

Rates of polymerization of diethyl fumarate and *trans*-ethyl cinnamate at high pressures

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The rates of polymerization of diethyl fumarate (DEF) and *trans*-ethyl cinnamate (EC), with azobisisobutyronitrile initiator, have been measured at 60°C and at pressures from 1 bar to 3000 bars. At ordinary pressure DEF polymerizes 68 times faster than EC. The rate of DEF polymerization is increased by pressure, the size of the effect being similar to that for monomers such as styrene and methyl methacrylate. The pressure-acceleration of the EC polymerization is exceptionally large and at the highest pressure its rate is nearly equal to that for DEF. Termination of EC chains appears to occur partly by reaction with initiator radicals. Freezing point vs. pressure curves have been obtained for each monomer.

(Keywords: polymerization; diethyl fumarate; diethyl cinnamate; pressure)

INTRODUCTION

There have been many studies of the effects of high pressure on the homopolymerizations of vinyl and vinylidene monomers; but few of the high pressure polymerization of 1,2-substituted alkenes. It has previously been reported¹⁻³ that the radical polymerizations of diethyl fumarate (DEF), and of *trans*-ethyl cinnamate (EC) occur more rapidly under pressure, in the range up to 10000 bar. The more detailed measurements on these two monomers, described below, permit a closer comparison with the other structural types.

FREEZING-PRESSURES OF DEF AND EC

As the normal melting points of DEF and EC are not far below room temperature some measurements were made to establish the thermodynamic freezing pressure of each monomer at 60°C (the reaction temperature). Samples of the monomers (about 50 cm³) were compressed to about 5000 bar, at constant temperature, in piston/cylinder equipment. Pressure was slowly reduced and the position of the piston (observed through a cathetometer telescope) plotted as a function of pressure. Melting was indicated by a change in slope, and the freezing-pressure could be estimated with an accuracy of about 2%. No 'superpressing' (failure of the solid phase to form on initial pressurization) was observed, though it was found to occur in some polymerization runs.

The melting temperatures (°C) and corresponding pressures (bars) so obtained are:

EC: 6.5°C, 1; 25.0°C, 900; 38.5°C, 1640; 60.3°C, 2960.
DEF: 0.6°C, 1; 30.0°C, 1720; 59.2°C, 3690.

The freezing curves are shown in *Figure 1*, with extrapolations to 100°C obtained from the relationship $P = a(\Delta t) + b(\Delta t)^2$. This is a good approximation⁴, provided that no solid-solid phase transition occurs in the region of extrapolation.

POLYMERIZATION PROCEDURE AND POLYMER PROPERTIES

Both monomers (which were vacuum-distilled under nitrogen) could be kept for long periods without polymer formation. Amounts of 5 to 10 cm³, containing azoisobutyronitrile (AIBN) initiator, were placed either in a glass tube over a mercury seal, or in a stainless steel tube fitted with an internal piston which carried an O-ring seal. The reaction tube was immersed in hydraulic fluid inside the pressure vessel, which was maintained at 60°C ± 0.1. Runs were normally of several hours duration, but extended to 20 h or longer for EC at the lower pressures. Most rate values were obtained from several runs taken to different conversions.

DEF polymer

The polymer was separated from the colourless, viscous product, either by precipitation in cold petroleum spirit (free of aromatics), or by the method of Bengough *et al.*⁵ In either case several reprecipitations were usually necessary to remove traces of monomer. The dried polymer was a white powder, melting at about 235°C; soluble in the monomer and in benzene, toluene, methanol, chloroform and carbon tetrachloride. I.r. and ¹H n.m.r. spectra indicated only slight traces of olefine double bond. Other workers^{5,6} have reported molecular weights in the range 3250 to 16 000 for polymer formed at 1 bar. We at first obtained anomalously low values, but the molecular weight of polymer produced at 3000 bar was determined to be 9600 (Knauer vapour pressure osmometer). Mass spectrometer measurements near the melting point gave many peaks from molecular fragments. The largest were at mass 45 (C₂H₅O) and at mass 471 (C₂₂H₃₁O₁₁).

EC polymer

In the EC polymerization a polymer-rich phase separated at low conversions, and above 6 or 7% conversion the product was a soft gel which had to be

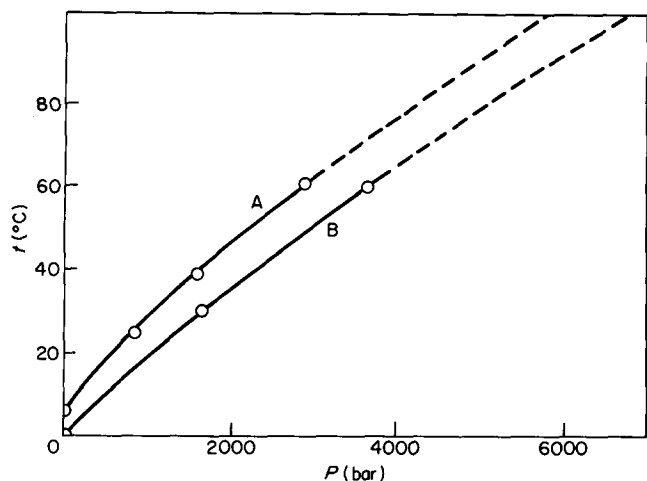


Figure 1 Melting point vs. pressure: (A) *trans*-ethyl cinnamate; (B) diethyl fumarate

pushed out of the tube. It had a green/pink opalescence which disappeared on heating to 100°C but returned on cooling; and was destroyed by addition of a solvent for the monomer. These effects are presumably due to a partially-oriented mesophase.

The product was stirred with chloroform and poured into methanol to separate the polymer. This was obtained as a white powder which melted or partially decomposed above 300°C, and then changed into a brick-red solid. Polymers obtained at pressures up to 1500 bars were soluble in chloroform and higher-pressure products were partially soluble. The limiting viscosity numbers of the solutions were measured as an indication of the trend of molecular weights with reaction pressure. (In earlier work^{3,7} M.wt. values of 4900 and 7600 were obtained for EC polymers.)

The results (Figure 2) show that the molecular weight is greater for polymers formed at the higher pressures. It also appears to be higher if the reaction is taken to 5% conversion rather than 3%, which may be related to the change in physical state of the system, or indicate chain transfer to 'dead' polymer.

RATES OF POLYMERIZATION

The rate measurements were made at 60°C. For experimental convenience the initiator concentration used in the rate vs. pressure study of DEF was 0.102 mol% of AIBN (1 g dm⁻³), while for the EC reaction it was 1.07 mol% (1.00 wt %).

Polymerization rates at 1 bar

The rate of polymerization of EC was found to be 0.020 wt% h⁻¹, and that for DEF to be 0.42. If the rate for DEF is adjusted to the same initiator concentration as for EC (using the $I^{0.5}$ relationship) its value becomes 1.36, so that under identical conditions at 1 bar DEF polymerizes 68 times faster than EC. The result for DEF agrees well with the rates of 0.42 and 0.44 wt% h⁻¹ obtained by Walling and McElhill⁸. No exact value for EC has previously been reported but Marvel and McCain's observation⁷ that with AIBN at 60°C it yields 10% of polymer in 'about a month' is in approximate agreement with our result.

Polymerization rates at high pressures

The results obtained for both monomers are shown in Figure 3 in which log₁₀ (relative rate) is plotted against pressure.

Values of relative rates at three pressures are also given in Table 1, together with corresponding results for the vinyl-type monomer styrene.

The effect of pressure on the rate of polymerization of styrene is typical of a group of vinyl and vinylidene monomers which includes vinyl acetate and methyl methacrylate¹⁰. The pressure-acceleration of the

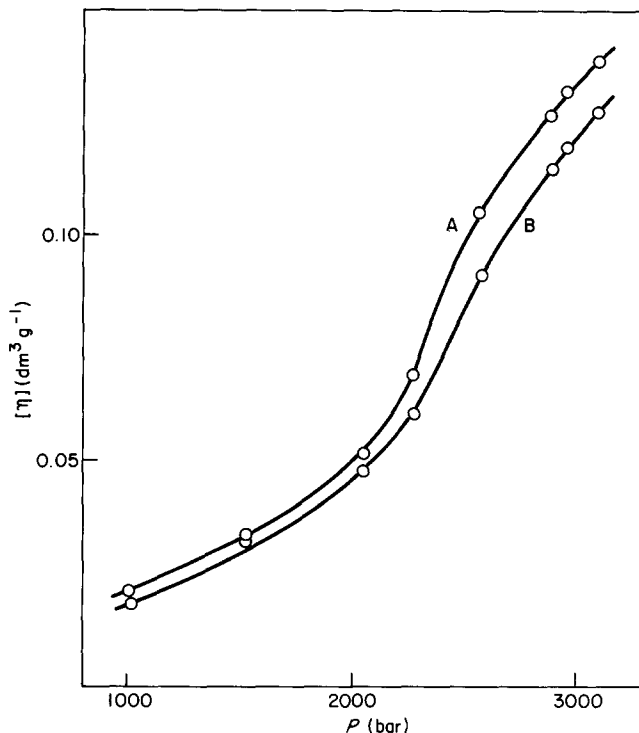


Figure 2 Relation between the pressure of polymerization and the limiting viscosity numbers of ethyl cinnamate polymers (in chloroform solvent at 16°C): (A) 5% conversion to polymer; (B) 3% conversion to polymer

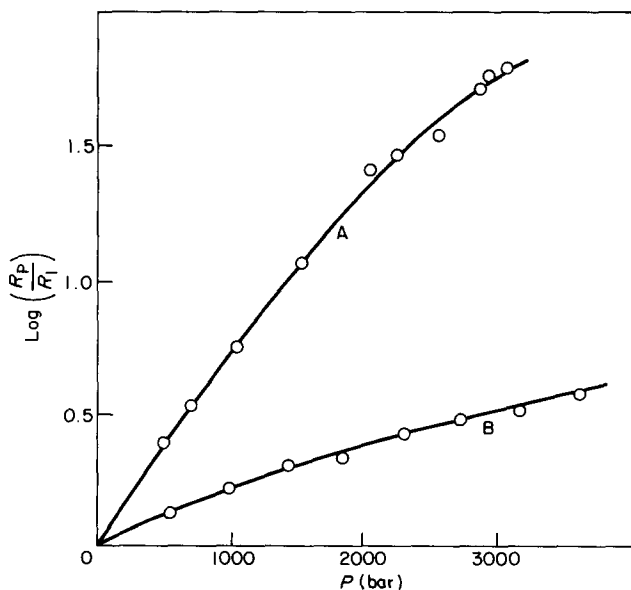


Figure 3 Dependence of initial rates of polymerization on pressure, at 60°C: (A) *trans*-ethyl cinnamate (AIBN = 1.07 mol%); (B) diethyl fumarate (AIBN = 0.102 mol%)

Table 1 Ratio of rate of polymerization at high pressure to rate at 1 bar (all at 60°C)

Monomer:	DEF	EC	Styrene ⁹
Initiator:	AIBN	AIBN	Benzoyl peroxide
P (bar)	R_p/R_1		
1	1	1	1
1000	1.57	5.0	1.95
2000	2.29	20.5	3.6
3000	3.05	55	6.0

polymerization of DEF generally resembles that for styrene. In contrast the very slow polymerization of EC is much more strongly accelerated, and at 3000 bars its rate (at the same concentration of initiator) approaches that of the DEF reaction.

Activation volumes of the polymerizations

The pressure-dependence of a reaction rate constant, k , is usually expressed as:

$$(d \ln k / dP)_T = -\Delta V^* / RT$$

where ΔV^* is the change of volume per mole when the transition state is formed from the reactants. The same form of equation, but with k replaced by R (the rate of polymerization) can be used to calculate an 'over-all' activation volume from the initial gradients of curves of the type shown in Figure 3. The values obtained for the monomers of Table 1 (in $\text{cm}^3 \text{mol}^{-1}$) are: DEF, -14 ; EC, -47 ; styrene, -19 ; with an accuracy of about ± 1 .

In radical polymerizations ΔV^* is a composite quantity⁴ which, in the simplest kinetic scheme, is given by

$$\Delta V^* = \Delta V_p^* + \Delta V_d^* / 2 - \Delta V_t^* / 2$$

where the subscripts indicate chain propagation, initiator dissociation, and the mutual termination of pairs of chains. The activation volume for dissociation of AIBN is a relatively small term which is positive (as dissociation is a bond-stretching and -breaking process). It is likely to have practically the same value in both DEF and EC. ΔV_t^* is a larger term which also has positive values (since termination is diffusion-controlled and pressure-retarded). The value will depend on chain-structure but it is improbable that the variation would be sufficient to explain the difference between the reactions of DEF and EC. The dominant term is ΔV_p^* , the activation volume for the addition of a monomer unit to the growing chain. This is generally somewhat less (numerically) than ΔV , the volume change when a mole of monomer is completely polymerized. The dilatometric results of Bengough *et al.*⁵ correspond to $\Delta V = -26.8$ for DEF. The density of EC polymer produced in our experiments was found to be 1.200 g cm^{-3} (density gradient column) at 22°C, which corresponds to $\Delta V = -21.6$. The similarity of the two results makes it unlikely that the exceptional pressure-acceleration of the EC polymerization is due to an abnormal value of ΔV_p^* .

Effects of initiator concentration on rate

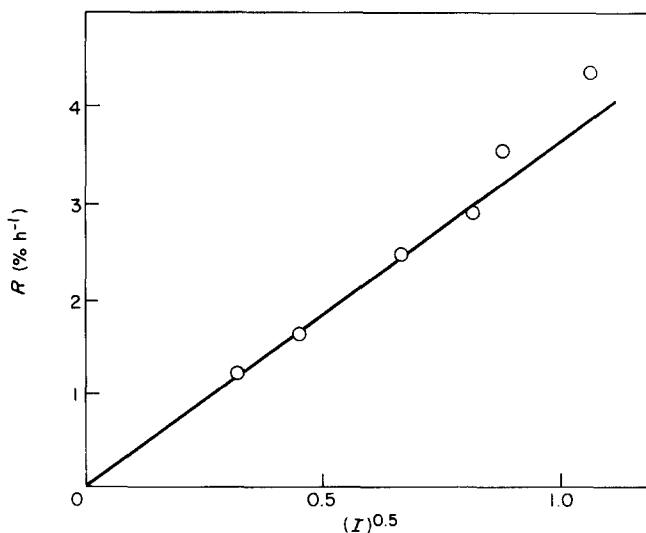
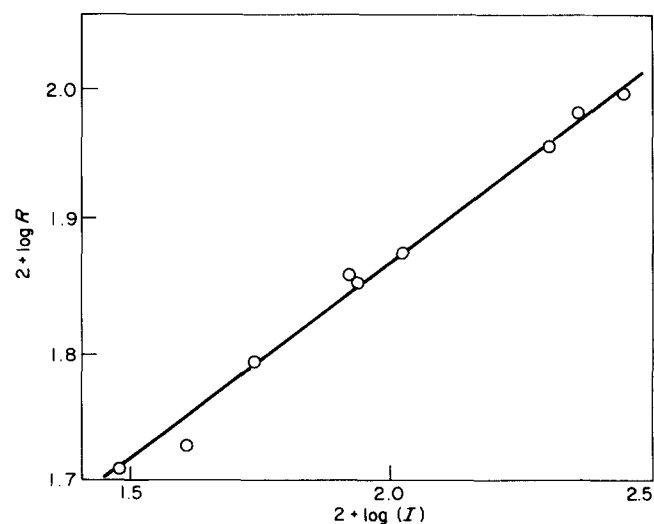
The rate of polymerization of DEF was measured for various concentrations of AIBN at 2750 bars and the results are shown in Figure 4. The plot is linear over most

of the range, and gives the normal value of 0.5 for the exponent of the initiator concentration in the rate equation. The divergence at rates above $3\% \text{ h}^{-1}$ is probably due to a small rise in temperature because of incomplete dissipation of the heat of reaction. In the reaction at 1 bar Walling and McElhill⁸ found the exponent to be 0.5, while Bengough *et al.*⁵ obtained 0.45.

The corresponding plot of results for EC at 2570 bars (AIBN concentrations of 0.297 to 2.84 mol%) is a curve, and a log/log plot (Figure 5) gives an exponent of 0.3. Bamford *et al.*¹¹ have shown that this type of deviation from normal kinetic behaviour occurs when a proportion of the growing chains is terminated by reaction with primary radicals from the initiator. It is not obvious that this could account for the exceptional pressure-acceleration of EC polymerization since a termination reaction which involves a small radical is likely to be less retarded at high pressure than termination between two large radicals.

Polymerization in the 'super-pressed' liquid

Five EC polymerizations were carried out very close to the freezing pressure (2950 bars, reaction time 7 h). Two


Figure 4 Effect of concentration of initiator (AIBN) on the rate of polymerization of diethyl fumarate at 2750 bars at 60°C

Figure 5 Logarithmic plot of rate of polymerization (wt% per hour) of *trans*-ethyl cinnamate vs. initiator concentration (mol% AIBN) at 2570 bars at 60°C

of the runs gave a rate of $1.12\% \text{ h}^{-1}$ which lies on the rate curve extrapolated from lower pressures. The other three gave much lower yields and it is estimated that freezing occurred after about one hour. At 3080 bars (8 h) three runs appeared normal, but in two others freezing apparently occurred after 0.5 to 0.75 h. At 3590 bars freezing appeared to take place after 0.5 h in one run, and 3 h in another. Earlier work^{2,3} on EC was carried out in the region in which the liquid phase is stable (*Figure 1*).

In previous work³ on DEF nearly complete polymerization was obtained at 10 000 bars, at 57°C, and at 5000 bars, at 60°C, which are both in the region in which the solid is thermodynamically stable. However, in two runs carried out at 9500 bars, at 60°C, we obtained yields of only 3.8 and 4.8% (less than the yield obtained at 1 bar in the same time).

The capricious behaviour of many organic liquids in respect of the liquid-to-solid phase transition at high pressures is well-known. Super-preserved liquid (or glassy) states may sometimes persist for very long periods.

CONCLUSIONS

The low rate of polymerization of EC at ordinary pressure, compared with that of DEF, is believed to be mainly due to the greater steric 'crowding' in the vicinity of the double bond, which is caused by the phenyl group.

The broad resemblance between the pressure-acceleration of DEF polymerization and that of a number of vinyl and vinylidene monomers indicates that there is a similar acceleration of chain propagation and retardation of the termination reaction in this case. A satisfactory explanation of the exceptionally large pressure-acceleration of the EC polymerization remains to be found, and a further study of this reaction is in progress.

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