

The copolymerization of methyl methacrylate and isoprene in the presence of ethyl aluminium sesquichloride: role of monomer complexes

J. R. Ebdon and N. P. Gabbott*

Department of Chemistry, University of Lancaster, Bailrigg, Lancaster, LA1 4YA, UK
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The kinetics of the spontaneous copolymerization of methyl methacrylate and isoprene in the presence of ethyl aluminium sesquichloride in toluene and at temperatures between 0° and 40°C have been investigated. Irreproducible fast initial rates of copolymerization are followed by slower reproducible rates. The structures of the copolymer and the accompanying Diels–Alder adduct have been determined by ¹H and ¹³C n.m.r.; the copolymers produced under a wide range of conditions are equimolar and highly alternating. The concentrations of various binary and ternary complexes have been assessed through ¹H n.m.r. chemical shift measurements; it is shown that the mechanism of copolymerization cannot involve simply the effective homopolymerization of ternary isoprene–methyl methacrylate–ethyl aluminium sesquichloride complexes.

Keywords Methyl methacrylate; isoprene; Et_{1.5}AlCl_{1.5}; copolymerization; kinetics; complexes

INTRODUCTION

Since the first demonstrations by Bamford and coworkers¹ that metal salts can influence the kinetics of radical polymerizations, and by Hirooka and colleagues² that organometal halides can catalyse the production of alternating copolymers from mixtures of donor and acceptor monomers, there have been several hundred reports concerned with studies of the influences of Lewis acids in general upon radical homo- and copolymerizations. This body of work has, from time to time, been reviewed (see, for example, refs. 3).

Of particular interest, because of their potential uses as synthetic elastomers, are alternating copolymers of acrylic and methacrylic monomers with dienes. Several such systems, involving the use of Lewis acid catalysts, have been studied, for example, by Gaylord⁴, Furukawa⁵, Kuran⁶ and coworkers and most recently by Bamford *et al.*⁷ Although there seems to be agreement concerning the general features of such copolymerizations, there is considerable disagreement about precise mechanisms, particularly as to the role of monomer–monomer and/or monomer–radical complexes in propagation steps.

Here we report some kinetic studies of the methyl methacrylate (MMA)/isoprene (IP)/ethyl aluminium sesquichloride, Et_{1.5}AlCl_{1.5} (EASC) copolymerization system.

EXPERIMENTAL

Purification of reagents

MMA (BDH Ltd) was freed from hydroquinone inhibitor by extraction with 10% aq. NaOH and was then

washed with distilled water and dried over MgSO₄. It was further purified by fractional distillation from CaH₂. The purified material was stored over CaH₂ in a refrigerator.

IP (Koch-Light Ltd) was dried with MgSO₄ and fractionally distilled from CaH₂ before use.

Solvents were dried and purified by standard methods.

EASC (Ventron Ltd) was used direct from the cylinder without further purification. All handling of EASC was carried out under a dry nitrogen atmosphere. Usually, EASC was dispensed as required into a reaction vessel as a stock solution in CHCl₃ or toluene and diluted *in situ* to give the required final concentration. Azobisisobutyronitrile (AZBN) was purified by recrystallization three times from ethanol.

Preparation and recovery of polymers

Radical copolymerizations of MMA and IP in solution in the absence of EASC were carried out in a conventional manner using reaction ampoules or dilatometers under vacuum with AZBN as initiator.

Most copolymerizations in the presence of EASC were performed at 25°C under N₂ in a stirred glass reaction vessel immersed in a thermostatted water bath and fitted with a rubber serum cap through which reagents could be introduced and samples withdrawn using a syringe fitted with a long needle. Some reactions involving EASC were carried out under vacuum by quickly introducing N₂ purged reagents into glass ampoules or dilatometers using small burettes or syringes and then attaching the reaction vessels to the vacuum line to remove all dissolved gases by the usual cycle of freezing, pumping and thawing operations. Finally, the ampoules or dilatometers were sealed off under vacuum with a glass-torch in the usual way.

Copolymers were recovered by precipitation of polymerization mixtures in an excess of stirred methanol. The

* Present address: Department of Chemistry, University of Technology, Loughborough, Leicestershire, UK

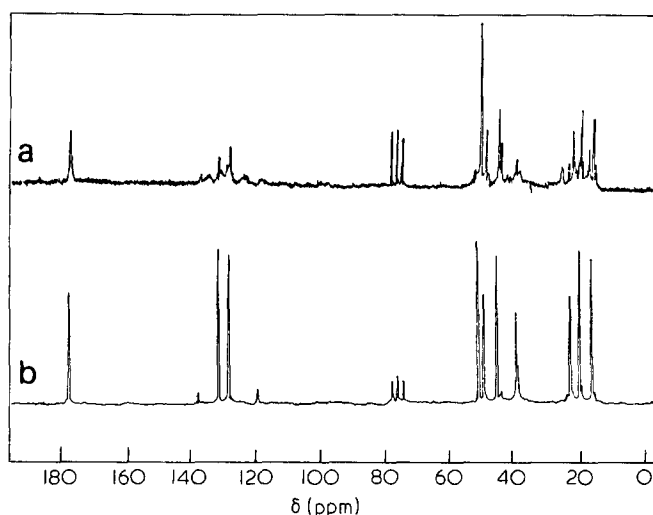


Figure 1 20 MHz ^{13}C n.m.r. spectra of (a) an equimolar random MMA/IP copolymer and (b) an equimolar alternating MMA/IP copolymer. Spectra recorded in CDCl_3 at $\sim 40^\circ\text{C}$

recovered polymers were dried by pumping under vacuum at room temperature overnight.

Recovery of Diels–Alder adducts

Diels–Alder adducts were detected in some IP/MMA/EASC reaction mixtures by gas chromatography. Samples of Diels–Alder adducts were recovered from such mixtures for subsequent characterization by removing residual solvents and monomers on a rotary evaporator at room temperature after first eliminating any copolymer by precipitation.

Spectroscopic measurements

To aid in characterization, ^1H n.m.r. spectra of products were recorded at 60 MHz and 220 MHz using Varian A60A and Varian HR220 spectrometers. Normally, spectra were recorded on 10% w/v solutions in CDCl_3 at ambient probe temperature (about 35°C). ^1H n.m.r. chemical shift measurements at 60 MHz were used also to assess the strength of complexing between various species. ^{13}C n.m.r. spectra of some copolymers were recorded on 10% w/v solutions in CDCl_3 at 20 MHz on a Varian CFT 20 spectrometer at ambient probe temperature (about 40°C). Typical operating conditions for the CFT 20 were: sweep width, 4000 Hz (200 ppm); pulse width, $12\ \mu\text{s}$, corresponding to a nuclear tip angle of $\sim 51^\circ$; acquisition time (and pulse repetition time), 0.51 s; number of pulses, typically $\sim 30\ 000$. Broad-band proton irradiation was used to remove C–H couplings. Proton and carbon chemical shifts are quoted relative to tetramethylsilane (TMS) internal standard.

Infra-red spectra of some copolymers were recorded on thin films cast from CHCl_3 solutions onto rock salt plates using a Perkin–Elmer 297 spectrometer.

Gel permeation chromatography

Molecular weight averages and molecular weight distributions for some copolymers were assessed by g.p.c. using a Waters Associates 502 chromatograph equipped with four columns each 30 cm in length and packed with Styragel of pore sizes 500, 10^3 , 10^4 and $10^5\ \text{\AA}$ respectively. The solvent was freshly distilled CHCl_3 at a flow rate of

$1\ \text{ml}\ \text{min}^{-1}$. A Miran II infra-red detector was used, tuned to the MMA carbonyl absorption band at $5.32\ \mu\text{m}$.

Gas-liquid chromatography

G.l.c. analysis for Diels–Alder adducts was carried out on Pye Unicam 104 and 204 chromatographs equipped with PEG-A coated Chromosorb stationary phases packed in steel columns 150 cm in length and 4 mm in diameter and with flame ionization detectors. The usual temperature conditions for the analysis of Diels–Alder adducts in monomer/solvent mixtures were: injector, 200°C ; detector, 300°C ; column held at 85°C for 8 min until all solvents and monomers had been eluted then quickly raised to 140°C to elute the Diels–Alder adducts. The carrier gas was N_2 at a flow rate of $30\ \text{ml}\ \text{min}^{-1}$.

RESULTS

Compositions and structures of products

In the absence of EASC, the copolymerization of MMA and IP initiated by AZBN ($1\ \text{g}\ \text{l}^{-1}$) in toluene at 60°C yields essentially random copolymers. Reactivity ratios of 0.18 (r_{MMA}) and 0.87 (r_{IP}) were determined by the Kelen–Tüdös method⁸ from the results of copolymerizations carried out at an overall monomer concentration of $4.8\ \text{mol}\ \text{l}^{-1}$ and over a feed range of 0.2–0.8 mol fraction of MMA. These reactivity ratios are close to those previously determined for this copolymerization in benzene⁹. The compositions of the copolymers were determined from the relative areas of peaks in their 60 MHz ^1H n.m.r. spectra by the previously reported method. The order of the copolymerization with respect to AZBN concentration at 60°C determined from dilatometric rates was 0.5 ± 0.1 over the range $[\text{AZBN}] = 1\text{--}10\ \text{g}\ \text{l}^{-1}$ at an approximately equimolar feed ($[\text{MMA}] = 2.36\ \text{mol}\ \text{l}^{-1}$, $[\text{IP}] = 2.48\ \text{mol}\ \text{l}^{-1}$).

In the presence of EASC at 25°C in toluene, whether under vacuum or N_2 , copolymerization of MMA and IP occurs spontaneously to give copolymers containing 50 mol% MMA irrespective of the feed composition (range investigated contained 25–90 mol% MMA), overall monomer concentration or EASC concentration. The n.m.r. spectra of the copolymers indicate that they possess a highly alternating arrangement of monomer units within the chains. The ^{13}C spectrum of such an alternating copolymer is compared with that of an equimolar ‘random’ copolymer prepared by conventional radical copolymerization in Figure 1. The spectrum of the alternating copolymer consists essentially of 10 sharp lines corresponding to the 10 carbon atoms of the uniquely situated MMA and IP units within the alternating sequences. Both the ^1H (Figure 2) and ^{13}C spectra of the alternating copolymers show that the IP units are almost entirely in 1,4- configurations; there are only very small vinylic resonances characteristic of 1,2- and 3,4- placements. Also it is believed from i.r. and n.m.r. evidence and by analogy with the alternating butadiene/MMA/ ZnCl_2 system that the IP units are predominantly of the *trans* type¹⁰. The presence of a prominent AB quartet type pattern within the ^1H spectrum of the alternating copolymer (four components between 1.9 and 2.6 δ) indicates that the 1,4-IP units are linked in a regular head-tail fashion. The AB quartet arises from the non-equivalent IP $\alpha\text{-CH}_2$ protons in such a linkage (underlined group in structure (I) below).

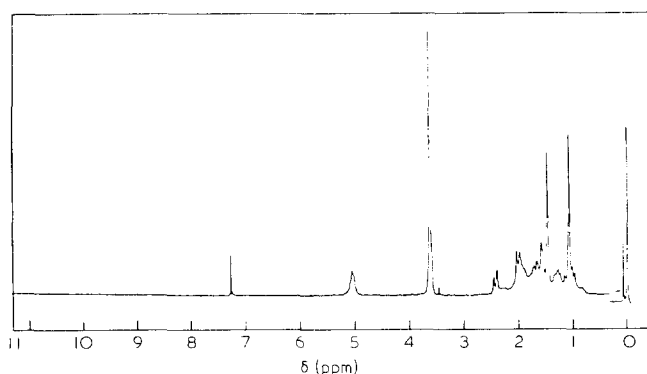


Figure 2 220 MHz ^1H n.m.r. spectra of an equimolar alternating copolymer. Spectrum recorded in CDCl_3 at $\sim 35^\circ\text{C}$

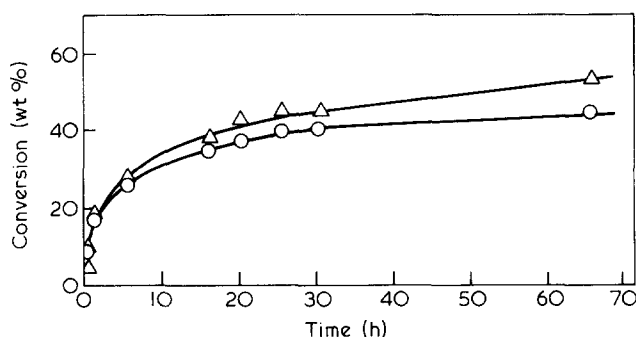
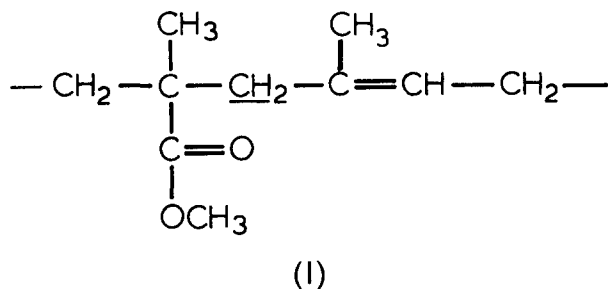
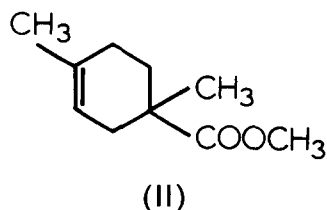


Figure 3 Conversion to alternating copolymer (O) and Diels-Alder adduct (Δ) in MMA/IP/EASC at 21.5°C . $[\text{MMA}] = 1.57 \text{ mol l}^{-1}$; $[\text{IP}] = 1.65 \text{ mol l}^{-1}$; $[\text{EASC}] = 0.15 \text{ mol l}^{-1}$; solvent, toluene



EASC catalyses also the production of a MMA-IP Diels-Alder adduct. Only one peak is visible within the g.l.c. trace of the adduct indicating the presence of a single component. The ^1H n.m.r. spectrum of the isolated product indicates this component to be 1,4-dimethyl-4-carbomethoxycyclohex-1-ene (II).



There is no evidence in the ^1H n.m.r. spectrum of an AB quartet pattern characteristic of the isolated methylene group within the alternative isomer (1,3-dimethyl-3-carbomethoxycyclohex-1-ene).

Kinetics of the copolymerizations in the presence of EASC

Spontaneous copolymerization of MMA and IP in the presence of EASC occurs in toluene, chloroform and n-hexane solvents. However, the latter two solvents are not suitable for use in kinetic studies; solutions of EASC in chloroform were found to be unstable and the alternating copolymer precipitates in n-hexane. Thus, toluene was used as solvent in all the kinetic experiments even though its use introduces certain complications in the form of monomer-solvent complexing (see later).

At temperatures at which the rate of production of alternating copolymer is reasonable for study (around 25°C), the Diels-Alder adduct is produced at a comparable rate (Figure 3). Thus dilatometry under vacuum cannot be used to monitor rates of copolymerization. Accordingly, all experiments aimed at elucidating the kinetics of the copolymerization were carried out under N_2 in the vessel from which samples could be removed by syringe. However, the use of this vessel can lead to irreproducibly rapid copolymerization over the first 5–10 min of reaction at 25°C . After these initial periods, reproducible lower rates of copolymerization are obtained. The cause of these fast initial rates is not known but they may arise from the introduction of traces of H_2O^{11} or O_2 ; the effects can be minimized by careful drying of solvents and monomers and by prolonged N_2 purging of reaction vessels and syringes. Experiments in which the fast initial rates were pronounced (e.g. Figure 4) were considered to be unsatisfactory for kinetic analysis; all kinetic parameters have been obtained from the steady 'slow' rates observed in experiments in which the 'fast' initial rates were only slightly higher and which did not persist to high conversion. Rates of spontaneous copolymerization have been measured as a function of (a) EASC concentration (expressed as moles of aluminium per litre), (b) MMA concentration, (c) IP concentration and (d) temperature. The data for (a) are presented in graphical form in Figure 5 and for (b), (c) and (d) in Tables 1, 2 and 3. The rate data (from the appropriate log-log plots) indicate the following orders of reaction: w.r.t. $[\text{EASC}]$, 1.35 ± 0.16 ; w.r.t. $[\text{MMA}]$, 0.26 ± 0.06 ; and w.r.t. $[\text{IP}]$, 0.03 ± 0.16 . The data at various temperatures (Table 3) are consistent with an overall activation energy for the copolymerization of $26 \pm 5 \text{ kJ mol}^{-1}$.

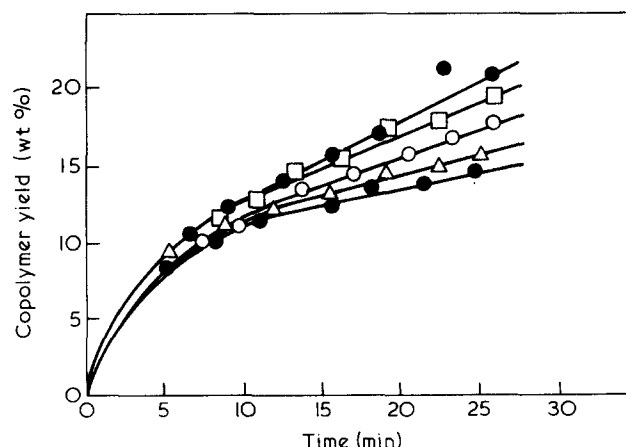


Figure 4 Copolymerization experiments at 25°C showing fast initial rates. $[\text{IP}] = 2.48 \text{ mol l}^{-1}$; $[\text{EASC}] = 0.94 \text{ mol l}^{-1}$; $[\text{MMA}] = 1.18\text{--}3.54 \text{ mol l}^{-1}$; solvent, toluene

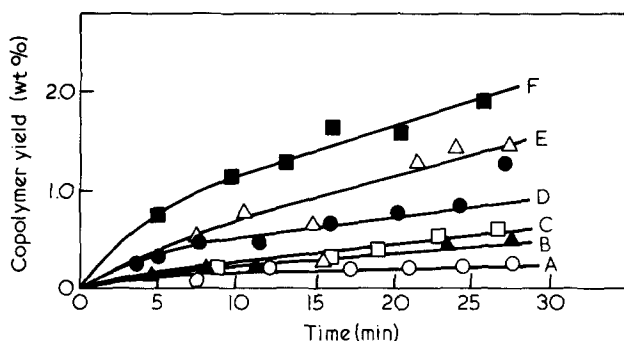


Figure 5 Copolymerization at 25°C with $[IP] = 2.48 \text{ mol l}^{-1}$, $[MMA] = 2.36 \text{ mol l}^{-1}$ and $[EASC] =$ (A) 0.20, (B) 0.32, (C) 0.33, (D) 0.48, (E) 0.64 and (F) 0.71 mol l^{-1} . Solvent, toluene

Table 1 Rate of copolymerization as a function of $[MMA]$ at 25°C in toluene

$[MMA]$ (mol l^{-1})	1.18	1.77	2.95	3.54
R_p (min^{-1})*	0.018	0.022	0.024	0.024

$[IP] = 2.48 \text{ mol l}^{-1}$, $[EASC] = 0.40 \text{ mol l}^{-1}$

* All copolymerization rates are quoted in wt fraction conversion to copolymer per minute

Table 2 Rate of copolymerization as a function of $[IP]$ at 25°C in toluene

$[IP]$ (mol l^{-1})	1.24	3.10	4.98
R_p (min^{-1})	0.014	0.017	0.014

$[MMA] = 2.36 \text{ mol l}^{-1}$, $[EASC] = 0.25 \text{ mol l}^{-1}$

Table 3 Rate of copolymerization as a function of temperature

T (K)	273.8	288.1	298.6	307.2	312.7
R_p (min^{-1})	0.020	0.028	0.060	0.053	0.086

$[MMA] = 2.36 \text{ mol l}^{-1}$, $[IP] = 2.48 \text{ mol l}^{-1}$, $[EASC] = 0.58 \text{ mol l}^{-1}$

The copolymerization was found to be inhibited by high concentrations ($\sim 10\%$ w/v) of the free-radical scavenger diphenylpicrylhydrazyl (DPPH). DPPH appears to be ineffective at the low concentrations normally used to inhibit radical polymerizations ($< 1\%$ w/v).

Molecular weights of copolymers prepared in the presence of EASC

Molecular weights and molecular weight distributions for copolymers prepared to high conversions from an approximately equimolar comonomer feed in the presence of EASC (the experiment illustrated in Figure 3) were assessed by g.p.c. \bar{M}_n and \bar{M}_w values obtained from the g.p.c. curves are given in Table 4. The g.p.c. columns were calibrated with polystyrene standards and the molecular weights were calculated by applying the Q -factor method¹² and assuming that $Q(\text{copolymer})/Q(\text{polystyrene}) = 33/47$. $Q(\text{copolymer})$ is obtained by taking the average molecular weight for an MMA unit and an IP unit (84.11) and dividing this by the average length of the five C–C bonds (four single and one double) contained within the backbone of one MMA unit and one 1,4-IP unit (2.515 Å). The molecular weights

calculated in this way will be overestimated but will be relatively correct.

The effect of AZBN on the alternating copolymerization

The addition of AZBN ($1\text{--}10 \text{ g l}^{-1}$) to mixtures of IP, MMA and EASC in toluene at 25°C results in increased rates of alternating copolymerization. Up to 7.5 g l^{-1} AZBN, the increase in rate is roughly proportional to the concentration of AZBN used, but beyond this concentration the increase in rate is particularly marked. In the presence of 1 g l^{-1} AZBN, the order of the copolymerization w.r.t. $[EASC]$ is no longer simple; measurements of rate of copolymerization as a function of $[EASC]$ with $[AZBN] = 1 \text{ g l}^{-1}$ produced curved \log_{10} rate vs. $\log_{10}[EASC]$ plots.

The molecular weights of alternating copolymers also are influenced by the presence of AZBN. Increasing the AZBN concentration from 1 g l^{-1} to 10 g l^{-1} with $[MMA] = 2.36 \text{ mol l}^{-1}$, $[IP] = 2.48 \text{ mol l}^{-1}$ and $[EASC] = 0.156 \text{ mol l}^{-1}$ reduced \bar{M}_n for the first formed polymer from 2.6×10^4 to 7.0×10^3 and reduced \bar{M}_w from 6.8×10^4 to 2.0×10^4 .

Complexing of monomers, solvent and EASC

The formation of donor–acceptor complexes in solution is often accompanied by the appearance of a new u.v. absorption band to longer wavelengths termed the charge-transfer band. Such complexing is sometimes accompanied also by changes in n.m.r. chemical shifts¹³. Either phenomenon can be used to assess the stoichiometry and strength of such complexing. In this work we have chosen to use 60 MHz ^1H n.m.r. to assess the importance of complexing in the binary systems MMA/IP, MMA/toluene and MMA/EASC and in the ternary systems IP/MMA/EASC and toluene/MMA/EASC.

Binary complexes. The addition of toluene (an electron donor) to solutions of MMA (an electron acceptor) in the inert solvent cyclohexane (CH) produces small but significant downfield shifts in the position of the MMA methoxyl proton resonance (δ_{OCH_3}). Measurements of these shifts as a function of MMA/toluene ratio followed by a plot of $\Delta_{\text{obs}} n_{\text{MMA}}$ vs. n_{MMA} (the n.m.r. equivalent of the u.v. continuous variation experiment) allows the stoichiometry of complexing to be determined¹⁴. Δ_{obs} is δ_{OCH_3} for MMA in CH minus δ_{OCH_3} for MMA in the toluene/CH mixture; n_{MMA} is the molar fraction of MMA. The result for MMA/toluene/CH at ambient n.m.r. probe tempera-

Table 4 Molecular weights of alternating copolymers as a function of conversion (experiment depicted in Figure 3) obtained by g.p.c.

Conversion to copolymer (wt%)	\bar{M}_n ($\times 10^{-3}$)	\bar{M}_w ($\times 10^{-3}$)
5.5	8.2	21.8
10.5	23.6	59.8
16.5	22.8	68.2
20.0	24.6	75.3
26.5	16.6	67.8
34.6	13.9	73.3
39.0	5.8	87.2
44.4	3.5	68.0

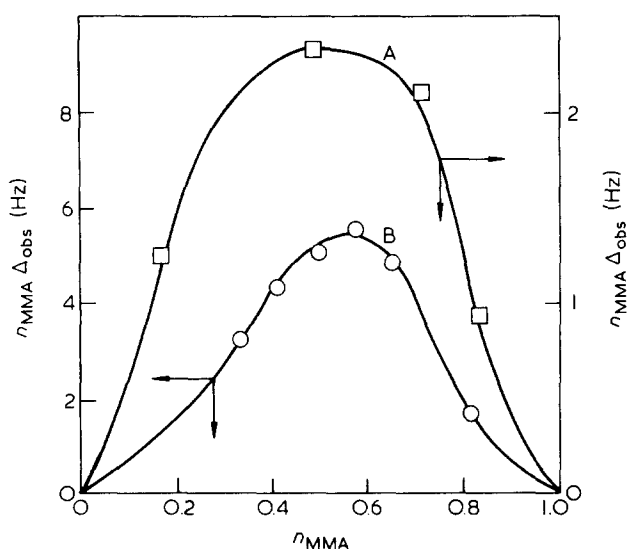
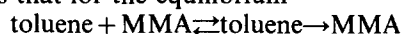


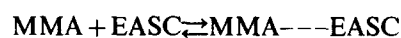
Figure 6 ^1H n.m.r. continuous variation experiments for (A) MMA/toluene/CH (MMA OCH_3 resonance monitored) and (B) MMA/EASC/CH (MMA $\alpha\text{-CH}_3$ resonance monitored) at 35°C . n_{MMA} = molar fraction of MMA in MMA/toluene and MMA/EASC mixtures. Total concentration of $[\text{MMA}] + [\text{toluene}] = 2.83 \text{ mol l}^{-1}$ in (A) and total concentration of $[\text{MMA}] + [\text{EASC}] = 3.8 \text{ mol l}^{-1}$ in (B)

ture (35°C) is illustrated in Figure 6A. The peak maximum at around $n_{\text{MMA}} = 0.5$ indicates a 1:1 interaction between MMA and toluene. The equilibrium constant for complexing has been obtained, using a now conventional n.m.r. approach¹⁵, by measuring Δ_{obs} for a series of mixtures of MMA with toluene in CH in which the MMA concentration was kept low and constant at 0.184 mol l^{-1} and in which the toluene concentration was varied over the range 1.63 to 9.05 mol l^{-1} . The plot of $1/[\text{toluene}]$ vs. $1/\Delta_{\text{obs}}$ (Figure 7) gives a straight line (again characteristic of 1:1 complexing) with an intercept on the ordinate equal to $-K$ (the equilibrium constant for complexing). Figure 7 indicates that for the equilibrium



in CH at 35°C , K is $0.27 \pm 0.051 \text{ mol}^{-1}$.

Addition of IP to mixtures of MMA and CH produces no significant changes in chemical shift and therefore it is assumed that complexing between the two monomers is negligible. However, the addition of EASC to mixtures of MMA and CH produces very marked changes in both δ_{CH_3} and δ_{OCH_3} . The appropriate continuous variation experiment (Figure 6B) indicates a 1:1 interaction, but the plot of $1/[\text{EASC}]$ vs. $1/\Delta_{\text{obs}}$ (Figure 7B) is nearly parallel to the ordinate, indicating very strong complexing between EASC and MMA. Extrapolation of this line indicates that for the equilibrium



in CH at 35°C , $K > 1001 \text{ mol}^{-1}$. It is assumed that the complexing between MMA and EASC involves coordination of the lone pair on the carbonyl oxygen of one molecule of MMA with a vacant orbital on an Al atom of EASC. Since EASC can be regarded as a mixture of monomeric and dimeric compounds in dynamic equilibrium ($\text{Et}_3\text{Al}_2\text{Cl}_3 \rightleftharpoons \text{Et}_2\text{AlCl} + \text{EtAlCl}_2$), the complex $\text{MMA} \text{---} \text{EASC}$ will be a mixture of species in each of

which one molecule of MMA is coordinated with each Al atom (1:1 stoichiometry). In representing this mixture of complexes with the single formula $\text{MMA} \text{---} \text{EASC}$, it is acknowledged that the spectroscopic and other properties of this system are average properties, and therefore that the equilibrium constant evaluated above is an average quantity.

Ternary complexes. The addition of an electron donor (D) to an electron acceptor (A) complexed with a Lewis acid (LA) can result in the formation of 1:1:1 ternary complexes which may be represented as $\text{D} \rightarrow \text{A} \text{---} \text{LA}$. Such complexes have been detected in several systems which give rise to alternating copolymers and might be expected in mixtures of toluene with MMA and EASC, and of IP with MMA and EASC. Since the equilibrium constant for the complexing of MMA with EASC is large, at all but the lowest concentrations equimolar mixtures of MMA and EASC can be regarded as consisting entirely of the 1:1 binary complex. Thus the formation of ternary complexes can be conveniently studied by investigating the spectroscopic properties of equimolar mixtures of MMA and EASC in an inert solvent to which various amounts of the donor compound (IP or toluene) have been added. ^1H n.m.r. continuous variation plots based on both MMA α -methyl and MMA methoxyl chemical shifts for the IP + $\text{MMA} \text{---} \text{EASC}$ and toluene + $\text{MMA} \text{---} \text{EASC}$ systems are shown in Figure 8. The Δ_{TC} values are based on the observed chemical shift differences, Δ_{obs} , but are corrected for the influence of binary complexing using

$$\Delta_{\text{TC}} = \Delta_{\text{obs}} - \Delta_{\text{BC}}$$

where Δ_{BC} represents the chemical shift of MMA in the binary complex minus the chemical shift of uncomplexed

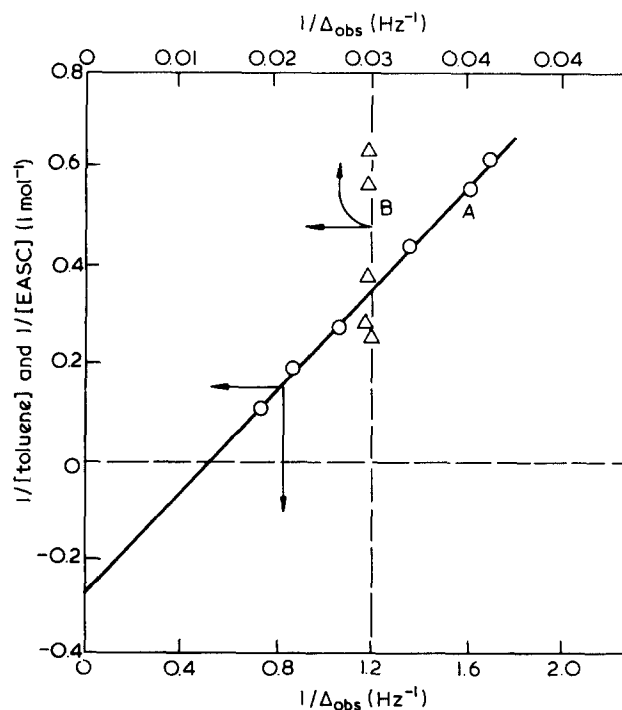


Figure 7 Obtaining the equilibrium constants for (A) $\text{MMA} + \text{toluene} \rightleftharpoons \text{MMA} \leftarrow \text{toluene}$ ($[\text{MMA}] = 0.18 \text{ mol l}^{-1}$ and (B) $\text{MMA} + \text{EASC} \rightleftharpoons \text{MMA} \text{---} \text{EASC}$ ($[\text{MMA}] = 0.44 \text{ mol l}^{-1}$) in CH at 35°C (δ_{OCH_3} measured)

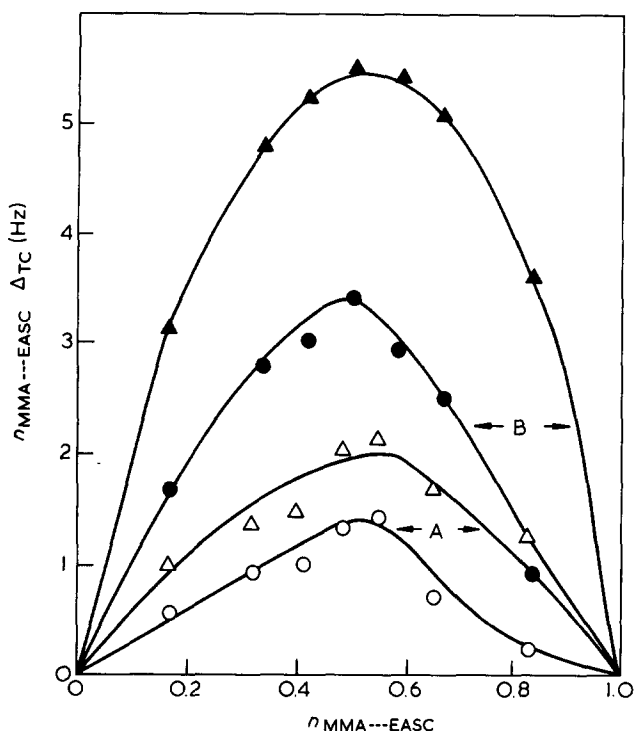
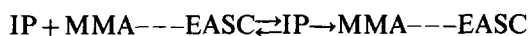


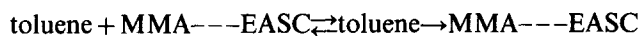
Figure 8 ^1H n.m.r. continuous variation experiments for (A) IP/MMA/EASC/CH (Δ , MMA OCH_3 resonance; \circ , MMA $\alpha\text{-CH}_3$ resonance) and (B) toluene/MMA/EASC/CH (\blacktriangle , MMA OCH_3 resonance; \bullet , MMA $\alpha\text{-CH}_3$ resonance). $n_{\text{MMA---EASC}}$ = molar fraction of 1:1 MMA/EASC complex in IP/MMA/EASC mixtures. Total concentration of $[\text{MMA}] + [\text{EASC}] + [\text{IP}] = 1.95 \text{ mol l}^{-1}$ in (A) and total concentration of $[\text{MMA}] + [\text{EASC}] + [\text{toluene}] = 2.26 \text{ mol l}^{-1}$ in (B)

MMA. For both ternary systems, the formation of 1:1:1 complexes is indicated.

Equilibrium constants for ternary complexing have been obtained from the intercepts of plots of $1/[\text{donor}]$ vs. $1/\Delta_{\text{TC}}$ (Figure 9) in a manner analogous to that used for the binary complexing. For the equilibrium



at 35°C , $K = 0.53 \pm 0.05 \text{ l mol}^{-1}$ and for



$K = 0.17 \pm 0.05 \text{ l mol}^{-1}$. (Note that these equilibrium constants are also average quantities for the reasons given above in the discussion of the significance of the equilibrium constant for binary complexing between MMA and EASC.)

DISCUSSION

We believe that the copolymerization of MMA and IP at 25°C in the presence of EASC involves radical initiation and propagation. This view is supported by the observation that rates of copolymerization are enhanced by the addition of AZBN, but that the average molecular weight is then lower, and that DPPH will inhibit the copolymerization, albeit only when used at higher-than-normal concentrations.

Molecular weights and molecular weight distributions

(Table 4) appear normal for a free-radical mechanism ($\bar{M}_w/\bar{M}_n \approx 3$ at up to 20% conversion) but the distribution broadens significantly at the highest conversion ($\bar{M}_w/\bar{M}_n \approx 20$ at 44.4% conversion). This broadening may arise through transfer to Diels-Alder adduct, amounts of which increase during the copolymerization experiment (Figure 3). The relatively low initial values of \bar{M}_n and \bar{M}_w at 5.5% conversion are associated with the higher initial rate of copolymerization and reflect the higher rates of initiation during this period.

Various detailed mechanisms have been advanced to explain the alternating copolymerizations of donor with acceptor monomers in the presence of metal halide and organometal halide Lewis acids. One of the more exotic mechanisms first proposed by Gaylord, but also supported by Furukawa, Hirai and others, involves the virtual homopolymerization of ternary monomer-monomer-Lewis acid complexes. However, we believe that our results do not support this mechanism for the copolymerization reported here. Our reasoning is given below.

An approximate value for the concentration of IP \rightarrow MMA---EASC ternary complex present in each of the copolymerization mixtures referred to in the results section can be calculated with the aid of a simple iterative computer program using the measured binary and ternary equilibrium constants. The system involves four competitive and consecutive equilibria, *viz.*

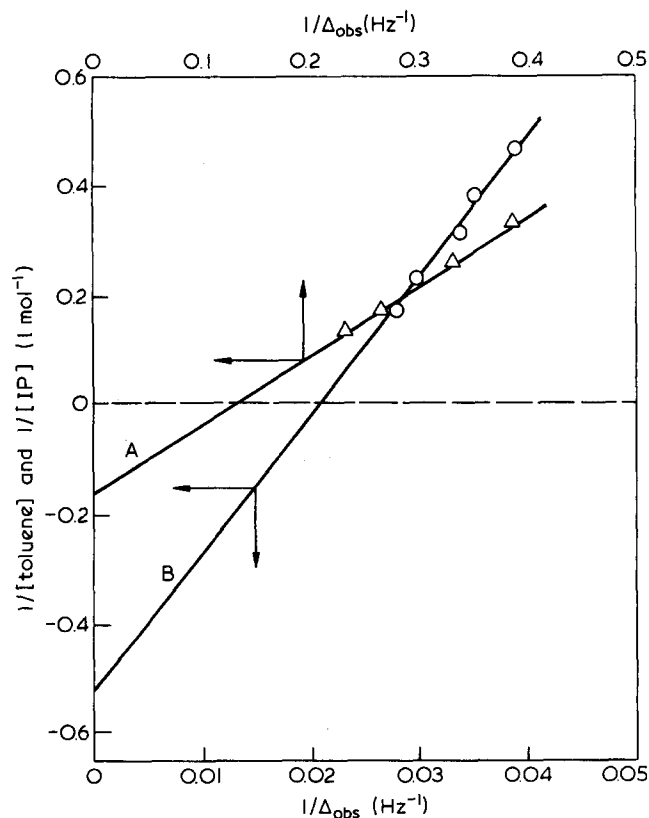
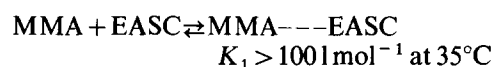


Figure 9 Obtaining the equilibrium constants for (A) $\text{MMA---EASC} + \text{toluene} \rightleftharpoons \text{toluene} \rightarrow \text{MMA---EASC}$ ($[\text{MMA---EASC}] = 0.40 \text{ mol l}^{-1}$) and (B) $\text{MMA---EASC} + \text{IP} \rightleftharpoons \text{IP} \rightarrow \text{MMA---EASC}$ ($[\text{MMA---EASC}] = 0.29 \text{ mol l}^{-1}$) (δ_{OCH_3} measured)

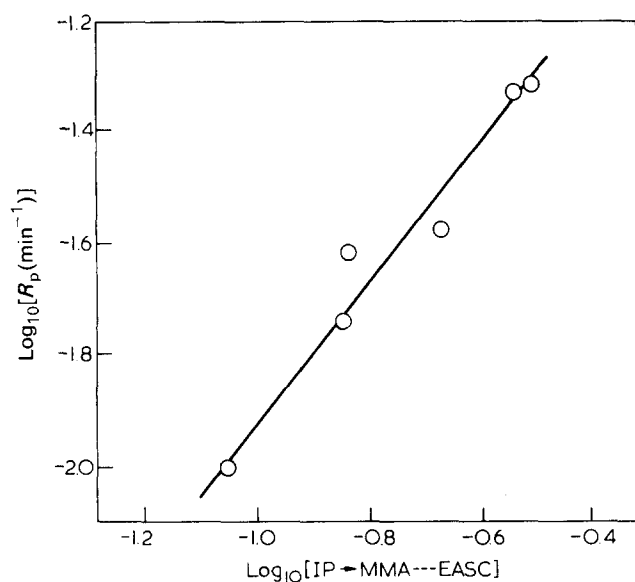
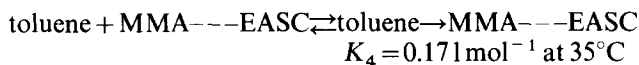
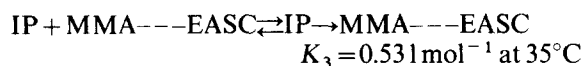
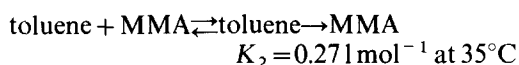


Figure 10 Log-log plot of rate of polymerization vs. ternary complex concentration, $[IP \rightarrow MMA---EASC]$. Data taken from experiments at constant $[MMA]$ and $[IP]$ but varying $[EASC]$ (Figure 5)

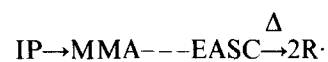


but the formation of the toluene \rightarrow MMA---EASC complex is important only insofar that it competes with the IP \rightarrow MMA---EASC for the available MMA---EASC binary complex. The calculated ternary complex concentrations will be slightly underestimated because the equilibrium constants relate to a temperature of 35°C whereas the copolymerization experiments were performed in the main at 25°C . Also it is assumed that the pattern of complexing in the copolymerization media will be the same as that in the cyclohexane solvent medium in which the complexing was studied.

If copolymerization propagation occurs predominantly by the incorporation of ternary complexes into the growing chain, it would be expected that rates of copolymerization would correlate in some simple way with ternary complex concentrations. However, as will be seen below, this was not the case for all the experiments reported here.

In the experiments in which $[EASC]$ was varied from 0.2 mol l^{-1} to 0.7 mol l^{-1} with $[MMA]$ and $[IP]$ constant (Figure 5), the concentration of the ternary complex, $[IP \rightarrow \text{MMA}---\text{EASC}]$, is calculated to vary from 0.09 to 0.31 mol l^{-1} , and a plot of \log_{10} rate vs. $\log_{10}[IP \rightarrow \text{MMA}---\text{EASC}]$ (Figure 10) is consistent with an order of reaction w.r.t. the complex of 1.36 ± 0.16 . This can be compared with the value of 1.5 found by Hirai and Komiyama¹⁶ for the order of reaction w.r.t. $[\text{styrene} \rightarrow \text{MMA}---\text{SnCl}_4]$ in the styrene/MMA/SnCl₄ copolymerization system, and could be interpreted in terms of a

mechanism involving a ternary complex in both initiation and propagation:



The observation that the order w.r.t. $[MMA]$ is close to zero is also consistent with this mechanism; when $[MMA] > [EASC]$, further additions of MMA have little effect on the concentration of the binary, $\text{MMA}---\text{EASC}$, complex and therefore have little effect also on the concentration of the ternary complex, $[\text{IP} \rightarrow \text{MMA}---\text{EASC}]$.

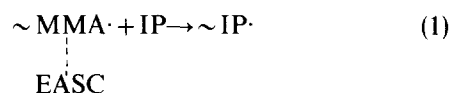
However, the observation that the order w.r.t. $[IP]$ is also approximately zero is *not* consistent with this ternary-complex mechanism. Varying $[IP]$ from 1.24 to 4.98 mol l^{-1} (Table 2) is calculated to produce a change in $[\text{IP} \rightarrow \text{MMA}---\text{EASC}]$ of from 0.065 mol l^{-1} to 0.166 mol l^{-1} , and yet over this range of $[IP]$ no change in rate of copolymerization is observed.

It is interesting to compare our results with those of Furukawa and coworkers¹⁷ for the alternating copolymerization in BD/MMA/EtAlCl₂/VOCl₃ (BD = butadiene). For this system, kinetic behaviour was found very similar to that described here, *viz.*,

$$\text{rate of copolymerization} \\ \propto [\text{EtAlCl}_2]^{1.5} [\text{VOCl}_3]^{0.5} [\text{MMA}]^0 [\text{BD}]^0$$

Furukawa proposed that copolymerization proceeded via a ternary complex, but recognized that the only way such a mechanism could be reconciled with an order of zero w.r.t. $[\text{BD}]$ was if the equilibrium constant for the formation of the ternary complex, $\text{BD} \rightarrow \text{MMA}---\text{EtAlCl}_2$, is much larger than that for the formation of the binary complex, $\text{MMA}---\text{EtAlCl}_2$. In view of our measurements on IP/MMA/EASC, this situation with regard to complexing in BD/MMA/EtAlCl₂ is most unlikely. Furukawa and coworkers did not report measured equilibrium constants for their system.

It is our view that alternation in IP/MMA/EASC arises largely because of favourable donor-acceptor interactions in the transition states for cross-propagation reactions involving complexed monomers and radicals, which as a consequence have low activation energies:



Low activation energies for such reactions would be reflected in a low overall activation energy as is the case here. Orders of reaction in copolymerizations are difficult to interpret, but orders w.r.t. $[MMA]$ and $[IP]$ of near zero are reconcilable with a scheme involving enhanced cross-propagation if $\text{MMA}---\text{EASC}$ is much more reactive than free MMA towards an isopropenyl radical (which on donor-acceptor grounds it would be expected to be) and if the overall rate of copolymerization is

determined by the rate of reaction (2) rather than by the rate of reaction (1). Bamford and Han⁷ have recently shown that cross-propagation is especially favoured in copolymerizations of methyl acrylate with BD and IP in the presence of EASC initiated photochemically with $Mn_2(CO)_{10}$.

There may be a contribution to growth also from complexed radicals of the type envisaged by Hirooka as being important in styrene/MMA/EASC copolymerization¹⁸. Hirooka has shown that such complexing can account for zero-order behaviour w.r.t. the donor monomer.

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