Hindered initiation, primary-radical termination and effects of pressure on polymerization rates

K. E. Weale

Department of Chemical Engineering and Chemical Technology, Imperial College, London SW7 2AZ, UK

The rates of polymerization of diethyl fumarate (DEF) and *trans*-ethyl cinnamate (EC) have been measured at 60°C, at various concentrations of the initiators azoisobutyronitrile (AIBN) and benzoyl peroxide (BPO), and at pressures from 1 to 3000 bar. In the EC/AIBN system at 1 bar the rate is nearly independent of initiator concentration and termination occurs almost entirely by reaction between growing chains and initiator radicals. The abnormally large initial pressure-acceleration of this polymerization can be explained in terms of the appropriate rate equation. Primary-radical termination is also of significance in the system EC/BPO, but not in the polymerization of DEF. The polymerization of each monomer is faster with BPO than with AIBN. It is concluded that in the initial reaction with EC the cyanoisopropyl radical is more hindered than are phenyl or benzoyloxy radicals. In the system DEF/AIBN initiation is hindered less strongly. There is some evidence of a related steric effect in the copolymerization of these monomers with methyl methacrylate.

INTRODUCTION

Measurements of the effects of pressure on the rates of polymerization of diethyl fumarate (DEF) and *trans*-ethyl cinnamate (EC), using the initiator azobisisobutyronitrile (AIBN), have been described previously[1]. It was found that both polymerizations are accelerated by increasing pressure in the range up to 3000 bar. For DEF the effect is broadly comparable with that for various mono-substituted and 1,1 di-substituted monomers, but the polymerization of EC, which is very slow, has an exceptionally large pressure-acceleration which cannot be explained in terms of known effects of pressure on the normal component processes. More detailed measurements have been made on these two systems, and on the same monomers, using the initiator benzoyl peroxide (BPO). There are large differences between the kinetic characteristics of the four polymerizations, and the abnormal effect of pressure on the EC/AIBN reaction can now be explained.

EXPERIMENTAL

The procedures were similar to those used previously[1]. Monomers were vacuum-distilled under nitrogen and redistilled at frequent intervals. Rates were measured at $60\pm0.1°C$, except where noted. Reactions at 1 bar were usually carried out with $10\,cm^3$ monomer in closed glass tubes (20 to $50\,cm^3$ reactant was used at very low initiator concentrations and for EC/solvent mixtures). At high pressures, about $8\,cm^3$ monomer was contained in a stainless steel tube, closed at one end and fitted with an internal piston by which pressure was transmitted from the surrounding fluid to the contents. DEF polymer was isolated by the method of Bengough *et al.*[2], and reprecipitated several times. EC polymer was separated by mixing the product with chloroform and pouring into excess methanol; after filtration through porosity 5 sintered glass it was washed repeatedly with methanol. Pressures up to 1400 bar were measured directly and were kept constant to within $\pm10\,bar$. Higher pressures were measured via a calibrated piston-intensifier system, with an accuracy of about 2%.

RATES OF POLYMERIZATION

Reaction rates for the four monomer/initiator pairs were measured over a range of concentrations at several pressures. In some cases extended runs were carried out to determine the forms of conversion vs. time curves.

Yields of polymer vs. time

Some conversion vs. time curves for the systems DEF/BPO and EC/BPO are shown in *Figure 1* at nearly identical values of *I*, the initiator concentration. DEF reacts much faster than EC, and its isobars have the usual curvature towards the time axis, which is attributable to depletion of the initiator and monomer as the reaction proceeds. (The half-life of BPO is about 80 h at 60°C, 1 bar, and is longer at higher pressures). In contrast the EC isobars are very nearly straight lines passing through the origin. An EC/AIBN isobar (not shown in the Figure) was determined at 1 bar, with $I = 0.0174\,mol\%$, and also found to be linear. Conversion was 0.36% at 20 h and 1.93% at 117 h (about 6 initiator half-lives). The unusual nature of the EC isobars is a consequence of other abnormal kinetic features which are discussed below.

The product from the longest run with DEF at 1 bar was principally a stiff, viscous material which contained 71.3% polymer, together with a minor amount of viscous fluid which contained 28% polymer. The longest run with
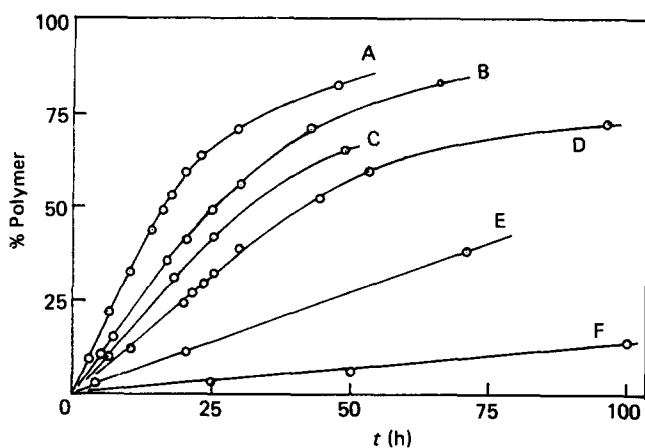
Figure 1 Yield of polymer vs. time (60°C) DEF/BPO ($I = 0.671$ mol%): A, 3000 bar; B, 1000 bar; C, 500 bar; D, 1 bar. EC/BPO ($I = 0.688$ mol%): E, 2700 bar; F, 1 bar

Table 1 Rates of polymerization at 1 bar, 60°C

Reaction system	Rate (mol% h⁻¹)	
	($I = 0.1$ mol%)	($I = 1.0$ mol%)
EC/BPO	0.060	0.13
EC/AIBN	0.020	0.019
DEF/BPO	0.47	1.48
DEF/AIBN	0.40	1.27
ST/BPO (ref. 3)	1.5	–
ST/AIBN (ref. 4)	3.1	–

EC at 2700 bar yielded a cylinder of faintly opalescent, friable, white solid which contained 37.9% polymer.

Polymerization rates at 1 bar

Rates of polymerization were obtained from runs at low conversions (corresponding to the initial slopes of conversion vs. time curves). A comparison between the four systems, and with styrene (ST), is given in *Table 1*.

EC polymerizes much more slowly than does DEF, whichever initiator is used. Also each of the two monomers polymerizes faster with BPO than with AIBN, which is the reverse of the normal order (cf. styrene). For DEF the rate is 1.17 times faster with BPO than with AIBN. For EC the difference is greater but varies with I, as described more fully below.

Effects of pressure on polymerization rates

The changes in rate of polymerization with pressure at constant (but not identical) initiator concentrations are shown for EC in *Figure 2*, and for DEF in *Figure 3*. The data for reactions with AIBN are from the earlier paper[1]. The exceptionally large pressure-acceleration in the EC/AIBN system and the different character of this curve are evident. The curves for the other systems, including EC/BPO, vary individually but form a group with general similarities.

The pressure coefficients of the rates, at 1 bar, are usually expressed as 'overall' activation volumes, ΔV_0^*, which are defined by the equation:

$$(\partial \ln \text{rate}/\partial P)_T = -\Delta V_0^*/RT \qquad (1)$$

and calculated from the initial slopes of plots of ln rate vs. P (cf. Figure 3 in ref. 1). The values obtained from the data are given in *Table 2*.

These may be compared with values of ΔV_0^* for six vinyl and vinylidene monomers determined by Ogo *et al.*[5,6], which range from -16 to -26. All the values refer to the initial slopes of ln rate vs. P plots, which have different degrees of curvature towards the P-axis. The curvature, i.e. the reduction in pressure-acceleration as the pressure is increased, is least for the EC/AIBN system.

Initiator concentration and the rates of DEF polymerizations

Rates of polymerization vs. $I^{0.5}$ for DEF with both initiators are shown in *Figure 4*. Within experimental error the data give straight lines passing through the
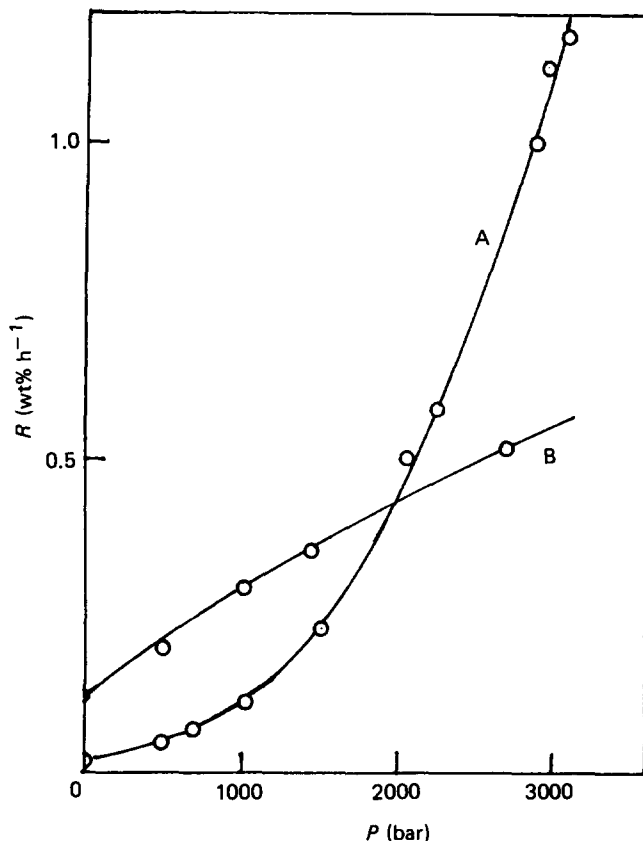

Figure 2 Rate of polymerization of EC vs. pressure (60°C): A, AIBN initiator (1.07 mol%); B, BPO initiator (0.688 mol%)
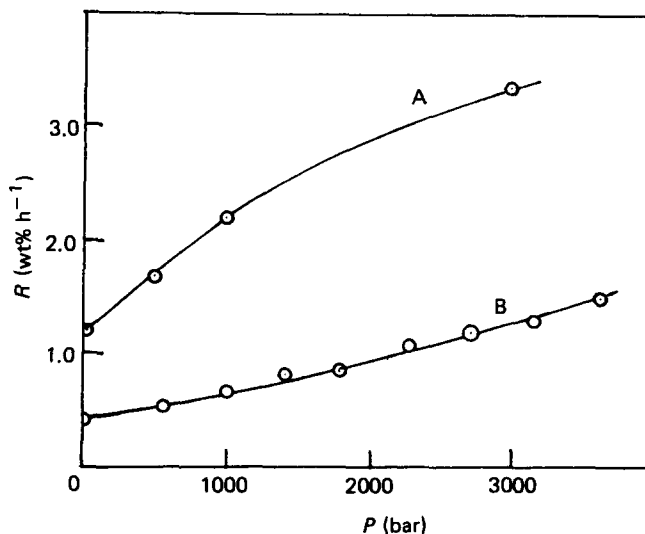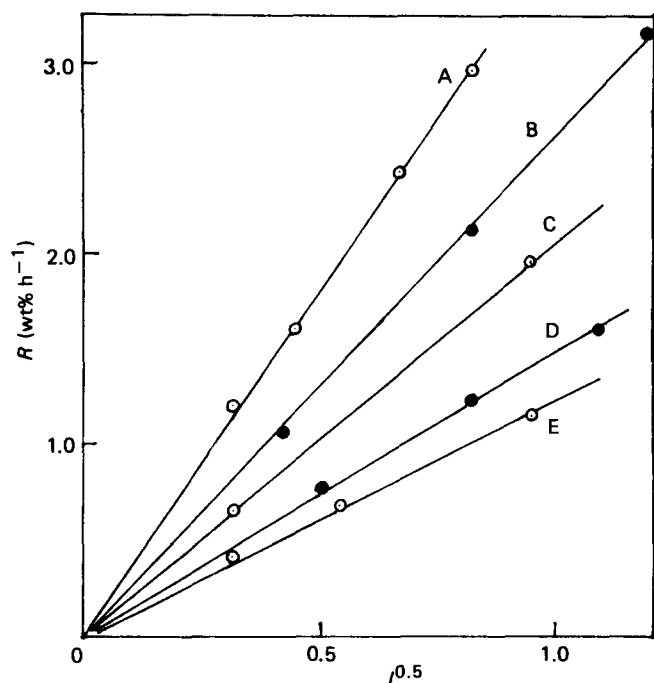

Figure 3 Rate of polymerization of DEF vs. pressure (60°C): A, BPO initiator (0.671 mol%); B, AIBN initiator (0.102 mol%)

Table 2 Overall activation volumes, ΔV_0^* (cm^3 mol^{-1}) at 60°C, 1 bar

DEF/AIBN	-14	EC/AIBN	-47
DEF/BPO	-18	EC/BPO	-27

Figure 4 Effect of initiator concentration on rate of polymerization of DEF (60°C). $\bigcirc$, AIBN: A, 2750 bar; C, 1000 bar; E, 1 bar. $\bullet$, BPO: B, 1000 bar; D, 1 bar

origin, in agreement with the normal kinetic equation. The pressure-acceleration of the reactions is therefore independent of I. At 1000 bar, as at 1 bar, the polymerization is somewhat faster with BPO than with AIBN.

Effect of initiator concentration on rates in the system EC/AIBN

In this, as in the other systems, no polymerization could be detected in the absence of an initiator. The rate of reaction in EC/AIBN at 1 bar is very slow and was usually obtained from yields of polymer in runs of about 20 h. The rates are shown in *Table 3*.

Apart from the result for the lowest initiator concentration the rate of polymerization varies remarkably little over a range in which I increases by a factor of 120. The polymerization at 1 bar thus has the characteristics of a system in which the growing chains are terminated almost exclusively by reaction with primary initiator radicals[7]. The linearity of the conversion vs. time relation, for $I = 0.174$, (discussed above), is clearly a consequence of the insensitivity of the rate to changes in I. At $I = 0.0052$ the rate is dropping more sharply towards zero and the conversion vs. time plot is probably curved towards the time axis. The rate was calculated from the yield of polymer obtained from 41.595 g EC (containing 2 mg AIBN) in 24 h (> 1 half-life) and may be appreciably lower than the true initial rate under these conditions.

Plots of rate vs. $I^{0.5}$ at 1 bar and four higher pressures are shown in *Figure 5*. The data at 2570 bar are those reported earlier[1], with further points at lower values of I. An increase in the reaction pressure increases the rate of

polymerization and also expands the region in which the rate is more strongly dependent on I towards higher values of I. At $I^{0.5} \approx 0.3$, the 1000 and 1400 bar curves level off and ΔV_0^* (*Table 2*), calculated from the initial increase of rate with pressure, becomes almost independent of I. At 2000 and 2570 bar the rate is approximately proportional to $I^{0.5}$ over a greater range, and at 2570 bar and high I the rate is more than 50 times the rate at 1 bar. The kinetic behaviour changes with increasing pressure from termination by primary radicals towards the normal mutual termination of pairs of chains.

*Effect of initiator concentration on rates in the system EC/BPO*

Rates of polymerization vs. $I^{0.5}$ for the EC/BPO system at three pressures are shown in *Figure 6*. The isobars are curved, indicating a marked departure from normal kinetics, but not to the extent found in EC/AIBN. At 1 bar rates are much higher than with AIBN initiator, but at 2700 bar they are rather lower than those for EC/AIBN at 2570 bar. As with EC/AIBN, the form of the rate vs. pressure curve varies with I. In spite of the stronger dependence of the rate on I, the conversion vs. time relation at 2700 bar is linear (*Figure 1*) and this is partly attributable to the approximate doubling of the half-life of BPO at this pressure.

Dependence of rate on temperature and monomer concentration for EC/AIBN at 1 bar

A polymerization in which chain termination occurs mainly by reaction with primary radicals should have an activation energy lower than normal; and the rate should be proportional to M^2, where M is the monomer concentration (see Discussion). A few measurements were made to examine these aspects, and rates of polymerization at two temperatures are given for all the systems in *Table 4*, (I was not identical for every system). These results confirm that the lowest temperature

Table 3 Rates of polymerization in EC/AIBN at 1 bar, 60°C

I (mol%)	Rate (mol% h^{-1})	I (mol%)	Rate (mol% h^{-1})
0.0052	(0.009)	0.61	0.023
0.0174	0.018	0.99	0.019
0.051	0.018		
0.102	0.026	1.07	0.020
0.204	0.027	2.10	0.017
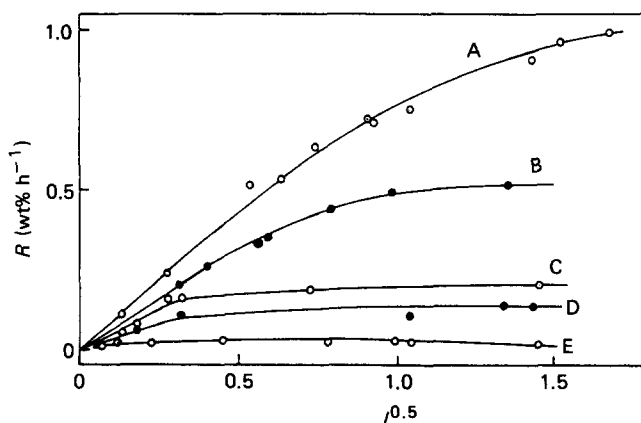
Figure 5 Effect of concentration of AIBN on rate of polymerization of EC (60°C): A, 2570 bar; B, 2000 bar; C, 1400 bar; D, 1000 bar; E, 1 bar
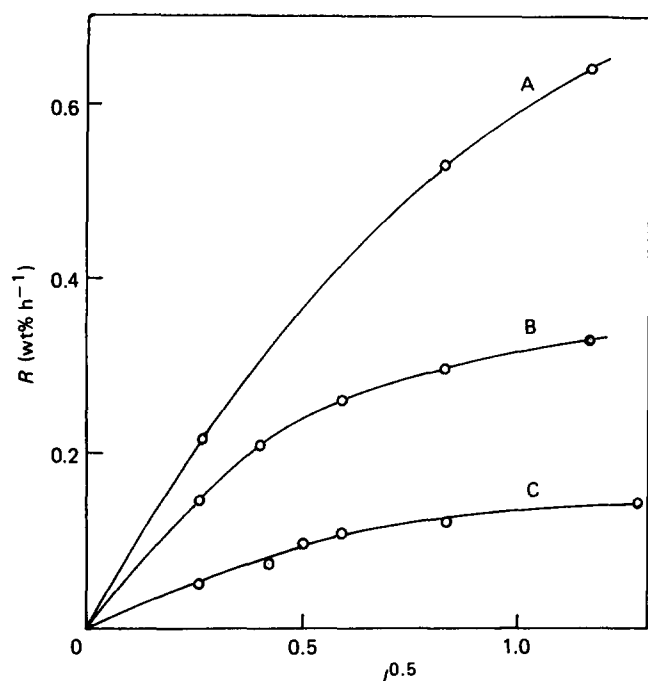
Figure 6   Effect of concentration of BPO on rate of polymerization of EC (60°C): A, 2700 bar; B, 1000 bar; C, 1 bar

Table 4   Effects of temperature change on rates of polymerization at 1 bar

System	Temp. (°C)	Rate (wt % h^{-1})	R_{80}/R_{60}
DEF/AIBN (ref. 7)	60	1.93	8.6
	80	16.6	
DEF/BPO	60	1.61	6.3
	80	10.2	
EC/BPO	60	0.12	4.7
	80	0.56	
EC/AIBN	60	0.020	3.2
	80	0.065	

coefficient of the rate occurs in the system EC/AIBN, which displays the greatest divergence from normal kinetics.

The effect of reduced M on the rate of polymerization in EC/AIBN was measured at 1 bar with methanol as the diluent, and with an initiator concentration of 0.5 g dm^{-3} (0.051 mol% in undiluted EC). The data (obtained in runs of 22 h) are shown in *Figure 7* for a concentration range of 2.53 to 5.90 mol dm^{-3}.

The lower points fall below the linear relationship, which could be due to increased experimental error (yields of polymer were only 35 and 24 mg for the lowest values of M), or to a reduction of initiator efficiency at low M; but to a reasonable approximation the rate of polymerization is proportional to M^2.

DISCUSSION

The four polymerization systems show a considerable range of kinetic behaviour, and the differences between them are a function both of monomer and initiator. It is therefore probable that the kinetic characteristics are determined largely by the initiation reactions between primary radicals and monomer, rather than by structural factors affecting propagation or transfer processes. The data can be interpreted on the basis that in the EC
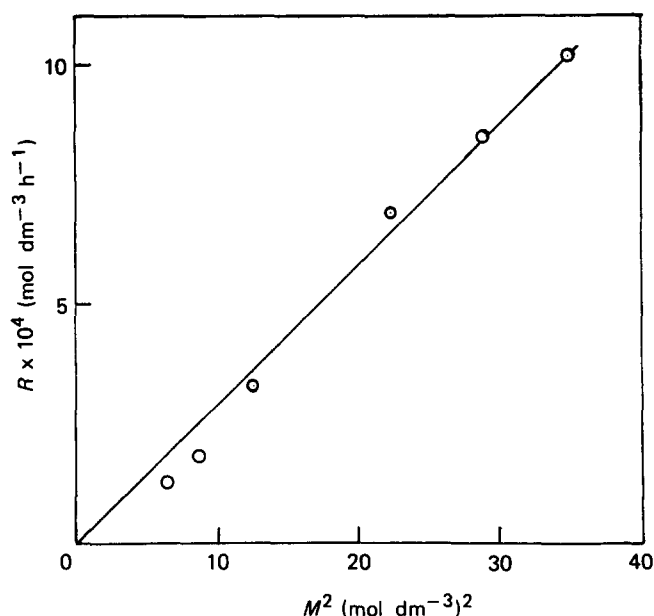

Figure 7   Effect of monomer concentration on rate of polymerization in EC/AIBN, with methanol as diluent, at 1 bar, 60°C

molecule the benzene ring and the ethylcarboxylate group together shield the double bond more effectively from radical addition than do the two ethylcarboxylate groups of DEF, and that with each monomer the cyanoisopropyl radicals from AIBN are more hindered than the initiator radicals from BPO.

Polymerization of EC at 1 bar

In the system EC/AIBN the presence of initiator radicals is necessary for polymerization but the rate is largely independent of their concentration over a wide range of I. Termination of growing chains by primary radicals appears to dominate the kinetics, and this can be attributed to an abnormally slow chain initiation reaction. Initiator radicals which fail to react with monomer react with growing chains to the exclusion of the usual mutual chain termination process. A study by Kharasch and Sage[8] of the radical-chain addition of CBrCl$_3$ to EC, (and also to β-methylstyrene) supports the view that addition of bulky radicals to some 1,2-substituted olefines is hindered. In both cases formation of the adduct was exceptionally slow. EC yielded 60% in three days at 75°C under continuous irradiation, and with fresh diacetyl peroxide added every 4 h. The initial step in this reaction is addition of CCl$_3$ to the C atom which carries the ethylcarboxylate group, and this is presumed to be the point of attack by polymerization initiator radicals. The cyanoisopropyl radical is bulkier than CCl$_3$, particularly along the axis of the protruding CN group, and so is likely to be more hindered. There is no direct evidence concerning the combination of (CH$_3$)$_2$C·CN radicals with EC polymer radicals carrying a phenyl group on the terminal carbon, but examination of space-filling models suggests that it is not strongly hindered. It may be noted that the MW of 7600 derived by Marvell and McCain[9] from the N content of polymer formed in the EC/AIBN system at 1 bar, 60°C, is calculated on the basis of two initiator residues per chain. The result is thus valid either for combination of chain pairs or for combination with initiator radicals, but would require revision if termination is by disproportionation.

In EC/BPO at 1 bar (*Figure 6*) the polymerization is considerably faster. The rate is dependent on I over the whole range, but the curvature of the isobar indicates that primary-radical termination takes place to a considerable extent. It can be inferred that BPO radicals are not as severely hindered as the cyanoisopropyl radical in addition reactions with monomer.

Pressure effects in the EC polymerizations

Kinetic equations have been developed[7,10] to describe polymerizations in which mutual termination of growing chains, and termination by primary radicals occur together. In principle these could be fitted to the curved isobars of the EC/BPO system but data on individual rate constants (and their variation with pressure) would be required.

It is more informative to consider the system EC/AIBN and to make the reasonable approximation that chain termination occurs only by reaction with primary radicals, both at 1 and 1000 bar, over the range in which the rate is practically independent of I (*Figure 5*). This permits a useful comparison with polymerizations which follow normal kinetics.

The kinetic equation for a normal radical polymerization (with the usual simplifying assumptions) is:

$$\text{Rate} = k_p (k_d/k_t)^{1/2} M I^{1/2} \qquad (2)$$

in which k_p, k_d and k_t are the rate constants for chain propagation, initiator dissociation and mutual termination of chains. The equation from transition-state theory for the pressure dependence of rate constants is:

$$(\partial \ln k/\partial P)_T = -\Delta V^*/RT \qquad (3)$$

and the combination of equations (2) and (3) gives:

$$\Delta V_0^* = \Delta V_p^* + \Delta V_d^*/2 - \Delta V_t^*/2 \qquad (4)$$

in which the subscripts denote the activation volumes for the component reactions of the polymerization. Experimental values for the terms on the right of equation (4) are available for a number of polymerizations[5,6] and agree well with values of ΔV_0^*.

For a polymerization in which termination is by reaction of chains with primary radicals, equation (2) is replaced by:

$$\text{Rate} = k_i k_p M^2/k_z \qquad (5)$$

in which k_i is the rate constant for the reaction between initiator radicals and monomer and k_z for the termination of chains by initiator radicals. The rate of the EC/AIBN polymerization at 1 bar has been shown to be approximately proportional to M^2 (*Figure 7*). Further, equation (5), in contrast to equation (2), does not contain k_d, which is associated with a much higher activation energy than the other rate constants; and the rate of the EC/AIBN polymerization has the lowest temperature coefficient of the four reactions (*Table 4*).

Combination of equations (3) and (5) gives:

$$\Delta V_0^* = \Delta V_i^* + \Delta V_p^* - \Delta V_z^* \qquad (6)$$

for polymerizations with termination by primary

radicals, and an estimate of ΔV_0^* can be made by comparisons with data for normal polymerizations[5,6]. Chain propagation has a compact transition state and is pressure accelerated. Values of ΔV_p^* for six polymerizations range from -17.9 to $-24.7 \, \text{cm}^3 \, \text{mol}^{-1}$, with a mean of -21.9. The mutual termination of polymeric radicals is a diffusion controlled process which can be retarded at 1 bar by increasing the viscosity of the reaction medium. As pressure increases the viscosities of liquid monomers and solvents it similarly retards termination and ΔV_t^* has values between 13.3 and $25.0 \, \text{cm}^3 \, \text{mol}^{-1}$ (mean 19.0) for the same polymerizations. The rate constant for the bond-breaking dissociation of AIBN falls as the pressure increases and ΔV_d^* is about 4 or $5 \, \text{cm}^3 \, \text{mol}^{-1}$. On the basis of the data it is reasonable to assume as a first approximation that for the two radical/monomer addition reactions $\Delta V_i^* \simeq \Delta V_p^* \simeq -20 \, \text{cm}^3 \, \text{mol}^{-1}$. The diffusion controlled termination reaction between a growing chain and a small primary radical is likely to be less retarded by pressure than the reaction between two macroradicals, so that ΔV_z^* can be assigned a value of 5 or $10 \, \text{cm}^3 \, \text{mol}^{-1}$. Equation (6) then yields an estimate of $\Delta V_0^* = -45$ or $50 \, \text{cm}^3 \, \text{mol}^{-1}$ for a polymerization with primary radical termination. This is similar to the experimental value $(-47 \, \text{cm}^3 \, \text{mol}^{-1})$ for the EC/AIBN system, and much more negative than ΔV_0^* for polymerizations which follow normal kinetics (cf. equation 4).

Although they involve rough approximations, these considerations support the view that the abnormally large initial pressure acceleration in EC/AIBN arises from the different forms of the two kinetic equations (2) and (5), and that there is no reason to assume any unusual effects of pressure on component reactions of the polymerization process.

Above 1000 or 1400 bar (*Figure 5*) the rate becomes dependent on I over the greater part of the experimental range and an interpretation which assumes reaction with primary radicals to be the only mechanism of chain termination is inadequate. The changeover towards mutual termination of chains is due to an increase in the ratio k_i/k_z (perhaps by a factor of $\simeq 30$ at 3000 bar). The increased rate of chain initiation causes an increase in the concentration of growing radicals and a decrease in the concentration of primary radicals (which reduces the probability of primary termination). These concentration changes increase the proportion of growing chains which terminate in pairs, and their effect is greater than the opposing decrease in the ratio of the diffusion controlled 'rate constants', k_t/k_z.

Polymerization of DEF

The rate of polymerization of DEF is closely proportional to $I^{0.5}$ with each initiator at each pressure (*Figure 7*) and the effect of pressure on the rate is thus independent of I. Replacement of the phenyl substituent by a second ethylcarboxylate group evidently reduces hindrance to initiation, and primary radical termination is not important within the experimental range.

There is a difference between the pressure acceleration of the two reactions (*Table 2*) and the value of ΔV_0^* for DEF/AIBN $(-14 \, \text{cm}^3 \, \text{mol}^{-1})$ is appreciably less negative than for vinyl and vinylidene monomers; but a comparison of particular interest concerns the rates at 1 bar. With BPO initiator (*Table 1*) the rate is 17% greater

than with AIBN, but the rate constant for dissociation of AIBN[11] in DEF at 60°C is $9.4 \times 10^{-6} s^{-1}$, and that for BPO[12] is $2.33 \times 10^{-6} s^{-1}$, so that polymerization with AIBN would be expected to be twice as fast as with BPO, as is the case for styrene. Since the chain growth and termination reactions are identical the difference lies in the initiation process. Considered in conjunction with the data for the EC systems this suggests that the cyanoisopropyl radical does encounter hindrance to addition with the DEF molecule, although this is insufficient for primary radical termination to be significant.

With BPO as initiator the rate of polymerization of DEF at 1 bar is about one-third of that for styrene. The values of k_p and k_t for DEF have not been determined but the result suggests that radicals derived from BPO are not conspicuously inefficient in initiating DEF polymerization. Bevington *et al.*[12], using ^{14}C-labelled BPO, showed that at 60°C not more than 2% of benzoyloxy radicals add to DEF, so phenyl radicals may be the main initiating species at 1 bar. It is known[13] that dissociation of benzoyloxy radicals to phenyl radicals and CO_2 is retarded by pressure, but the influence of this on pressure acceleration in DEF/BPO cannot be assessed without data on the relative reactivities of the two radicals towards the monomer.

Hindered addition in copolymerizations with DEF and with EC

There should be parallels to the results described above in the polymerization of other β-substituted styrenes, but no published data have been found. An analogous effect should also occur in two-component copolymerizations between a 1,1-disubstituted monomer and either DEF or EC. If the substituents are not too small a copolymer chain radical which carries two groups on its terminal C atom will be hindered in adding to a DEF molecule, and

more severely hindered in its addition to EC. Data are available for copolymerizations with methyl methacrylate (MMA). DEF copolymerizes readily with a number of vinyl monomers and the systems show an alternating tendency, i.e. both reactivity ratios are <1. For MMA with DEF, however, the reactivity ratios[14] are $r_{MMA} = 40.4 \pm 0.2$, $r_{DEF} = 0.03 \pm 0.02$, so that for most of the range of reactant compositions the copolymer consists mainly of sequences of MMA units separated by one or, very occasionally, two DEF units. EC can copolymerize with styrene ($r_{ST} = 2.7 \pm 0.3$, $r_{EC} = 0.05$), but the polymer formed in the EC/MMA system is reported to be pure poly-MMA[15]. The results for these monomer pairs are thus in accord with the steric interpretation.

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