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### The Site of Initiation in Vinyl Chloride Polymerization

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## The Site of Initiation in Vinyl Chloride Polymerization

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### ABSTRACT

Doubly labeled (3H and 14C) benzoyl peroxide has been used to study the relative incorporation of phenyl and benzoyloxy initiating radicals in PVC polymerized in bulk and over a range of monomer concentrations in dichloroethane solutions. From the results it is concluded that (a) transfer occurs between phenyl radicals and the solvent, (b) that vinyl chloride is a relatively unreactive monomer, and (c) that the main site of initiation in the earlier stages of the bulk polymerization is the continuous monomer phase. Explanations are suggested for the very high ratio of benzoyloxy to phenyl incorporation in polymers formed by polymerization of monomer dissolved in preformed PVC films and for the decreased benzoyloxy to phenyl ratio obtained with increasing initiator concentration.

### INTRODUCTION

It is well established that the apparent autocatalytic rate increase that occurs in the heterogeneous bulk polymerization of acrylonitrile is due to the ever-increasing concentration of "occluded" polymer radicals that is produced by the great hindrance to termination in the precipitated polymer phase.

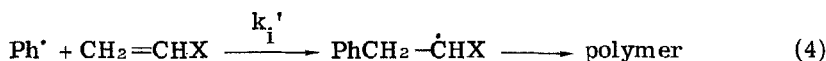
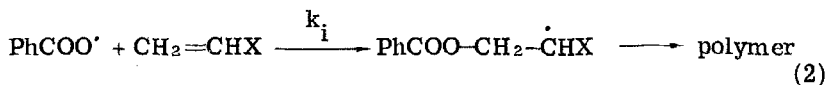
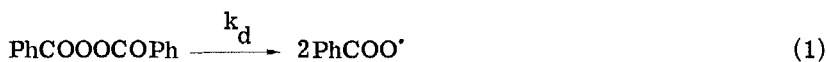
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Due to the relatively large concentration of monomer in the precipitated polymer phase in vinyl chloride polymerization, occluded radicals do not occur. Nevertheless, the high viscosity of this phase gives a lower termination rate constant and hence a greater polymerization velocity than would be the case in the bulk monomer phase. The generally accepted explanation for the increase of polymerization rate found for vinyl chloride is that as more polymer is formed, the volume of the polymer rich phase increases and so more of the monomer is found in this region of rapid polymerization and less in the continuous monomer phase. Various mechanisms which show variations in detail have been proposed, and there appears to be some uncertainty about the degree of migration of growing radicals from one phase to another and about the location of the initial formation of the growing radicals. For instance, the initial radicals could be formed entirely in the continuous monomer phase, resulting in growing polymer radicals which then migrate to the polymer rich phase, or extensive initiation of polymerization might occur in the polymer-rich phase itself [1-3].

In previous experiments in this laboratory, samples of the suspended polymer phase had been removed from heterogeneous vinyl chloride polymerizations in which initiation was due to carbon-14 labeled benzoyl peroxide. Radioassay had shown the polymer phase to be highly radioactive, and it was concluded that a large proportion of unreacted initiator had been abstracted into the polymer-rich phase. This would appear, then, to support the idea that in this system at least initiation in the polymer-rich phase must be important and from the extent of the benzoyl peroxide abstraction it was thought that in the later stages of the polymerization most of the initiation would be occurring in the polymer-rich phase.

In order further to investigate the site of initiation, it was decided to make use of the competition between the reaction of benzoyloxy radicals with monomer and the decomposition of benzoyloxy radicals to phenyl radicals that has been well investigated in other systems by Bevington and his collaborators [4]. The reactions involved in the initiation of polymerization by benzoyl peroxide are



From this scheme and assuming a stationary state for the concentration of phenyl radicals, it follows that the ratio,  $p$ , of benzoyloxy groups to phenyl and benzoyloxy groups in the polymer must be given by

$$1/p = 1 + (k_e/k_i)(1/[CH_2=CHX]) \quad (5)$$

Values of  $p$  can be obtained if polymerization experiments are carried out with carbon-14 labeled initiator in which for one set of experiments the carbon-14 label is in the benzene ring and for another set of experiments the carbon-14 label is on the carbonyl group. It is relatively simple to calculate  $p$  from the activities of the two lots of polymers produced. If  $p$  values are obtained over a range of monomer concentrations, it should be possible to obtain the ratio  $(k_e/k_i)$  and then, for a polymerization carried out in a system of unknown monomer concentration, this unknown concentration should be obtainable from the  $p$  value. A variation on this experiment is to use double-labeled benzoyl peroxide in which the phenyl group is labeled with tritium and the carbonyl group is labeled with carbon-14. Using this technique it was hoped that from the  $p$  values found in the heterogeneous bulk polymerization, the monomer concentration at the site of initiation would be obtained and hence, some conclusion about the site of initiation could be reached.

## EXPERIMENTAL

Doubly labeled benzoyl peroxide was made from a mixture of benzoic acid labeled with tritium in the ring and benzoic acid labeled with carbon-14 in the carboxyl group. The acid was converted to the acid chloride which was then reacted with sodium peroxide to give the crude product. This was purified by solution in acetone and precipitated with methanol. (We are indebted to Dr W. Brendlein, Darmstadt, for preparing this initiator.)

1,2-Dichloroethane from BDH Ltd. was dried over calcium chloride and distilled. The middle fraction boiling at 83 to 84°C was used as a solvent for the polymerizations. Vinyl chloride, kindly given to us by BP Chemicals Ltd., was dried by passing the vapor over magnesium perchlorate. It was outgassed and distilled on the vacuum line; the middle fraction (one-third) was further outgassed and used for the polymerizations.

### Solution Polymerizations

These were carried out in ~15 cm<sup>3</sup> dilatometers. Initiator was introduced in acetone solution which was distilled off. The calculated

volume of dichloroethane was added and outgassed by freezing, pumping, and thawing cycles. Vinyl chloride was condensed into the solvent from a 5-L gas storage bulb using a calibrated manometer to obtain the correct amount. The dilatometer was then sealed off. The masses of all the constituents were checked by weighing at each stage. The polymerization was effected in a 60°C thermostat, the course of the reaction was followed with a cathetometer, and after 10% conversion the reaction was quenched in liquid nitrogen and the polymer precipitated into a large excess of methanol.

### Heterogeneous Polymerizations

These were carried out in ampules containing no solvent to about 10% conversion. After quenching in liquid nitrogen, the excess monomer was allowed to escape, the polymer was dissolved in deperoxidized tetrahydrofuran and precipitated into methanol.

### Polymerization in PVC Films

Some study was made of initiator incorporation in polymers formed by polymerization of vinyl chloride monomer dissolved in PVC films. PVC films containing from 4 to 10% labeled initiator were cast on glass plates from solutions in deperoxidized tetrahydrofuran. After prolonged drying in vacuum, strips of film ( $\sim 25 \times 30$  mm) were weighed and introduced into ampules. Sealing off constrictions, A, were then made above the samples as shown in Fig. 1, and after outgassing on the vacuum line, about 2 g of pure vinyl chloride was introduced into the lower section cooled in liquid nitrogen as shown in the figure. After sealing off at A, the ampules were placed in a thermostat at 60°C for 40-90 min.

After quenching in liquid nitrogen, the unreacted monomer was allowed to escape, the film was evacuated for an hour, and a rough measure of the extent of polymerization was obtained by weighing. The film was dissolved in pure tetrahydrofuran and precipitated into methanol.

### Radioactive Assay

The tritium and carbon-14 activities of the initial benzoic acids, initiator, and isolated polymer were determined by liquid scintillation counting with a Nuclear Enterprises Ltd. 6500 double channel twin tube liquid scintillation counter. Scintillation solutions consisted of 10 cm<sup>3</sup> of Nuclear Enterprises Ltd. NE 220 scintillator, 1 cm<sup>3</sup> of pure cyclohexanone, and 1 cm<sup>3</sup> of the unknown in cyclohexanone solution. In order to eliminate the effects of quenching, the count rates

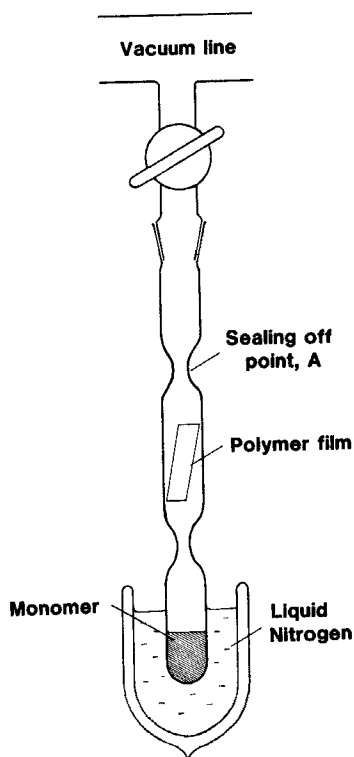


FIGURE 1.

for this solution were compared with one in which the pure cyclohexanone was replaced with a "standard" tritium solution of tritium-labeled toluene in cyclohexanone and one in which the replacement was with "standard" carbon-14 labeled hexadecane in cyclohexane. By using a low energy counting channel which responded mainly to the tritium and a high energy one for carbon-14, it was possible to obtain relative figures for the tritium and carbon-14 activities of the initiator, the initiator precursors (labeled benzoic acid), and the polymers. These enabled the benzoyloxy and phenyl contents of the polymers to be calculated.

A possible source of error arises in the work from the inclusion of uncombined initiator in the polymer. The polymer was purified by solution in deperoxidized tetrahydrofuran, precipitation into methanol, and drying. It was found that constant activity was obtained after five precipitations, and so subsequently this was used as a standard purification before activity determination.

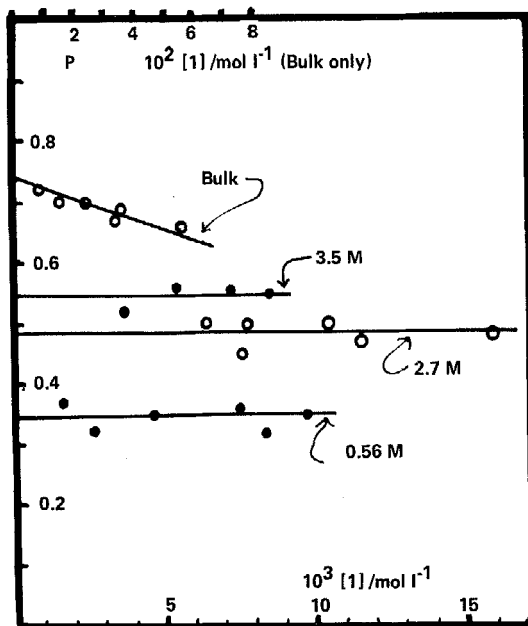


FIG. 2. Dependence of  $p$  (benzoyloxy to benzoyloxy + phenyl ratio) on initiator concentration  $[I]$ . Monomer concentrations are indicated on each plot.

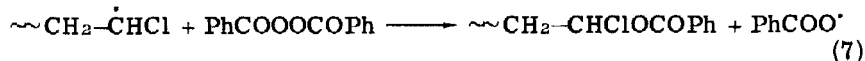
## RESULTS AND DISCUSSION

### Solution Polymerization

It is well known from the increased rate of benzoyl peroxide decomposition that occurs in the absence of radical traps that induced decomposition of benzoyl peroxide occurs readily. At high initiator concentration this could lead to competition between initiator and monomer molecules for the phenyl radicals to give higher  $p$  values.



Alternatively, transfer to initiator



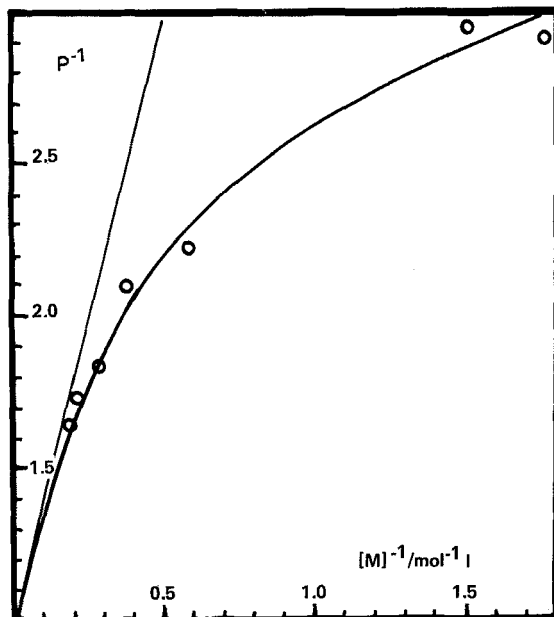


FIG. 3. Dependence of  $p$  (benzoyloxy to benzoyloxy + phenyl ratio) on monomer concentration  $[M]$ .

could lead to higher  $p$  values. These reactions would lead to  $p$  values that increase with increasing initiator concentrations particularly at low monomer concentrations. Figure 2 shows that at both low (0.56 mol/L) and higher monomer concentrations,  $[M]$ , the value of  $p$  is independent of the initiator concentration in the solution polymerizations.

Figure 3 shows a plot of  $1/p$  against  $1/[M]$ . The linear relationship expected from Eq. (5) only appears to hold at high monomer concentrations. The leveling out of the plot at high values of  $1/[M]$  has been observed in styrene polymerization by Bevington and Ito [5], who attributed the effect to a conversion of phenyl radicals to benzene by transfer to the solvent as shown in



Bevington and Ito's analysis leads to the relationship

$$\frac{p}{[M](1-p)} = \frac{k_i}{k_e} + \frac{k_i k_f' [\text{SH}]}{k_e k_i' [M]} \quad (9)$$



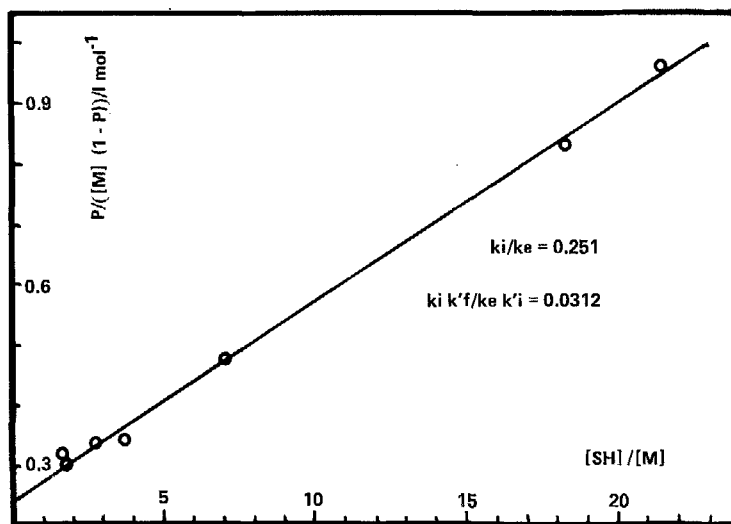


FIGURE 4.

and so the plot in Fig. 4 enables values of 3.98 mol/L to be obtained for  $k_e/k_i$  and 0.124 for  $k'_f/k'_i$ . This last figure is quite an appreciable transfer constant and reflects the low reactivity of vinyl chloride monomer. At low solvent concentrations  $[SH]$  and high monomer concentrations, transfer to solvent must become unimportant and, in fact, for  $[SH]/[M] = 0$ , Eq. (9) reduces to Eq. (5). In agreement with this, it is interesting to see that the slope at the origin in Fig. 3 is in fact  $\sim 4$  mol/L in agreement with the  $K_e/K_i$  value for Fig. 4.

The  $k_e/k_i$  value for vinyl chloride is fairly large, and Table 1 compares this with the figures obtained by Bevington [4] for other monomers. The ratios in the last column give the relative reactivities of the different monomers to the benzoyloxy radical and thus again confirm the low reactivity of vinyl chloride monomer which is only one-tenth as reactive as styrene.

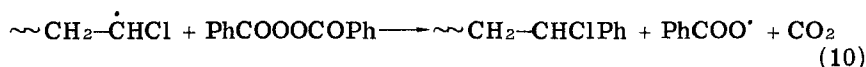
### Bulk Polymerization

The top curve in Fig. 2 shows that, unlike the solution polymerization, there is a steady variation in the benzoyloxy to phenyl + benzoyloxy ratio,  $p$ , with initiator concentration. The initiator concentrations are, however, 3 to 6 times as great as for the solution polymerization, and this could account for the difference. The decrease in  $p$  with

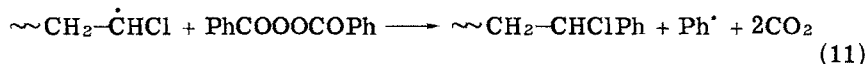
TABLE 1. Relative Reactivities of Various Monomers toward Benzoyloxy Radicals

Monomer	$k_e/k_i$	$k_i/k_i$ (VCM)
Styrene	0.4	10.0
Vinyl acetate	1.1	3.6
Methyl methacrylate	3.4	1.2
Vinyl chloride	4.0	1.0

increasing initiator concentration is surprising. Reactions (6) and (7) would both lead to an increase. The observed variation in  $p$  suggests that reactions such as



or



could occur! The fall in  $p$  is not very large and extrapolation to zero initiator concentration gives a  $p$  value of 0.73 which, when combined with the value of 3.98 for  $k_3/k_i$ , leads by substitution in Eq. (5) to an  $[M]$  value of 10.8 mol/L. This is much larger than the monomer concentration in the swollen polymer (6 mol/L). It almost approaches the value for the pure monomer (13 mol/L), suggesting that at this low conversion (10%), initiation is mainly in the continuous monomer phase.

#### Polymerization of Monomer Dissolved in Polymer Film

The use of Eq. (5) to obtain the monomer concentration at the site of initiation assumes that in the monomer "diluted" with polymer, negligible transfer occurs from phenyl to polymer.  $k_f'$  for the polymer is likely to be less than for dichloroethane. Also, since the monomer concentration comes out at about 11 mol/L, any error involved in using Eq. (5) instead of Eq. (9) is likely to be small. Nevertheless, it was decided to measure  $p$  for the polymerization of monomer dissolved in the polymer when the initiation was also confined to the polymer phase.

TABLE 2. Values of P (ratio of benzoyloxy to phenyl + benzoyloxy groups) in PVC Formed by Polymerization of Monomer Dissolved in PVC Film

Initiator concentration [ I ]		
% in film	~ mol/L	p
4.20	0.14	0.96
4.80	0.16	0.96
4.90	0.16	0.96
7.50	0.25	0.91
8.50	0.28	0.81
10.04	0.33	0.85

Due to the small proportion of new polymer formed in the PVC sheet, determination of absolute values for the incorporation of phenyl and of benzoyloxy radicals was not possible but there was no difficulty in obtaining values for  $p$ . The figures obtained are shown in Table 2. As in the case of the bulk polymerization,  $p$  decreases with increasing initiator concentration, but instead of the expected value for 6 molar monomer of about 0.6, the values larger than those expected for the 13 mol/L concentration of pure monomer were obtained. The  $p$  value of 0.73 for the bulk polymerization is quite different from the high value obtained in these experiments, and so the conclusion that initiation in our bulk polymerization occurs mainly in the continuous monomer phase is still valid. Nevertheless, it is necessary to suggest causes for the high  $p$  values in Table 2.

One possibility is that the polymer matrix surrounding the benzoyloxy radicals increases the activation energy needed for Reaction (3) and so decreases the probabilities of formation of phenyl radicals. A similar matrix effect has been postulated by Hass [6] to account for the decreased rate of decomposition of benzoyl peroxide in PVC film compared with benzene solution. Another possibility is that contrary to expectation, practically all the phenyl radicals that are formed undergo transfer, extracting hydrogen from the polymer to form benzene so that the only radicals incorporated are benzoyloxy ones. At high initiator concentration, phenyl radicals from Reactions (10) and (11) or from primary radical transfer would be incorporated and lead to a fall in  $p$ .

#### ACKNOWLEDGMENTS

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