Studies of absolute rate coefficients in alternating copolymerization by observation of pre- and after-effects

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Expressions are presented for pre- and after-effects in some photo-initiated copolymerizations leading to strongly alternating copolymers. The mechanisms considered include alternation arising from dominant cross-propagation and from homopolymerization of a ternary complex containing both monomers, as well as from a generalized version of the former in which the ternary complex is involved in propagation. Determination of pre- and after-effects by dilatometry is discussed, in particular the necessity of allowing for thermal perturbations during polymerization, which may easily exceed the quantities being measured. A method for making corrections for these perturbations is developed and two ways of plotting experimental data for this purpose are described. In both pre- and after-effects data are plotted in the same diagram to increase the precision. The techniques are applied to the copolymerization of methyl acrylate and styrene, and of methyl methacrylate and styrene, in the presence of the Lewis acid ethylaluminium sesquichloride. Initiation was effected by light with $\lambda = 365$ nm. The resulting values of $k_{ba}k_t'^{-1}$ (k_{ba}, k_t' are the velocity coefficients for propagation of a styryl radical with an acrylate type monomer (complexed with the Lewis acid), and for second order termination, respectively) agree satisfactorily with literature values when comparison is possible (i.e. for the system $Et_3Al_2Cl_3$/MA/St). For this case, combination of the above with literature data on steady-state measurements permits evaluation of the propagation coefficients: $k_{ba} = 5.6 \times 10^3$, $k_{ab} = 37.3 \times 10^3$ $mol^{-1} dm^3 s^{-1}$. Progress in the kinetic analysis of these copolymerizations is currently impeded by the shortage of quantitative information about the binary and ternary equilibria involved.

(Keywords: Lewis acid; monomer complexes; interactions with radicals; dilatometry; non-isothermal effects; reaction mechanisms)

INTRODUCTION

A knowledge of the cross-propagation rate coefficients in free-radical polymerization is important in strongly-alternating reactions, since it can provide information on the nature of the propagation process. Usually, when alternation is not marked, these coefficients are evaluated from homopropagation coefficients with the aid of the appropriate monomer reactivity ratios; however, this procedure is inapplicable to strongly alternating systems since the reactivity ratios are close to zero and are very difficult to determine accurately.

The studies of Hirooka and his colleagues[1-6] led to the recognition of an important class of alternating reactions, in which a mixture of monomers with donor and acceptor types of behaviour (representatives of Hirooka's A and B monomer groups[4,5], respectively) are copolymerized in the presence of a Lewis acid, generally a metal halide. These systems have been much studied, but there are few determinations of absolute rate coefficients of the component reactions. Probably the most complete study of the absolute propagation coefficients to date is that of Bamford and Malley[7] on the methyl acrylate/styrene/ethylaluminium sesquichloride system, in which the kinetic chain life-times were estimated by conventional use of intermittent illumination. The photoinitiating system was manganese carbonyl ($Mn_2(CO)_{10}$) + carbon tetrachloride, used with light of wavelength 436 nm. The authors gave reasons for believing that the rate of initiation $\mathscr{I}$ is the same as that holding with simple vinyl monomers under the same conditions; hence simple calibration experiments provided a knowledge of $\mathscr{I}$ in the alternating reaction. Both propagation coefficients were found to have high values at 25°C: $k_{ba} = (8.5$ or $9.4) \times 10^3$ and $k_{ab} = (39$ or $57) \times 10^3$ mol^{-1} dm^3 s^{-1} according to the details of the polymerization mechanism assumed (methyl acrylate and styrene are denoted by A and B, respectively).

It has been known for a long time that observations of photochemical pre- and after-effects may be used to evaluate the ratio $k_p k_t^{-1}$ in homopolymerization (k_p, k_t being the rate coefficients of propagation and second order termination, respectively)[8]. The method has received little attention, however; the work of Burnett[9] on pre-effects in styrene polymerization is probably the best-known early example. As far as the writers are aware there have been no applications of the technique to copolymerization. It has the advantage of not requiring a knowledge of the rate of initiation. (Note that the 'viscosity method' for evaluating absolute rate coefficients in polymerization reactions, being essentially a technique for measuring pre- and after-effects by viscosity changes[10], shares this advantage.) The most direct way of observing such effects

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employs dilatometry, which (like viscosity) is particularly valuable in that it permits determination of the small degrees of conversion involved. However, a dilatometer behaves as a sensitive thermometer, and (as realized by Burnett) the observed pre- and after-effects are likely to contain major contributions arising from temperature changes when polymerization is started or interrupted.

In the course of extended work on alternating copolymerization in the presence of ethylaluminium halides, Hirooka observed in these laboratories that reaction rates are greatly enhanced by illumination with u.v. light; indeed in the absence of oxygen and light the reactions occur only slowly. He also noted that the rates of the photoinitiated polymerizations are proportional to the square root of the incident intensity. The reactions therefore appeared to be amenable to direct study by observation of pre- and after-effects, without added photoinitiator. It will become apparent later that these alternating copolymerizations, in view of their relatively high rates of propagation, are particularly suitable for investigations of this kind.

These matters are considered in the present paper. We have derived a method which permits first-order correction for perturbing thermal effects and applied it to the copolymerizations in toluene solution of methyl acrylate + styrene and methyl methacrylate + styrene in the presence of ethylaluminium sesquichloride.

The pre- and after-effects in alternating copolymerization

In this section we derive expressions for pre- and after-effects which are analogous to those holding for homopolymerization. We use the simple cross-propagation mechanism (cf. Bamford and Malley[7]) set out in *Scheme 1*, in which A and B represent the two vinyl monomers, I is the initiator and other symbols have their conventional meanings. Since we consider very strong alternation, homopropagations are omitted; chain transfer is not included. It is our opinion that this mechanism is the most appropriate for our system and conditions[11]; see also p. 000. In the light of the results of Bamford and Malley[7], we believe it is sufficient for present purposes to assume a single rate coefficient for the three diffusion-controlled termination processes.

Scheme 1 is general for copolymerization with dominant cross-propagation; however, this paper is concerned with the copolymerization of acrylic monomers with styrene in the presence of a Lewis acid which complexes with the former. The observations of Hirooka and his colleagues[3–6] reveal that for such systems it is the complexed monomer which enters predominantly into the alternating copolymerization; thus we shall take A to represent complexed methyl acrylate (MA) or methacrylate (MMA) and B to denote styrene.

$$
\begin{array}{llll}
 & \mathrm{I} \xrightarrow{h\nu} \mathrm{R}_0^{\cdot} & & \text{(a)} \\
\mathrm{R}_0^{\cdot}+ & \mathrm{A} \rightarrow \sim\!\mathrm{A}^{\cdot} & \left.\begin{matrix}\\ \\ \end{matrix}\right\} \mathscr{I} & \text{(b)} \\
\mathrm{R}_0^{\cdot}+ & \mathrm{B} \rightarrow \sim\!\mathrm{B}^{\cdot} & & \text{(c)} \\
\sim\!\mathrm{A}^{\cdot}+ & \mathrm{B} \rightarrow \sim\!\mathrm{B}^{\cdot} & k_{ab} & \text{(d)} \\
\sim\!\mathrm{B}^{\cdot}+ & \mathrm{A} \rightarrow \sim\!\mathrm{A}^{\cdot} & k_{ba} & \text{(e)} \\
\sim\!\mathrm{A}^{\cdot}+ & \sim\!\mathrm{A}^{\cdot} \rightarrow \text{polymer} & \left.\begin{matrix}\\ \\ \\ \end{matrix}\right\} k_t' & \text{(f)} \\
\sim\!\mathrm{A}^{\cdot}+ & \sim\!\mathrm{B}^{\cdot} \rightarrow \text{polymer} & & \text{(g)} \\
\sim\!\mathrm{B}^{\cdot}+ & \sim\!\mathrm{B}^{\cdot} \rightarrow \text{polymer} & & \text{(h)}
\end{array}
\qquad (1)
$$

Under stationary conditions, the relative concentrations of ~A· and ~B· radicals are given by

$$\frac{[\mathrm{A}\cdot]}{[\mathrm{B}\cdot]}=\frac{k_{ba}[\mathrm{A}]}{k_{ab}[\mathrm{B}]} \qquad (2)$$

and for long chains this ratio will be effectively maintained under non-stationary conditions. Hence, in general, we have for the total radical concentration $[\mathrm{Z}\cdot]$

$$[\mathrm{Z}\cdot]=[\mathrm{A}\cdot]+[\mathrm{B}\cdot]=\lambda[\mathrm{B}\cdot] \qquad (3)$$

where

$$\lambda=1+\frac{k_{ba}[\mathrm{A}]}{k_{ab}[\mathrm{B}]} \qquad (4)$$

Further, in the stationary state

$$\mathscr{I}=k_t'[\mathrm{Z}\cdot]^2 \qquad (5)$$

and the rate of polymerization ω is given in general by

$$\omega\equiv-\frac{\mathrm{d}[\mathrm{M}]}{\mathrm{d}t}=-\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t}-\frac{d[B]}{dt}=2k_{ba}[\mathrm{A}][\mathrm{B}\cdot]$$

$$=\frac{2k_{ba}}{\lambda}[\mathrm{A}][\mathrm{Z}\cdot] \qquad (6)$$

from relation (3). (M represents total monomer concentration.)

We suppose that in pre-effect determinations, the rate of chain-starting is increased instantaneously at time $t=0$ from $\mathscr{I}_1$ to $\mathscr{I}_2$. The stationary total radical concentrations corresponding to these values are $[\mathrm{Z}\cdot]_1$ and $[\mathrm{Z}\cdot]_2$ respectively; the latter is not, of course, established instantaneously at $t=0$. The pre-effect ΔM_p, which represents the reduction in monomer conversion attributable to the failure of the radical concentration instantly to attain its final concentration at $t=0$, is given by

$$\Delta M_p=\int_{t=0}^{\infty}(\omega_2-\omega)\mathrm{d}t=\frac{2k_{ba}[\mathrm{A}]}{\lambda}\int_{t=0}^{\infty}([\mathrm{Z}\cdot]_2-[\mathrm{Z}\cdot])\mathrm{d}t \qquad (7)$$

The integral in relation (7) may be simply evaluated by expressing dt in terms of $[\mathrm{Z}\cdot]$ with the aid of relation (8), valid for $t\geqslant 0$

$$\frac{\mathrm{d}[\mathrm{Z}\cdot]}{\mathrm{d}t}=\mathscr{I}_2-k_t'[\mathrm{Z}\cdot]^2 \qquad (8)$$

and noting from relation (5) that $\mathscr{I}_2/k_t'=[\mathrm{Z}\cdot]_2^2$; we thus find that

$$\Delta M_p=\frac{2k_{ba}[\mathrm{A}]}{\lambda k_t'}\int_{[\mathrm{Z}\cdot]_1}^{[\mathrm{Z}\cdot]_2}\frac{\mathrm{d}[\mathrm{Z}\cdot]}{[\mathrm{Z}\cdot]_2+[\mathrm{Z}\cdot]}$$

$$=\frac{2k_{ba}[\mathrm{A}]}{\lambda k_t'}\ln\frac{2[\mathrm{Z}\cdot]_2}{[\mathrm{Z}\cdot]_2+[\mathrm{Z}\cdot]_1} \qquad (9)$$

It is convenient to express the ratio of the final to the initial (stationary) radical concentrations as ϕ. From relation (6) it follows that ϕ also represents the ratio of final to initial rates of copolymerization,

$$\phi=[\mathrm{Z}\cdot]_2/[\mathrm{Z}\cdot]_1=\omega_2/\omega_1 \qquad (10)$$

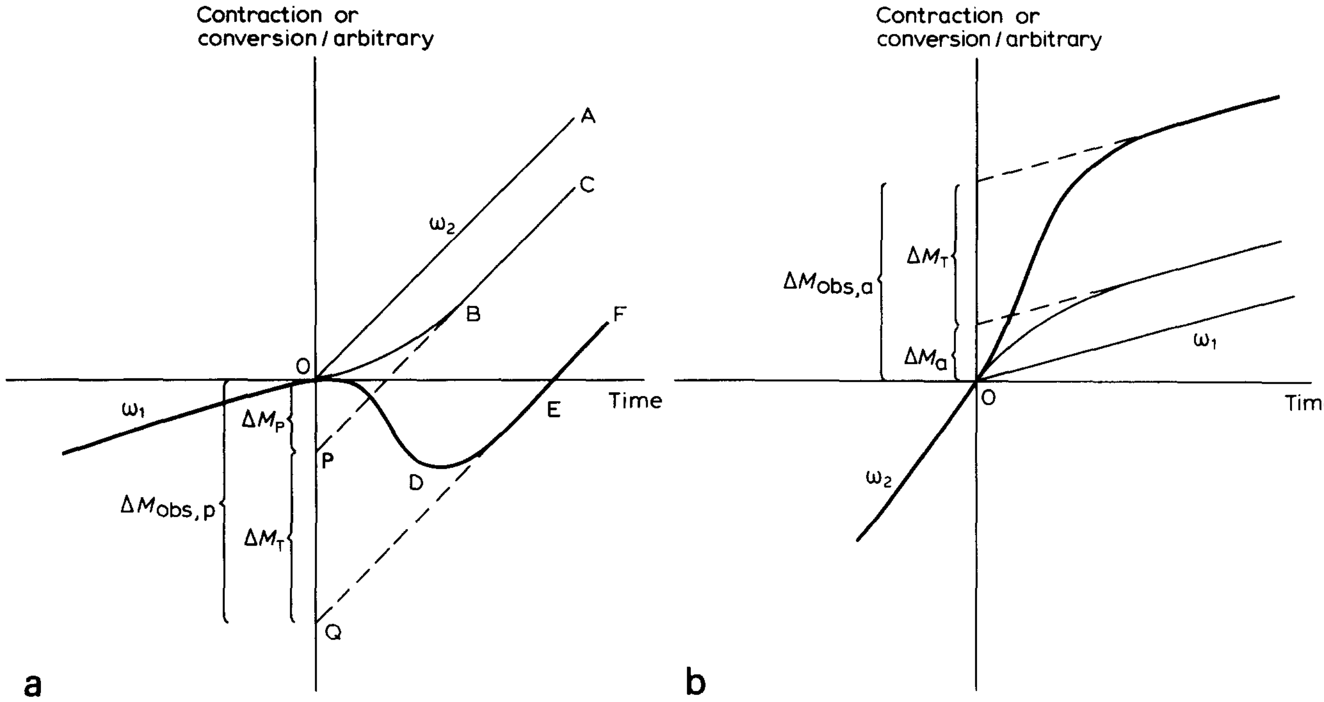

Figure 1 Diagrammatic representation of thermal effects in dilatometric determinations of (a) pre- and (b) after-effects in polymerization

We thus obtain from relation (9)

$$\Delta M_p = \frac{2k_{ba}[A]}{\lambda k_t'} \ln \frac{2\phi}{\phi+1} \qquad (11)$$

This expression is, necessarily, symmetrical in [A] and [B]; for limiting conditions of monomer composition it reduces to relations (12a) and (12b), respectively.

$$\Delta M_p = \frac{2k_{ab}[B]}{k_t'} \ln \frac{2\phi}{\phi+1}, \quad k_{ba}[A] \gg k_{ab}[B] \qquad (12a)$$

or

$$\frac{2k_{ba}[A]}{k_t'} \ln \frac{2\phi}{\phi+1}, \quad k_{ba}[A] \ll k_{ab}[B] \qquad (12b)$$

To observe the after-effect, the rate of initiation is reduced instantaneously at $t=0$ to a lower value, say from $\mathscr{I}_2$ to $\mathscr{I}_1$. An expression for the after-effect ΔM_a, which represents the excess polymerization occurring after $t=0$ attributable to the fact that the radical concentration does not instantly assume its final (lower) value, may be derived in a manner similar to that presented for ΔM_p. Thus we have

$$\Delta M_a = \int_{t=0}^{\infty} (\omega - \omega_1)\,\mathrm{d}t = \frac{2k_{ba}[A]}{\lambda k_t'} \ln \frac{\phi+1}{2} \qquad (13)$$

ϕ being defined by relation (10). The limiting forms of relation (13) will be evident from relations (12a) and (12b).

Note that both ΔM_p and ΔM_a are taken as positive and ϕ is always >1. For the sake of completeness we give in equation (14) the appropriate expressions for the pre- and after-effects in general copolymerization (in which homopropagations are included), since these do not seem to have been recorded in the literature. They have been derived as illustrated above.

$$\Delta M_p = \frac{U}{\lambda k_t'} \ln \frac{2\phi}{\phi+1} \qquad (14a)$$

$$\Delta M_a = \frac{U}{\lambda k_t'} \ln \frac{\phi+1}{2} \qquad (14b)$$

where

$$U = 2k_{ba}[A] + (\lambda - 1)k_{aa}[A] + k_{bb}[B] \qquad (14c)$$

Corrections for thermal effects in dilatometry

Illumination of a dilatometer containing a polymerizable monomer and a photoinitiator may bring about phenomena of the type illustrated in *Figure 1*. The dilatometer is supposed to be immersed in a bath at constant temperature and irradiation is started at $t=0$. In *Figure 1(a)* the low rate of initiation for $t<0$ produces the small rate of polymerization ω_1; if there were no pre-effect this would change instantaneously at $t=0$ to the higher rate ω_2 (corresponding to line OA). The existence of the pre-effect means that achievement of this rate is delayed, so that under strictly isothermal conditions the system follows the path OBC. Back-extrapolation of the final linear portion CB to $t=0$ gives an intercept OP corresponding to the true pre-effect ΔM_p. The onset of reaction, however, is accompanied by heat evolution so that the temperature of the reaction mixture rises and the liquid starts to expand along OD; in dilatometry this would correspond to a negative conversion. Eventually a new thermal equilibrium is established at a temperature slightly above the thermostat temperature and conversion proceeds linearly (along EF) at a rate ω_2. Back-extrapolation of FE to $t=0$ gives an intercept $\mathrm{OQ} = \Delta M_{\mathrm{obs},p}$ comprising the true pre-effect + the perturbation arising from thermal changes ΔM_{T}, i.e.

$$\Delta M_{\mathrm{obs},p} = \Delta M_p + \Delta M_{\mathrm{T}} \tag{15}$$

ΔM_{T}, like the other quantities in this equation, is taken as positive. An equation identical in form to equation (15) holds for after-effect experiments, as will be apparent from a perusal of *Figure (1b)*.

Our problem is to estimate or remove ΔM_{T}, so that ΔM_p may be derived from the observed $\Delta M_{\mathrm{obs},p}$ or $\Delta M_{\mathrm{obs},a}$.

Changes in reactant concentrations and variations in rates of polymerization arising from the small temperature changes will be neglected. In the simplest model convection is supposed to be dominating, so that the temperature of the contents of the dilatometer is effectively uniform. Heat loss from the reactants is determined by a single conduction layer between the liquid and the thermostat (in the ideal case the dilatometer walls) with thermal conductivity K, thickness l and surface area S. For present purposes we are concerned only with steady states of the system, although quantitative treatment of the intermediate states (along ODE) would reveal the development of the pre-effect in time. In any steady state the rates of heat production and heat loss must balance so that

$$\frac{\Delta H_p \omega V}{1000} = \frac{KS}{l}(T - T_0) \tag{16}$$

Here ΔH_p is the heat of polymerization, V (ml) the dilatometer volume, and T, T_0 the temperatures of the reaction medium and thermostat, respectively. As usual, ω is expressed in mol dm^{-3} s^{-1}. By applying equation (16) to the slow and fast reactions (ω_1, ω_2 in *Figure 1*) we find

$$T_2 - T_1 = \frac{\Delta H_p V l}{1000KS}(\omega_2 - \omega_1) = \frac{\Delta H_p V l \omega_1}{KS}(\phi - 1) \tag{17}$$

where T_1,T_2 are the temperatures corresponding to the initial and final steady states, respectively. This temperature rise produces a volume change

$$\Delta V = \beta V(T_2 - T_1) \tag{18}$$

β being the coefficient of thermal expansion of the dilatometer contents, which will cause a rise of the meniscus height in the dilatometer $\Delta h = \Delta V/a$ if a is the cross-section of the capillary. This will of course correspond to an apparent reduction in conversion ΔM_{T}, the two being related by a factor c dependent on the nature of the monomer(s) being polymerized. Thus we have from relations (17) and (18)

$$\Delta M_{\mathrm{T}} = \frac{c\Delta V}{a} = \left\{\frac{c\beta V^2 \Delta H_p l}{1000aKS}\right\}\omega_1(\phi - 1) \tag{19}$$

The term in braces in relation (19) is constant for a given monomer (mixture) and dilatometer. This model therefore leads to a result of the form

$$\Delta M_{\mathrm{T}} = D\omega_1(\phi - 1) \tag{20a}$$

where

$$D = \frac{c\beta V^2 \Delta H_p l}{1000aKS} \tag{20b}$$

At the other extreme a model may be constructed in which convection is negligible, the temperature profile in the dilatometer and the thermal perturbation ΔM_{T} depending on the thermal conductivities of the reaction mixture and the dilatometer walls (K',K, respectively). If the dilatometer is cylindrical and end-effects are insignificant this model may readily be treated exactly; it leads to a result of the form relation (20a) with D given by

$$D = \frac{c\beta V \Delta H_p}{1000a}\left\{\frac{r^2}{4K'} + \frac{Vl}{KS}\right\} \tag{21}$$

where r is the radius of the dilatometer. As might be anticipated, values of D given by relation (21) are considerably bigger than those obtained from relation (20b).

The intermediate situation, in which both convection and conduction contribute significantly is much more complicated. Dimensional analysis suggests that ΔM_{T} is first order in the rate of heat generation $\omega_1(\phi - 1)\Delta H_p$, i.e. that relation (20a) is applicable.

Consequently, we believe that use of relation (20a) as a basis for eliminating thermal perturbations is generally justifiable. We may note that these perturbations must vanish for $\phi = 1$; the simplest assumption to make, without recourse to any special model, is that they are proportional to $\phi - 1$ as in relation (20a). For present purposes this is all that is necessary, since we are not concerned with theoretical estimation of D. Thus, in general, we write

$$\Delta M_{\mathrm{obs}} = \Delta M_p \text{ (or } \Delta M_a) + D\omega_1(\phi - 1) \tag{22}$$

Equation (22) should be valid regardless of the detailed nature of the polymerization mechanism, provided, of course, that a stationary state is achieved on illumination. Here we are particularly concerned with the cross-propagation mechanism, for which ΔM_a and ΔM_p are given by equations (11) and (13), respectively. With the aid of these equations we find for the pre- and after-effects:

$$\Delta M_{\mathrm{obs},p} = \frac{2k_{ba}[\mathrm{A}]}{\lambda k_t'}\ln\frac{2\phi}{\phi + 1} + D\omega_1(\phi - 1) \tag{23a}$$

$$\Delta M_{\mathrm{obs},a} = \frac{2k_{ba}[\mathrm{A}]}{\lambda k_t'}\ln\frac{\phi + 1}{2} + D\omega_1(\phi - 1) \tag{23b}$$

Evaluation of $k_{ba}k_t'^{-1}$

Equations (23a) and (23b) contain the two unknowns $k_{ba}/\lambda k_t'$ and D, while the remaining four quantities $\Delta M_{\mathrm{obs},p}$ (or $\Delta M_{\mathrm{obs},a}$), [A], ϕ and ω, are known or measurable. Therefore, in principle, two appropriate determinations of the ΔM_{obs} suffice for the evaluation of $k_{ba}/\lambda k_t'$ and D. A convenient method of plotting the equations may be derived by writing them as in equations (24a) and (24b):

$$Y_p = \frac{2k_{ba}}{\lambda k_t'} + DX_p \tag{24a}$$

$$Y_a = \frac{2k_{ba}}{\lambda k_t'} + DX_a \tag{24b}$$

The functions X_p, X_a, Y_p, Y_a which are defined in (25), may all be evaluated experimentally.

$$X_p=\frac{\omega_1(\phi-1)}{[\mathrm{A}]\ln\frac{2\phi}{\phi+1}} \qquad X_a=\frac{\omega_1(\phi-1)}{[\mathrm{A}]\ln\frac{\phi+1}{2}}$$
$$Y_p=\frac{\Delta M_{\mathrm{obs},p}}{[\mathrm{A}]\ln\frac{2\phi}{\phi+1}} \qquad Y_a=\frac{\Delta M_{\mathrm{obs},a}}{[\mathrm{A}]\ln\frac{\phi+1}{2}} \qquad (25)$$

As already stated $\phi>1$, so that no physical significance can be attached to the X and Y values in relation (25) for $\phi\leqslant 1$. Plots of Y_p *versus* X_p and Y_a *versus* X_a based on equations (24) and (25) should be linear with

$$\text{slope}=D \qquad (26)$$

and intercept on Y axis $=2k_{ba}/\lambda k_t'$ (regardless of the fact that portions of the graph have no physical meaning).

This procedure may be applied to a series of measurements either of pre- or after-effects. However, to minimize errors, we strongly recommend that both series are plotted on the same diagram. Since they give straight lines with identical intercepts and slopes, the combined plot should be a single straight line, from which $k_{ba}/\lambda k_t'$ may be found from relation (26). We have used this technique in the work described later.

A variant in which $k_{ba}/\lambda k_t'$ is determined from the slope of a linear plot instead of from a rather small intercept would have obvious advantages. For this purpose equations (23) and (25) may be written in the forms

$$\frac{\Delta M_{\mathrm{obs},p}}{\omega_1(\phi-1)}=\frac{2k_{ba}}{\lambda k_t'}\frac{1}{X_p}+D \qquad (27a)$$

$$\frac{\Delta M_{\mathrm{obs},a}}{\omega_1(\phi-1)}=\frac{2k_{ba}}{\lambda k_t'}\frac{1}{X_a}+D \qquad (27b)$$

and the left sides plotted against $1/X_p$ or $1/X_a$. An example of this procedure will be provided subsequently.

EXPERIMENTAL

Materials

Styrene was purified by washing with 10% aqueous sodium hydroxide and water, then drying over calcium chloride under nitrogen. The monomer was distilled in vacuum and stored over calcium hydride.

Methyl acrylate was washed with an aqueous solution containing 5% sodium hydroxide and 20% sodium chloride, then with 20% aqueous sodium chloride. After cooling to −78°C and separating ice, the monomer was dried over calcium chloride under nitrogen. It was distilled in vacuum and stored over calcium hydride.

Methyl methacrylate was purified similarly and partially polymerized over calcium hydride. Toluene of analytically pure grade was stored over sodium. A commercial 25% toluene solution of ethylaluminium sesquichloride from Aldrich Chemical Company was stored in small glass ampoules.

Apparatus and techniques

All experiments were carried out in a laboratory illuminated by inactive (sodium) light.

Dilatometers were of conventional design, with cylindrical reaction vessels and capillaries of 1 mm internal diameter (Veridia); their volumes were approximately 1 or 10 ml. Each dilatometer was attached to a preparation reservoir of about 10 or 50 ml volume. In this the components were mixed in a nitrogen atmosphere in the order: toluene, ethylaluminium sesquichloride, methyl acrylate or methacrylate, styrene. After degassing on the vacuum line by the conventional freeze/thaw technique the reaction mixture was poured into the dilatometer and frozen. The dilatometer was then sealed off, with the pressure about 10^{-5} mm Hg.

The light source was a high pressure mercury arc (Mazda 250 watt type ME/D), used with glass lenses to produce a parallel beam and a light filter to isolate 365 nm. Three gauzes of different transmissions (48.4%, 41.4% and 17.1%) were employed to adjust the light intensity.

The dilatometers were immersed in a thermostat at 25° ± 0.001°C.

RESULTS AND DISCUSSION

Experimental data on measurements of $M_{\mathrm{obs},p}$ and $M_{\mathrm{obs},a}$ for various values of ω_1 and ω_2 are presented in *Tables 1–5*; *Table 1* refers to $\mathrm{Et_3Al_2Cl_3}$/MMA/St and the remainder to $\mathrm{Et_3Al_2Cl_3}$/MA/St systems.

Equilibrium constants for binary complex formation between acrylic monomers and ethylaluminium sesquichloride are generally high[11]; for example, in the case of MMA in cyclohexane at 35°C, it exceeds 100 mol dm^{-3}, being too high to evaluate conventionally from n.m.r. observations[12]. A similar situation probably exists with MA[4–6]. It is therefore often assumed that in mixtures containing excess acrylic monomer effectively all the aluminium exists as the binary complex (compare refs. 7 and 13). *Table 6* presents some recent values[14] of equilibrium constants for $\mathrm{Et_3Al_2Cl_3}$/MMA/St in toluene solution together with the corresponding calculated complex concentrations. Clearly the simple

Table 1 Pre- and after-effects—PMT-11. Initial concentrations/mol dm^{-3}: St 0.8, MMA 0.8, al 0.6 [A] = 0.6 mol dm^{-3} throughout

$10^5\ \omega_1$ (mol dm^{-3}s^{-1})	$10^5\ \omega_2$ (mol dm^{-3}s^{-1})	Φ	$10^3\ \Delta M_{\mathrm{obs,\,p}}$ (mol dm^{-3})	$10^3\ \Delta M_{\mathrm{obs,\,a}}$ (mol dm^{-3})
0.944	8.93	9.46	6.47	
0.995	8.93	8.97		7.89
0.995	5.82	5.85	4.05	
0.952	5.82	6.11		4.60
0.952	3.39	3.56	1.92	
0.877	3.39	3.87		2.63
0.877	6.12	6.98	3.94	
0.775	6.12	7.90		5.82

Table 2 Pre- and after-effects—PMT-9. Initial concentrations/mol dm^{-3}: St 0.4, MA 0.4, al 0.3

[A]/ (mol dm^{-3})	$10^5\,\omega_1$ (mol dm^{-3}s^{-1})	$10^5\,\omega_2$ (mol dm^{-3}s^{-1})	Φ	$10^3\,\Delta M_{\mathrm{obs,p}}$ (mol dm^{-3})	$10^3\,\Delta M_{\mathrm{obs,a}}$ (mol dm^{-3})
0.2745	1.057	16.91	16.00		22.32
0.2515	1.057	8.56	8.10	9.21	
0.230	0.906	8.56	9.45		11.81
0.2185	0.906	7.98	8.81	9.32	
0.199	0.777	7.98	10.27		11.27
0.186	0.777	4.46	5.74	4.88	
0.1685	0.673	4.46	6.63		5.74
0.161	0.673	9.85	14.64	10.89	
0.1225	0.4605	9.85	21.39		13.98

Table 3 Pre- and after-effects—AMH-4. Initial concentrations/mol dm^{-3} : St 0.4, MA 0.4, al 0.15 [A] = 0.15 mol dm^{-3} throughout

$10^5\,\omega_1$ (mol dm^{-3}s^{-1})	$10^5\,\omega_2$ (mol dm^{-3}s^{-1})	Φ	$10^3\,\Delta M_{\mathrm{obs,p}}$ (mol dm^{-3})	$10^3\,\Delta M_{\mathrm{obs,a}}$ (mol dm^{-3})
2.11	6.50	3.08	1.86	3.08
2.31	6.50	2.81		3.08
2.31	23.27	10.07	7.50	
2.04	23.27	11.41		4.19
2.04	9.32	4.57	3.02	
2.11	9.32	4.42		2.91
2.11	16.17	7.66	5.24	
2.29	16.17	7.06		3.90
2.29	6.87	3.00	2.04	

Table 4 Pre- and after-effects—AMH-3. Initial concentrations/mol dm^{-3}: St 0.4, MA 0.4, al 0.15 [A] = 0.15 mol dm^{-3} throughout

$10^5\,\omega_1$ (mol dm^{-3}s^{-1})	$10^5\,\omega_2$ (mol dm^{-3}s^{-1})	Φ	$10^3\,\Delta M_{\mathrm{obs,p}}$ (mol dm^{-3})	$10^3\,\Delta M_{\mathrm{obs,a}}$ (mol dm^{-3})
0.848	11.36	13.40	2.83	
0.848	11.36	13.40		2.93
0.848	19.78	23.33	4.95	
0.848	19.78	23.33		6.47
0.848	14.01	16.52	3.78	
0.848	14.01	16.52		5.26
0.848	17.78	20.97	4.35	
0.848	17.78	20.97		5.44
0.848	5.36	6.32	1.38	
0.716	5.36	7.49		2.08

Table 5 Pre- and after-effects—AMH-2. Initial concentrations/mol dm^{-3}: St 0.4, MA 0.4, al 0.006 [A] = 0.06 mol dm^{-3} throughout

$10^5\,\omega_1$ (mol dm^{-3}s^{-1})	$10^5\,\omega_2$ (mol dm^{-3}s^{-1})	Φ	$10^3\,\Delta M_{\mathrm{obs,p}}$ (mol dm^{-3})	$10^3\,\Delta M_{\mathrm{obs,a}}$ (mol dm^{-3})
0.636	3.19	5.02	4.45	
0.559	3.19	5.71		5.15
0.559	1.24	2.22	1.55	
0.429	1.24	2.89		1.29
0.429	2.61	6.08	4.03	
0.391	2.61	6.68		4.02
0.391	1.38	3.55	2.57	
0.360	1.38	3.83		1.84
0.360	1.07	2.97	1.46	
0.314	1.07	3.41		1.52
0.314	3.25	10.35	5.46	
0.222	3.25	14.64		6.90

Table 6 Equilibrium constants and complex concentrations

Complex	Equilibrium constant[14] and conditions	10^2 concentration in PMT–11 (mol dm^{-3})
$AlEt_{1.5}Cl_{1.5}$——MMA	>100 mol^{-1} dm^3 cyclohexane solution 35°C	9.64
$AlEt_{1.5}Cl_{1.5}$——MMA . . . St	2.61 mol^{-1} dm^3, toluene solution, 40°C	15.9
$AlEt_{1.5}Cl_{1.5}$——MMA . . . Tol	0.50 mol^{-1} dm^3, toluene solution, 40°C	34.4

Table 7 Values of $k_{ba}/\lambda k_t'$. PMT–11 refers to $Et_3Al_2Cl_3$/MMA/St, the others to $Et_3Al_2Cl_3$/MA/St

Series	PMT–11	PMT–9	AMH–4	AMH–3	AMH–2
$10^3 k_{ba}/\lambda k_t'$	1.0	4.2	3.1	2.2	2
λ		1.1 – 1.05	1.006	1.06	1.02
$10^3 k_{ba}/k_t'$	1.0†	4.5*	3.1	2.3	2

† assuming $\lambda = 1$

* using mean λ

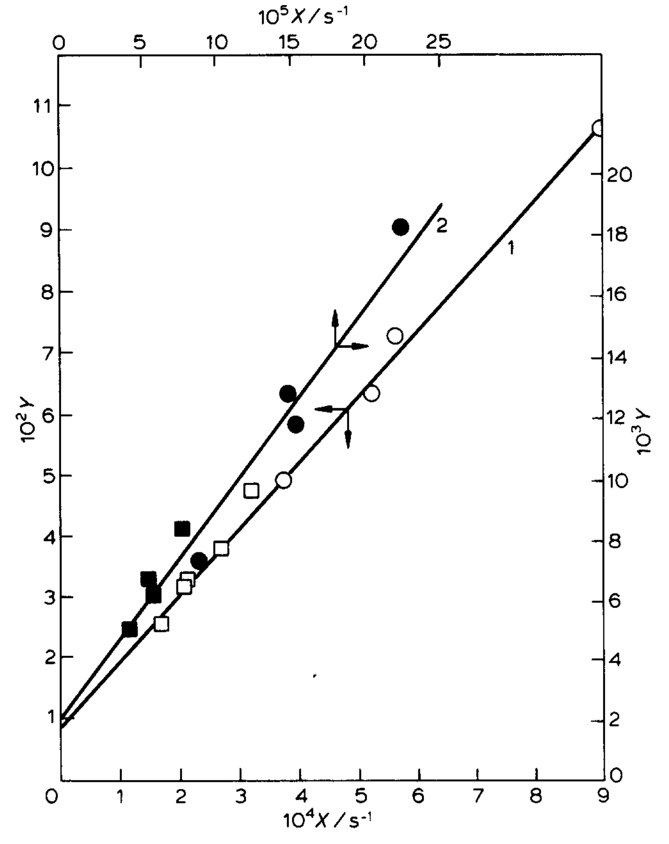

Figure 2 Combined plots for $Et_3Al_2Cl_3$/MA/St and $Et_3Al_2Cl_3$/MMA/St systems (PMT-9, *Table 2* and PMT-11, *Table 1*, respectively) see equations (24) and (25): curve 1 PMT-9: ○ pre-effect, □ after-effect; curve 2 PMT-11: ● pre-effect, ■ after-effect

binary complex al–MMA is not a major constituent, both the ternary complexes al–MMA···St and the complex including toluene al–MMA···Tol are considerably more abundant (al represents an aluminium atom in a complex). However, the equilibrium constants quoted are considerably higher than many to be found in the literature[11], and it may be advisable to wait for further conformation. We suggest that the toluene complex probably behaves in copolymerization like the simple binary complex, and should be included with the latter. In this even the 'binary complex' amounts to 73% of the total aluminium. Unfortunately no corresponding data are available for methyl acrylate systems. In the following we have adopted the conventional practice of equation [A] with the concentrations of the minor component, i.e. either with the concentration of acrylic monomer or with [al]($=2[Et_3Al_2Cl_3]$), depending on whether [al] or [monomer] is the greater. For the experiments in *Tables 1, 3–5* the latter condition prevails, so that [A] = [al] and is effectively constant during a series of runs. For PMT-9 in *Table 2*, [MA] > [al] initially, but non-stationary phases were not studied until appreciable conversion had occurred, so that this situation was reversed. Therefore in PMT-9 [A] was calculated for each run from the overall conversion.

The data presented permit evaluation of the functions X and Y (equation (25)) so that combined after- and pre-effect plots of Y *versus* X based on equation (24) can be constructed. The parameter $k_{ba}/\lambda k_t'$ has been evaluated from the intercepts on the Y axes. Examples of such plots are given in *Figure 2* for PMT-11 and PMT-9 and all the values of $k_{ba}/\lambda k_t'$ are collected in *Table 7*.

To illustrate the application of equation (27) we give in *Figure 3* a plot for PMT-9 based on this equation. The data give a fairly well defined straight line of slope 9.3×10^{-3}, corresponding to $k_{ba}/(\lambda k_t')=4.7\times10^{-3}$. This may be compared to 4.2×10^{-3} derived by the intercept method (*Figure 2* and *Table 7*). We are of the opinion that use of equation (27) is worthy of further exploration and, depending on the quality of the experimental data, is capable of giving more reliable values of $k_{ba}/(\lambda k_t')$ than equation (24). For the case of PMT-9 in *Figure 3* the error in the slope depending on how the line is drawn seems unlikely to exceed ±20%. Note that the slope in *Figure 2* (curve 1) and the intercept in *Figure 3* both give D, the thermal parameter defined in equation (20a). The two values are 115 s, and 111 s, respectively, in satisfactory conformity.

From the stationary-state observations of Bamford and Malley[7] on the $Et_3Al_2Cl_3$/MA/St system at 25°C we find that $k_{ba}/k_{ab}=0.15$, hence

$$\lambda = 1 + 0.15\frac{[A]}{[B]} \tag{28}$$

Clearly in the present experiments λ is close to unity;

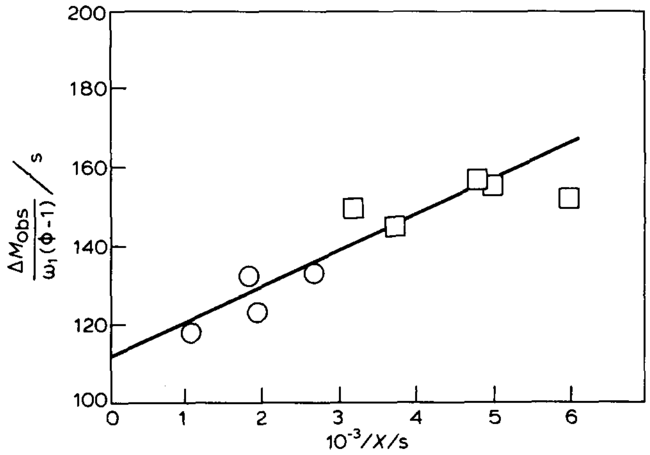

Figure 3 Plot for $Et_3Al_2Cl_3$/MA/St (PMT-9, *Table 2*) based on equation (27): ○ pre-effect, □ after-effect

values calculated from relation (28) are, however, given in *Table 7* and used to evaluate $k_{ba}k_t'^{-1}$ from $k_{ba}/\lambda k_t'$. λ is not known for the methyl methacrylate system and we have assumed it to be unity.

We believe the results for AMH-2, in which a very low concentration of aluminium was used, are the least reliable of those presented in *Table 7*. The mean value of $k_{ba}k_t'^{-1}$ for the $Et_3Al_2Cl_3$/MA/St systems is given in *Table 8* and used in conjunction with the value of $k_{ba}k_t'^{-1/2}$ from stationary state experiments[7], to estimate the absolute magnitudes of k_{ba} and k_t'. k_{ab} has also been calculated with the aid of the known value of k_{ba}/k_{ab} (see above).

Agreement with the results of Bamford and Malley[7] is probably as good as could be expected. The propagation coefficients, although somewhat lower than those of the earlier workers, are nevertheless high and exceed by one or two orders of magnitude the corresponding coefficients in the absence of Lewis acid ($k_{ba}=59$[15,16], $k_{ab}=3289$[16,17] $\text{mol}^{-1}\,\text{dm}^3\,\text{s}^{-1}$, respectively). Clearly these results are consistent with the basic premises of the cross-propagation mechanism of alternating copolymerization.

Alternative mechanisms

On the other hand, according to the ternary complex mechanism, as elaborated by Furukawa, Hirai and their colleagues, the alternating copolymerization is to be regarded as the homopolymerization of a ternary complex composed of the Lewis acid and both monomers[11]. There are good reasons for believing that this is not a major mechanism for the type of systems discussed in this paper, under existing conditions. Chief among these is that concentrations of ternary complex are often too low for compatibility with the observed kinetics[7,11].

If the equilibrium constants for a system are known, so that ternary complex concentrations may be estimated, the kinetic parameter $k_pk_t^{-1}$ appropriate for the ternary complex mechanism may be deduced from pre- and after-effect observations by application of the relations holding for homopolymerization. The familiar expressions[8] for the pre- and after-effects in the homopolymerization of monomer M are given in equation (29).

$$\Delta M_p=\frac{k_p[\text{M}]}{k_t}\ln\frac{2\phi}{\phi+1}$$

$$\Delta M_a=\frac{k_p[\text{M}]}{k_t}\ln\frac{2}{\phi+1} \qquad (29)$$

Proceeding as described earlier, from equations (22) and (29) we deduce equations (30a) and (30b) corresponding to equations (24a) and (24b).

$$Y_p=\frac{k_p}{k_t}+DX_p \qquad (30a)$$

$$Y_a=\frac{k_p}{k_t}+DX_a \qquad (30b)$$

Here X_a, X_p, Y_a, Y_p are given by equation (25) with [M] substituted for [A]; the remaining symbols ω_1, ω_2 and ϕ retain their earlier significance. Combined pre- and after-effect plots of the type described earlier may be constructed with the aid of equation (30) and hence $k_pk_t^{-1}$ evaluated.

There are few data in the literature which permit the application of these equations to alternating copolymerizations. For purposes of illustration we use the recent data of Ebdon[14] given in *Table 6* for $Et_3Al_2Cl_3$/MMA/St and suppose that copolymerization in this system (PMT-11) follows the ternary-complex mechanism exclusively (a most improbable assumption in our opinion). According to *Table 6*, $[\text{M}]=15.9\times10^{-2}\ \text{mol dm}^{-3}$ (the ternary complex concentration) and from the combined plot based on the data in *Table 1* we find that $k_pk_t^{-1}=7.4\times10^{-3}$.* Thus if $k_t{\sim}2\times10^6\ \text{mol}^{-1}\ \text{dm}^{-3}\ \text{s}^{-1}$, $k_p{\sim}1.5\times10^4\ \text{mol}^{-1}\ \text{dm}^3\ \text{s}^{-1}$.

Although the ternary complex mechanism in its original form may not be applicable to many systems under 'normal' conditions, there can be little doubt of the existence of ternary complexes in reaction mixtures and it seems likely that under suitable conditions of concentration such species would participate in copolymerization by reacting with propagating chains. If the complex C is designated A···B two major propagation processes involving it may be envisaged: these are shown below as 1(i) and (j). Both ends of the complex molecule are supposed to be reactive, so that alternation is preserved in these processes. Generalization of scheme (1) by inclusion of these propagations appears to us a reasonable step; it was indeed done by Zubov *et al.*[11,13]. The expanded scheme has four propagation reactions:

Table 8 Reaction parameters for $Et_3Al_2Cl_3$/MA/St

	This work	Ref. 7
$10^3\,k_{ba}/k_t'$	3.0	2.0
$10^{-3}\,k_{ba}/\text{mol}^{-1}\text{dm}^3\text{s}^{-1}$	5.6	8.5
$10^{-3}\,k_{ab}/\text{mol}^{-1}\text{dm}^3\text{s}^{-1}$	37.3	57.0
$10^{-6}\,k_t'/\text{mol}^{-1}\ \text{dm}^3\text{s}^{-1}$	1.9	4.3

($k_{ba}k_t'^{-1/2} = 4.1\ \text{mol}^{-1/2}\,\text{d}^{3/2}\text{s}^{-1/2}$ [7])

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* This result may be obtained immediately from *Figure 2* by noting that the intercept on Y in the new combined plot is greater than that in *Figure 2* by the factor $0.6/(15.9\times10^{-2})$.

$$\left.\begin{array}{llll} \sim\mathrm{A}\cdot+\mathrm{B} & \longrightarrow\sim\mathrm{B}\cdot & k_{ab} & \text{(d)} \\ \sim\mathrm{B}\cdot+\mathrm{A} & \longrightarrow\sim\mathrm{A}\cdot & k_{ba} & \text{(e)} \\ \sim\mathrm{A}\cdot+\mathrm{B}\cdots\mathrm{A} & \longrightarrow\sim\mathrm{ABA}\cdot & k_{ac} & \text{(i)} \\ \sim\mathrm{B}\cdot+\mathrm{A}\cdots\mathrm{B} & \longrightarrow\sim\mathrm{BAB}\cdot & k_{bc} & \text{(j)} \end{array}\right. \qquad (1)$$

Under stationary conditions the rate of polymerization is given by

$$\omega=-\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t}-\frac{\mathrm{d}[\mathrm{B}]}{\mathrm{d}t}=\frac{\mu}{\lambda}\left(\frac{\mathscr{I}}{k_t'}\right)^{1/2} \qquad (31)$$

and the pre- and after-effects by

$$\left.\begin{array}{l} \Delta M_p=\dfrac{\mu}{\lambda k_t'}\ln\dfrac{2\phi}{\phi+1} \\[2ex] \Delta M_a=\dfrac{\mu}{\lambda k_t'}\ln\dfrac{\phi+1}{2} \end{array}\right. \qquad (32)$$

in which

$$\mu=2\{k_{ba}[\mathrm{A}]+(\lambda-1)k_{ac}[\mathrm{C}]+k_{bc}[\mathrm{C}]\} \qquad (33)$$

and λ is defined in equation (4).

The functional dependencies of ω in equations (31) and (33) are examinable in steady-state experiments. From pre- and after-effect observations similar to those described $\mu/(\lambda k_t')$ may be evaluated and this, with the aid of the known parameters in equation (31), could lead to $k_{ab}k_t'^{-1}$, $k_{ba}k_t'^{-1}$, $k_{ac}k_t'^{-1}$ and $k_{bc}k_t'^{-1}$.

Progress in the study of these alternating copolymerizations requires more extensive data on complex formation, so that kinetic relations such as equation (31) may be tested and discussion generally placed on a more secure quantitative basis.

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