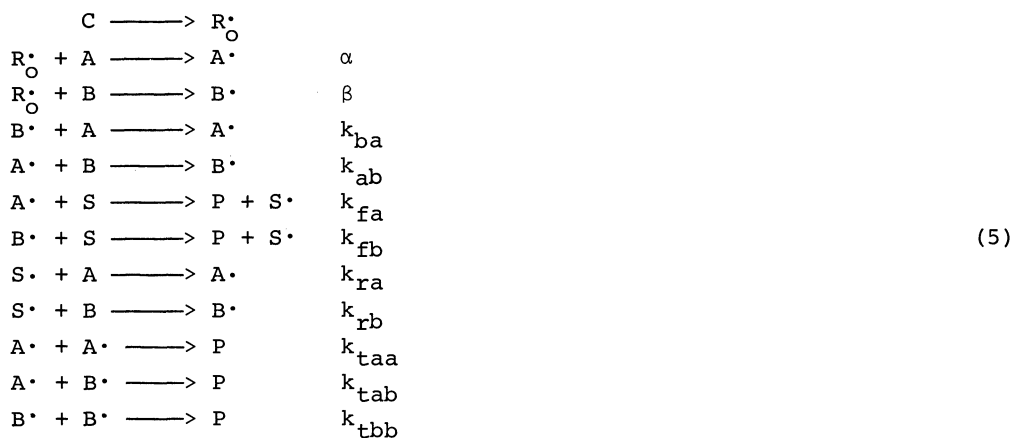
Fig. 6. Dependence of \bar{P}_n on $[CBr_4]$: plot according to equation (7). $[styrene] = [methyl\ acrylate] = 0.4\ mol\ dm^{-3}$; toluene solution, $25^\circ C$. Initiator: $Ni(CO)_2\{P(OPh)_3\}_2$ ($5.2 \times 10^{-5}\ mol\ dm^{-3}$) + CCl_4 ($0.1\ mol\ dm^{-3}$). $[Al_2Et_3Cl_3] = 0.03\ mol\ dm^{-3}$.

0.240 and $0.676\ mol^{-1}dm^3$ for $[Al_2Et_3Cl_3] = 0.075$ and $0.030\ mol\ dm^{-3}$, respectively. From the data in Table 3 and Figs. 5 and 6 we draw the following conclusions. (i) Rates of polymerization are not greatly affected by the presence of carbon tetrabromide, although there is a tendency for the rate to be somewhat depressed by CBr_4 . A similar effect, associated with chain-transfer to carbon tetrahalides has been frequently reported in the literature (Ref. 1 and 26). (ii) The activity of carbon tetrabromide in chain-transfer is markedly greater at the lower concentration of EASC.

Kinetics and mechanism

A major objective of this work is to explore the applicability of the simple mechanism in which monomer units of the two types (A and B) are added successively to the propagating chains, alternation being the result of the predominance of cross-propagation reactions. The component reactions, including chain-transfer to species S, are set out in (5). Initiating radicals R_\circ are formed from the initiator C, (rate f), P represents dead polymer and $\alpha + \beta = 1$. Termination by combination is assumed, this seeming most appropriate for the two monomers under consideration; our general conclusions are not affected by this assumption.

Conventional stationary-state treatment leads to relations (6) and (7) for long chains.



$$\omega \left(\equiv - \frac{d([A] + [B])}{dt} \right) = 2k_{ba}[A] \left(\frac{f}{k_t} \right)^{\frac{1}{2}} \quad (6)$$

$$\frac{1}{\bar{P}_n} = \frac{(f/k_t)^{\frac{1}{2}}}{4k_{ba}[A]} + \frac{1}{2} \left\{ \frac{k_{fa}}{k_{ab}} [A] + \frac{k_{fb}}{k_{ba}} [B] \right\} \frac{[S]}{[A][B]} \quad (7)$$

In these equations

$$k_t = k_{tbb} + 2k_{tab} \frac{k_{ba}[A]}{k_{ab}[B]} + k_{taa} \left(\frac{k_{ba}[A]}{k_{ab}[B]} \right)^2 \quad (8)$$

We note that (6) is consistent with the experimental finding of Hirooka (Ref. 2), expressed by (9)

$$\omega = k[MA \cdot \cdot al][MA]_{free}^0 [St]^0 \quad (9)$$

if [A] represents complexed methyl acrylate [MA · · al], and k_t is effectively independent of [A] and [B], i.e. if termination occurs predominantly between styryl radicals (free or complexed) so that, effectively, $k_t = k_{tbb}$. If complexing between methyl acrylate and $Al_2Et_3Cl_3$ is strong, as proposed by Hirooka (Ref. 2 and 22), $[A] = [al] = 2[Al_2Et_3Cl_3]$ so long as $[al] < [A]$; the proportionality between ω and $[Al_2Et_3Cl_3]$ thus predicted by (6) is confined to the middle portion of the range of $[Al_2Et_3Cl_3]$ in the present experiments (Fig. 4) for reasons already discussed.

With the aid of (6) and the data in Fig. 4 we may evaluate $k_{ba} (f/k_t)^{\frac{1}{2}}$ and hence $k_{ba} k_t^{-\frac{1}{2}}$, since f is known. Results are presented in Table 4.

TABLE 4. Kinetic parameters derived from rates of polymerization at 25°C. $[MA] = [St] = 0.4 \text{ mol dm}^{-3}$, toluene solution. Initiating system as in Table 3. $f = 3.8 \times 10^{-8} \text{ mol dm}^{-3} \text{ s}^{-1}$.

$[Al_2Et_3Cl_3]$ (mol dm ⁻³)	0.075	0.030
ω (mol dm ⁻³ s ⁻¹)	2.04×10^{-4}	0.61×10^{-4}
$k_{ba} (f/k_t)^{\frac{1}{2}}$ (s ⁻¹)	6.80×10^{-4}	5.08×10^{-4}
$k_{ba} k_t^{-\frac{1}{2}}$ (mol ^{-1/2} dm ^{3/2} s ^{-1/2})	3.49	2.61

Values of $k_{ba} k_t^{-\frac{1}{2}}$ are somewhat different for the two values of $[Al_2Et_3Cl_3]$, reflecting the approximate nature of the proportionality between ω and $[Al_2Et_3Cl_3]$, noted above, which may indicate a small amount of primary radical termination at the lower value of $[Al_2Et_3Cl_3]$.

We now consider the data in Figs. 5 and 6. According to (7) the slope of the $1/\bar{P}_n$ versus $[CBr_4]$ plot is

$$\frac{1}{2} \left\{ \frac{k_{fa}}{k_{ab}[B]} + \frac{k_{fb}}{k_{ba}[A]} \right\} \quad (10)$$

For systems free from Lewis acids, the first term in (10) is equal to $r_{AA}/2[B]$. Neither r_A nor C_A has been determined at 25°C, but we may assume approximate values of 0.18 and 0.3, respectively (see Table 1 and Ref. 18(b)) and so obtain

$$\frac{k_{fa}}{2k_{ab}[B]} = 0.068 \text{ mol}^{-1} \text{ dm}^3 \quad (11)$$

Complexation of $\sim A \cdot$ with a Lewis acid would reduce its activity towards CBr_4 (k_{fa}) and increase its rate of addition to monomer B (k_{ab}) (Ref. 15), so

that (11) gives a maximum value for $k_{fa}/(2k_{ab}[B])$ in the present systems. This term therefore makes only a rather small contribution to the observed slopes in Figs. 5 and 6. In the absence of more precise data, we believe that no important error will be introduced by using (11) in combination with (10) to calculate k_{fb}/k_{ba} from the chain-transfer data. We take [A] to refer to complexed methyl acrylate and follow Hirooka (Ref. 2) in setting $[A] = 2[Al_2Et_3Cl_3]$. Results are presented in Table 5.

TABLE 5. Kinetic parameters derived from chain-transfer to CBr_4 at 25°C.

$[Al_2Et_3Cl_3]$ (mol dm ⁻³)	0.075	0.030
slope of $1/\bar{P}_n$ versus $[CBr_4]$ plot (mol ⁻¹ dm ³)	0.240	0.676
k_{fb}/k_{ba}	0.052	0.073
$k_{fb}k_t^{-1/2}$ (mol ^{-1/2} dm ^{3/2} s ⁻¹)	0.18	0.19

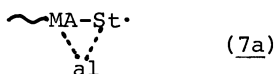
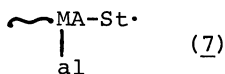
Combination of the data for $k_{ba}k_t^{-1/2}$ and k_{fb}/k_{ba} in Tables 4 and 5, respectively, yields the values of $k_{fb}k_t^{-1/2}$ in Table 5. An estimate of the corresponding figure for the styrene + methyl acrylate copolymerization in the absence of Lewis acid may be obtained from the transfer constant of radical (4) ($\sim MA-St\cdot$) in Table 2 (302) and $k_p k_t^{-1/2}$ for the homopolymerization of styrene (Ref. 28). The transfer constant in Table 2 is probably almost independent of temperature, hence, in the absence of Lewis acid,

$$k_{fb}k_t^{-1/2} = 302 \times 8.3 \times 10^{-3} = 2.5 \text{ mol}^{-1/2} \text{ dm}^{3/2} \text{ s}^{-1/2} \quad (12)$$

Thus the presence of the Lewis acid brings about a reduction in the value of $k_{fb}k_t^{-1/2}$ by a factor of approximately 14. If k_t is unaltered (i.e. in both cases it is equal to k_t for styrene homopolymerization) this factor also represents the reduction in k_{fb} attributable to the Lewis acid. However, it is unlikely that the k_t values are similar, and for a variety of reasons we might expect k_t in the system with Lewis acid to be smaller than that for styrene; we should, therefore, regard the factor 14 as the minimum reduction in k_{fb} .

We are presently engaged in determining the absolute value of the termination coefficient and intend to report the results in due course. Our measurements to date indicate that k_t is close to $3 \times 10^6 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$. On this basis $k_{fb} = 312 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$, a value approximately 43 times smaller than that for $\sim MA-St\cdot$ radicals deduced from Table 2.

These findings are understandable in terms of complexation of $\sim MA-St\cdot$ radicals by the Lewis acid to give



A strong penultimate-unit influence might be anticipated in (7); electron-withdrawal would reduce transfer activity towards CBr_4 and steric factors and perhaps interaction between the unpaired spin and the Al atom (7a) would also operate in the same sense.

Taking $k_t = 3 \times 10^6 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ we find from Table 4 that $k_{ba} = 6045 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$. This high value is probably mainly attributable to complexation of methyl acrylate, which thereby becomes much more powerfully electron-attracting. It is important to stress that the apparent insensitivity of these copolymerizations to conventional transfer agents stems not only from the

lower value of k_{fb} mentioned above, but also from the high rate coefficient k_{ba} of the competing propagation.

In conclusion we present in Table 6 a collection of propagation coefficients relevant to this system.

TABLE 6. Propagation coefficients corrected as far as possible to 25°C.

Reaction	Rate coefficient ($\text{mol}^{-1}\text{dm}^3\text{s}^{-1}$)
$\sim\text{MA}\cdot + \text{St}$	3289 (Ref.12 and 29)
$\sim\text{MA}-\text{St}\cdot + \text{MA}$ $\begin{array}{c} \\ \text{al} \end{array}$ $\begin{array}{c} \\ \text{al} \end{array}$	6045
$\sim\text{St}\cdot + \text{MA}$	59 (Ref. 12 and 27)
$\sim\text{St}\cdot + \text{St}$	44 (Ref. 27)
$\sim\text{MA}\cdot + \text{MA}$	592 (Ref. 29)

These data illustrate that the high rate of the $\sim\text{B}\cdot + \text{A}$ type reaction brought about by complexing makes alternating addition of monomer units to growing chains the predominant propagation. Although the effects of complexing on the other propagation steps are not yet known, we believe our analysis shows that all the experimental data can be accommodated in this way, i.e. in terms of scheme (5).

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