Photoinitiated polymerization of *N*-vinylcarbazole in the presence of azobisisobutyronitrile

Richard G. Jones and Reza Karimian
University Chemical Laboratory, University of Kent at Canterbury,
Canterbury CT2 7NH, UK
(Received 11 September 1979)

Azobisisobutyronitrile is a photosensitizer of the polymerization of *N*-vinylcarbazole in benzene solution at $\lambda = 365$ nm. At low concentrations of initiator, a low molecular weight polymer is the dominant product, but, as the initiator concentration is raised, this is replaced progressively by a high molecular weight fraction. Kinetic mechanisms compatible with the experimental observations are proposed and indicate that the high and low molecular weight fractions are formed distinctively through the intermediacy of radical and cationic species, respectively arising from the quenching by the initiator of the first excited singlet and triplet states of the monomer.

INTRODUCTION

Recent interest in the polymerization of *N*-vinylcarbazole (VCZ) following electron transfer from the monomer to well-characterized electron acceptors[1,2] has overshadowed studies of its polymerization in the presence of common free radical initiators. Both the thermal[3,4,5] and photoinitiated[6] polymerizations of VCZ in the presence of benzoyl peroxide, however, are now recognized to propagate through two non-interactive mechanisms, one of which is radical, and the other almost certainly cationic. On the other hand, polymerizations initiated by azobisisobutyronitrile (AZBN) are considered to propagate through a radical mechanism[1,3] only, although if carried out in the presence of an additive which is amenable to accepting an electron, cationic propagation has been observed[7]. In this paper we report evidence

(i) of propagation by a non-radical mechanism for the photosensitized polymerization of VCZ in the presence of AZBN in benzene solution;

(ii) suggesting that this arises from the quenching of triplet state VCZ by AZBN.

EXPERIMENTAL

Materials

Zone-refined VCZ monomer was supplied by Fluka AG of Switzerland. Solvents were purified by standard procedures and AZBN was purified by successive recrystallization from anhydrous methanol.

Apparatus and procedures

Rates of polymerization were obtained dilatometrically and average molecular weights and distributions were obtained using gel permeation chromatography. The apparatus, procedures and essential experimental considerations have been described previously[6].

Nitrogen evolution was followed using a 1mm diameter gas burette attached to a 50 ml round-bottomed flask containing 30 ml aliquots of the solution being irradiated. Prior to irradiation, the solution and apparatus were de-aereated by flushing with dry nitrogen.

RESULTS

Absorption and fluorescence studies

As reported previously[6], at wavelengths >300 nm, VCZ has two absorption maxima (323 and 338 nm) with extinction coefficients of 4350 and 6600 $dm^3\ mol^{-1}\ cm^{-1}$. At the chosen wavelength of irradiation for the present study, 366 nm, which is on the outer edge of the first band, the extinction coefficient in benzene solution is 3.6 $dm^3\ mol^{-1}\ cm^{-1}$. In this region of the spectrum, AZBN displays a weak absorption band with an extinction coefficient of 11.6 $dm^3\ mol^{-1}\ cm^{-1}$ at 366 nm. No association between VCZ and AZBN in the ground state was evident from absorption studies on benzene solutions at concentrations up to those used in the subsequent polymerization studies.

AZBN quenches the fluorescence of VCZ efficiently. Figure 1 is a Stern–Volmer representation of a typical set of data after correction for absorption by AZBN at both the excitation and emission wavelengths. The quenching constant obtained from the slope of this plot is 52 $dm^3\ mol^{-1}$. Spectrofluorometric studies on benzene solutions at concentrations up to those used in the subsequent polymerization studies revealed no new emission bands that might be attributed to the formation of an exciplex of VCZ and AZBN.

Plots of the reciprocal of the VCZ fluorescence lifetime against AZBN concentration were linear and gave a bimolecular quenching rate constant of $8.81 \times 10^9\ dm^3\ mol^{-1}\ s^{-1}$ and a singlet state lifetime of 5.99 ns in aereated benzene solution. The product of these constants is 53 $dm^3\ mol^{-1}$ in excellent agreement with the value obtained from the slope of *Figure 1*.

0032–3861/80/070832–05$02.00

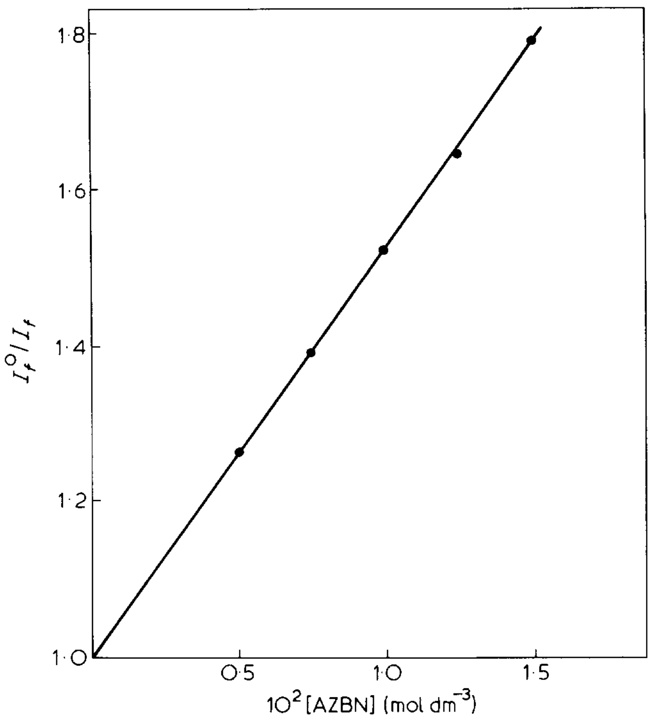

Figure 1 Stern–Volmer plot of the quenching of the fluorescence of VCZ (2 X 10^{-4} mol dm^{-3}) by AZBN in benzene solution at 303 K. λ_{excit} = 337 nm, λ_{emiss} = 370 nm

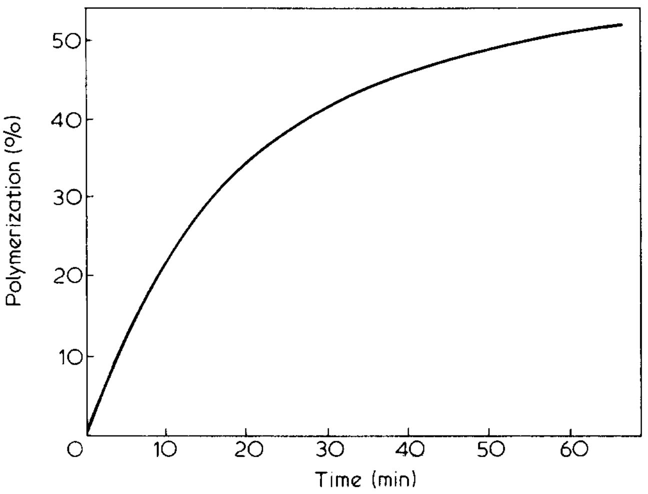

Figure 2 Typical contraction *versus* time curve for the photosensitized polymerization of VCZ (1 mol dm^{-3}) in the presence of AZBN (8 X 10^{-3} mol dm^{-3}) in benzene solution at 303K

Polymerization Studies

No polymerization was observed in benzene solution at 303K unless the solution was both illuminated and contained AZBN. A typical conversion *versus* time curve for the polymerization is shown in *Figure 2*. It is readily seen that the polymerization is rapid, and the yield high. No photochemical 'after-effect' was observed.

The dependence of the initial rate of polymerization on the AZBN concentration, the monomer concentration and the incident light intensity was determined by plotting $\log_{10} R_p$ against $\log_{10}$ (*concentration*) or $\log_{10}$ (*intensity*). For a ten-fold range of monomer concentrations up to 1 mol dm^{-3} and an eight-fold initiator concentration range up to 8 x 10^{-2} mol dm^{-3}, the rate expression (1) was obtained†:

$$R_p = KI_0^{0.55}\,[\mathrm{AZBN}]^{0.25}\,[\mathrm{VCZ}]^{2.0} \qquad (1)$$

where K = 0.082 for the concentrations expressed in mol dm^{-3} and I_0 is in einstein dm^{-3} s^{-1}.

Figure 3 shows the gel permeation chromatograms of polymers prepared at an initial monomer concentration of 1 mol dm^{-3} but over a range of AZBN concentrations. The corresponding molecular weight data are listed in *Table 1*.

The breadth of the distributions, together with the observation that polymers prepared at initial AZBN concentrations in the vicinity of 10^{-3} mol dm^{-3} are clearly bimodal, suggest that polymerization propagates through two non-interacting mechanisms. That leading to the low molecular weight fraction dominates at low AZBN concentrations, whilst that which leads to the high molecular weight fraction dominates at high initial AZBN concentrations.

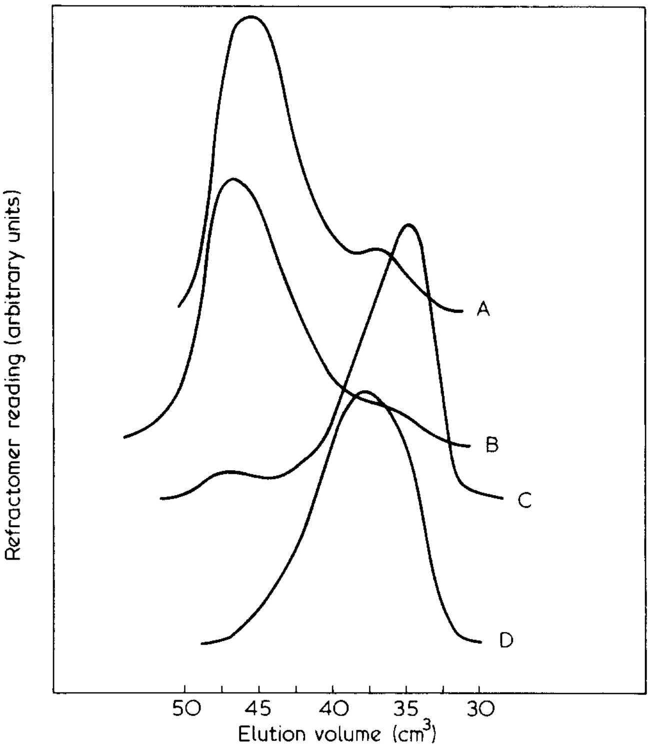

Figure 3 Gel permeation chromatograms of samples of poly (VCZ) prepared in benzene solution at 303K at respresentative AZBN concentrations (in mol dm^{-3}). A, 10^{-4} ; B, 7 X 10^{-4}; C, 10^{-3}; D, 6 X 10^{-3} [VCZ] = 1 mol dm^{-3}

Table 1 Molecular weights of poly(VCZ) from chromatograms of *Figure 3*

[AZBN] mol dm^{-3}	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
10^{-4}	5670	36 850	6.5
7 X 10^{-4}	3620	22 600	6.3
10^{-3}	28 900	323 000	11.2
6 X 10^{-3}	38 500	174 000	4.5

---

† Polymerizations at low AZBN concentration and less than maximum illumination had such low initial rates that they were difficult to estimate, hence the incident light intensity exponent was obtained only at a constant AZBN concentration of 7 X 10^{-3} mol dm^{-3} and is not asserted to hold the same value at other concentrations

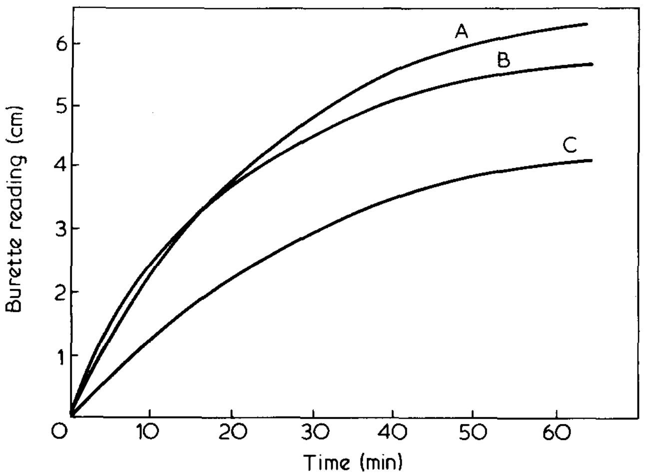

Figure 4 Nitrogen evolution from the photolysis of solutions of AZBN (10^{-2} mol dm^{-3}) in the presence of VCZ in benzene solution at 303K VCZ concentrations in mol dm^{-3}: A, 0; B, 10^{-2}; C, 0.3

Nitrogen evolution studies

Because of the optical irregularity of the vessel used for nitrogen evolution studies, no significance should be attached to any feature of these results other than the relative yields and the time required to attain them. These experiments were of a preliminary nature, and such a vessel was chosen simply to facilitate irradiation of a sufficiently large volume of solution as would lead to volume changes of a magnitude that could be estimated using a simple gas burette.

The results are plotted in *Figure 4*, from which it can be seen that the time over which nitrogen is evolved is comparable with the period over which polymerization occurs (see *Figure 2*), and that the presence of VCZ suppresses the yield in comparison with that obtained from irradiation of a solution that contains only AZBN.

DISCUSSION

Over the range of concentrations used in the polymerization studies, the fraction of the light that was absorbed by VCZ rather than AZBN was never less than 0.93. The spectrophotometric studies revealed no complex formation between VCZ and AZBN either in the ground state or the excited state; thus, it is concluded that the dominant primary photochemical process is the excitation of VCZ, and that any chemical change arises from the subsequent reaction of AZBN with either the first excited singlet (S_1) or triplet (T_1) states of the monomer.

From the fluorescence studies, it is clear that S_1 reacts with AZBN. Since the concentration of the latter increases as the relative amount of the *high* molecular weight polymeric product becomes larger, it is reasonable to infer that in benzene solution this reaction (i.e. the quenching of S_1 by AZBN) leads to *radical* intermediates capable of initiating the polymerization of the VCZ in the following radical scheme; where, VCZ is represented by M, the cyanoisopropyl group by R and excited states are distinguished by asterisks.

Radical scheme

(i) excitation:

$$\mathrm{M} + h\nu \longrightarrow {}^1\mathrm{M}^*$$

(ii) excited state decay (both radiative, non-radiative and including that through intersystem crossing to T_1):

$${}^1\mathrm{M}^* \xrightarrow{k_1} \mathrm{M}$$

(iii) energy transfer (quenching of S_1 by AZBN):

$${}^1\mathrm{M}^* + \mathrm{AZBN} \xrightarrow{k_2} \mathrm{M} + {}^1\mathrm{AZBN}^*$$

(iv) de-activation of ^{1}AZBN*:

$${}^1\mathrm{AZBN}^* \xrightarrow{k_3} \mathrm{AZBN}$$

(v) initiation:

$${}^1\mathrm{AZBN}^* + \mathrm{M} \xrightarrow{k_4} \mathrm{RM}\cdot + \mathrm{R}\cdot + \mathrm{N}_2$$

$$\mathrm{R}\cdot + \mathrm{M} \longrightarrow \mathrm{RM}\cdot$$

(vi) propagation:

$$\mathrm{RM}_i\cdot + \mathrm{M} \xrightarrow{k_p} \mathrm{RM}_{i+1}$$

(vii) termination:

$$\mathrm{RM}_i\cdot + \mathrm{RM}_j\cdot \xrightarrow{k_t} \text{polymer}$$

Assuming instantaneous stationary state conditions for all radicals and excited states and that $k_3 \gg k_4$ [M], the rate of radical polymerization (R_{pr}) can be represented by equation (2):

$$R_{pr} = \frac{k_p}{k_t^{1/2}} \left(\frac{2I_a k_2 k_4\,[\mathrm{AZBN}]}{k_3(k_1 + k_2[\mathrm{AZBN}])} \right)^{1/2} [\mathrm{M}]^{3/2} \qquad (2)$$

where I_a is the intensity of light absorbed by VCZ.

For low optical extinctions (the design of the dilatometer bulb[6] was such that the absorbance was never greater than 0.36), I_a is proportional to the incident light intensity, I_0, and to [M]. Therefore, it follows that:

$$R_{pr} = K_r I_0^{1/2} \left(\frac{[\mathrm{AZBN}]}{k_1 + k_2[\mathrm{AZBN}]} \right)^{1/2} [\mathrm{M}]^2 \qquad (3)$$

From the known values of k_1 and k_2 (the reciprocal of the singlet state lifetime and the bimolecular quenching rate constant respectively), it can be shown through a plot of $\log_{10} R_{pr}$ *versus* $\log_{10}$ [AZBN] that this rate expression would give rise to an apparent initiator concentration exponent of 0.41 over the range of AZBN concentrations employed. Although the monomer concentration exponent and the incident light intensity exponent of equation (3) are in sensible agreement with the experimental values, it *is* clear that the observed initiator concentration exponent is too small to explain the polymerization solely in terms of radical initiation through the quenching of S_1. Furthermore, even if account is taken of the small amount of direct excitation of AZBN that must inevitably occur, this would have the effect of increasing rather than decreasing the apparent initiator concentration exponent.

However, it is clear from the gel permeation chromato-

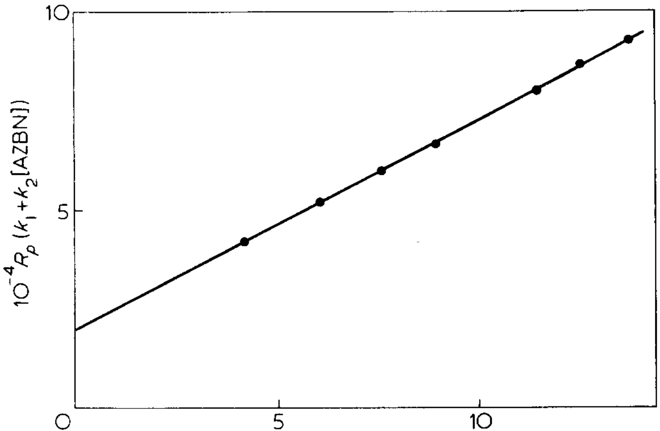

Figure 5 Linear plot of the variation of the rate of polymerization with AZBN concentration, according to the form of equation (7)

grams that another mechanism of polymerization occurs and is dominant at low AZBN concentrations. Since, as the concentration of AZBN is lowered, the steady state concentration of T_1 will increase (T_1 being formed by intersystem crossing from S_1, a reaction which competes with the quenching of S_1 by AZBN), it is reasonable to postulate that this second, non-interacting, mechanism is initiated through the intermediacy of T_1. It is further proposed that this polymerization propagates through the cationic centre of a close ion-pair, which in benzene solution would be expected to be unstable and thus only give rise to polymer of low molecular weight. Taking account of the depleted yields of nitrogen from AZBN when it is photolysed in the presence of VCZ, we therefore represent the complete polymerization by reactions (i) to (vii) together with the following:

Cationic scheme

(viii) intersystem crossing:

$$^1\mathrm{M}^* \xrightarrow{k_5} {}^3\mathrm{M}^*$$

(ix) triplet state deactivation:

$$^3\mathrm{M}^* \xrightarrow{k_6} \mathrm{M}$$

(x) charge transfer (quenching of T_1 by AZBN):

$$^3\mathrm{M}^* + \mathrm{AZBN} \xrightarrow{k_7} \mathrm{M}^{+\cdot}, \mathrm{AZBN}^{-\cdot}$$

(xi) donor–acceptor complex deactivation:

$$\mathrm{M}^{+\cdot}, \mathrm{AZBN}^{-\cdot} \xrightarrow{k_8} \mathrm{M} + \mathrm{AZBN}$$

(xii) initiation:

$$\mathrm{M}^{+\cdot}, \mathrm{AZBN}^{-\cdot} \xrightarrow{k_9} \mathrm{RM}^{+} \cdot\cdot\, \mathrm{RN}_2^{-}$$

(xiii) propagation:

$$\mathrm{RM}_i^{+} \cdot\cdot\, \mathrm{RN}_2^{-} + \mathrm{M} \xrightarrow{k'_p} \mathrm{RM}_{i+1}^{+} \cdot\cdot\, \mathrm{RN}_2^{-}$$

(xiv) termination:

$$\mathrm{RM}_i^{+} \cdot\cdot\, \mathrm{RN}_2^{-} \xrightarrow{k'_t} \mathrm{RM}_i\mathrm{N}_2\mathrm{R}$$

If instantaneous stationary state conditions of all transient species are assumed again, then the rate of cationic polymerization (R_{pc}) is given by equation (4):

$$R_{pc} = \frac{k'_p}{k'_t}\left(\frac{I_a k_5 k_7 k_9 [\mathrm{AZBN}]}{(k_8 + k_9)(k_1 + k_2[\mathrm{AZBN}])(k_6 + k_7[\mathrm{AZBN}])}\right)[\mathrm{M}] \tag{4}$$

Since k_7 is likely to be of the same order as k_2, and $k_6 \gg k_1$ (T_1 being longer-lived than S_1) it follows than k_7 [AZBN] $\gg k_6$ over the range of concentrations employed. Substituting for I_a as previously, equation (4) reduces to:

$$R_{pc} = K_c I_0 (k_1 + k_2\,[\mathrm{AZBN}])^{-1}\,[\mathrm{M}]^2 \tag{5}$$

The overall rate of polymerization is then given by equation (6):

$$\begin{aligned} R_p &= R_{pr} + R_{pc} \\ &= K_r I_0^{1/2}\left(\frac{[\mathrm{AZBN}]}{k_1 + k_2\,[\mathrm{AZBN}]}\right)^{1/2}[\mathrm{M}]^2 \\ &\quad + \frac{K_c I_0\,[\mathrm{M}]^2}{k_1 + k_2\,[\mathrm{AZBN}]} \end{aligned} \tag{6}$$

Consistent with the chromatographic evidence, at low concentrations of AZBN the ionic mechanism is dominant; but, as the concentration is increased, the denominator of the second term of equation (6) ensures that R_{pc} tends to zero whilst R_{pr} increases.

The observed monomer concentration and incident light intensity exponents are understood by inspection of equation (6), and the initiator concentration exponent will be lower than the value of 0.41 so far calculated, by virtue of the contribution to its value from the apparent negative exponent that would arise from the R_{pc} term. The observed dependence is better recognized to correlate with equation (6), however, by rearranging it to the form of equation (7):

$$\begin{aligned} R_p(k_1 + k_2[\mathrm{AZBN}]) &= K_c I_0[\mathrm{M}]^2 \\ &\quad + K_r I_0^{1/2}[\mathrm{AZBN}]^{1/2}(k_1 + k_2[\mathrm{AZBN}])^{1/2}[\mathrm{M}]^2 \end{aligned} \tag{7}$$

Figure 5 is a plot of the experimental data in the linear form thus indicated. From the slope and intercept of *Figure 5*, the values $K_r = 2.43 \times 10^3$ mol^{-1} einstein$^{-1/2}$ dm$^{9/2}$ s$^{-1/2}$, and $K_c = 4.07 \times 10^7$ mol^{-1} einstein^{-1} dm^6 s^{-1} are obtained. Substitution back into equation (6) of the appropriate AZBN and monomer concentrations, and values of I_0 over the range that was used to evaluate the intensity exponent enables the calculation of values of R_p which are plotted as $\log_{10}R_p$ *versus* $\log_{10}I_o$ in *Figure 6*. The slope of this plot, 0.56, is in excellent agreement with the observed light intensity exponent. The experimental points are included for comparison.

In the course of the derivation of equation (6), it was assumed that $k_3 \gg k_4$ [M]. From K_r, the reported values of k_p and k_t for the radical polymerization of VCZ (2×10^3 and 5.1×10^8 dm^3 mol^{-1} s^{-1}, respectively,)[2] and the avail-

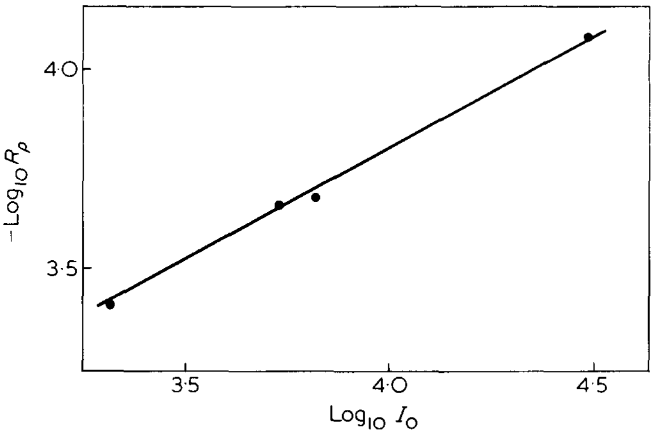

Figure 6 Variation of $\log_{10} R_p$ with $\log_{10} I_0$ calculated from data derived from *Figure 5*, for [VCZ] = 1 mol dm^{-3} and [AZBN] = 7 × 10^{-3} mol dm^{-3} with experimental points included for comparison

able data, it can be shown that $k_3 = 20\,k_4$ so that at a VCZ concentration of 1 mol dm^{-3} the assumption is clearly justified. By the nature of the species that have been postulated to be involved, the efficiency of initiation of the cationic fraction of the polymerization should be quite low, i.e. $k_8 > k_9$. If we assume:

(a) a 'most-probable' distribution for the low molecular weight fraction;

(b) an absence of chain transfer reactions during the formation of this fraction so that, according to the proposed mechanism, the degree of polymerization is given by $k'_p\,[\text{M}]\,/\,k'_t$;

(c) that the quantum yield for intersystem crossing for VCZ ($k_5 k_1^{-1}$) is similar to the value 0.36 quoted for carbazole[8];

then, from K_c and the available data it can be shown that $k_8 = 16\,k_9$.

CONCLUSION

The previously reported[6] polymerization of VCZ photosensitized by benzoyl peroxide which also exhibited characteristics of both radical and cationic polymerization was explained in terms of singlet state quenching (leading to radical polymerization) and excitation of a ground state complex of the monomer and benzoyl peroxide (leading to ionic polymerization). The present work does not invalidate the previously proposed mechanism, so far as it went. However, re-examination of the reported 'erratic' behaviour of the initiator concentration exponent at low concentrations of benzoyl peroxide, and of the chromatograms of polymers prepared at these concentrations, leads to the possible conclusion that the ionic polymerization in the other system is initiated in the same manner as reported here for the AZBN system, as well as through direct excitation of a charge transfer complex.

REFERENCES

1 Ellinger, J. P. *Adv. Macromol. Chem.* 1968, **1**, 169
2 Tazuke, S. *Pure Appl. Chem.* 1973, **34**, 329
3 Jones, R. G., Catterall, E., Bilson, R. T. and Booth, R. G. *J. Chem. Soc. Chem. Comm.* 1972, 22
4 Bevington, J. C. and Dyball, C. J. *J. Chem. Soc. Faraday I*, 1975, **71**, 2226
5 Bevington, J. C. and Dyball, C. J. *J. Polym. Sci., Polym. Chem. Edn.* 1976, **14**, 1819
6 Al-Abidin, K. M. Z. and Jones, R. G. *J. Chem. Soc. Faraday I*, 1979, **75**, 774
7 Olaj, O. F., Breitenbach, J. W. and Kauffmann, H. F. *Polym. Lett.* 1971, **9**, 877
8 Lamola, A. A. *Ph D Thesis*, California Institute of Technology, Pasadena, California, USA, 1965