Reactions of Dibenzoyldiazene. Part 1. Cycloaddition and the Inhibition and Retardation of Vinyl Addition Polymerizations

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The cycloaddition of dibenzoyldiazene to a selection of monomers with electron-rich vinyl groups has been shown to compete with its capability as an inhibitor of their polymerization by a free-radical mechanism. Cycloaddition to monomers with electron-deficient vinyl groups does not occur, and dibenzoyldiazene acts solely as a retarder of their polymerization. Kinetic mechanisms compatible with the experimental observations are proposed.

Although exhaustive studies of azo compounds as initiators of free radical polymerization have been carried out over the years, diacyldiazenes (RCON=NCOR) have received scant attention. Bevington and Stamper[1] studied the thermal polymerizations of methyl methacrylate initiated by dibenzoyldiazene† and recognized that degradative chain transfer to the initiator was pronounced, and the present authors in a preliminary communication[2] reported that in the presence of monomers with electron-rich vinyl groups, the same compound acted as an inhibitor of polymerization whilst also undergoing an inverse Diels–Alder cycloaddition to the monomer. The initiation of the polymerization of acrylonitrile by dibenzoyldiazene has been reported,[3] but there have been no other definitive studies of which the present authors are aware.

In this short series of papers we report (i) our earlier work in full, together with a new study of the retardation of the polymerization of methyl methacrylate, and (ii) studies that shed light on the complexity of the reactions of radicals with dibenzoyldiazene.

Experimental

Materials.—Dibenzoyldiazene (DBDZ) was prepared by the oxidation of dibenzoylhydrazine with lead tetra-acetate in acetonitrile solution. After reaction for 30 min, the solution was filtered and the product precipitated by addition to stirred distilled water. Three-fold recrystallization from carbon tetrachloride was carried out without allowing the temperature to rise above 313 K, thus avoiding thermal decomposition of the product. After drying *in vacuo*, the m.p. was 391—392 K (lit.,[4] 392—384 K) (Found: C, 70.5; H, 4.7; N, 11.4. Calc. for $C_{14}H_{10}N_2O_2$: C, 70.6; H, 4.2; N, 11.8%).

N-Vinylcarbazole monomer (Fluka AG) was used without further purification. Other monomers, the solvents, and azobisisobutyronitrile were purified by standard procedures.[5]

Apparatus and Procedures.—Rates of polymerization were obtained dilatometrically. The dilatometer consisted of a borosilicate glass bulb of 11 ml capacity attached to a 1 mm i.d. capillary. For the purpose of preparation, prior to filling the dilatometer with solution the open end of the capillary was connected *via* a side arm to a vessel which in turn could be attached to a vacuum line. Grease-free taps and connections were used throughout the vacuum system and solutions were outgassed to a static pressure of $< 10^{-4}$ Torr at liquid nitrogen temperature by repeated freeze–pump–thaw cycles. Preparative work was carried out in solutions that were deaereated by flushing with argon.

For high-performance liquid chromatography, Waters Associates (ALC/GPC 201) equipment was used. In gel permeation mode, μ-Styragel columns were used together with benzene as the mobile phase. Column calibration was carried out with narrow molecule weight distribution samples of polystyrene.

The equipment with which spectra were obtained was as follows: u.v.–visible, Pye Unicam SP 8000; i.r., Perkin-Elmer 237; n.m.r., JEOL PTF-100.

Results

The reactions of catalytic amounts (0.02 mol dm^{-3}) of dibenzoyldiazene (DBDZ) with a range of vinyl monomers [*N*-vinylcarbazole (NVC), styrene (STY), *p*-methoxystyrene (PMS), vinyl acetate (VA), and methyl methacrylate (MMA)] were investigated in a variety of solvents (benzene, diethyl ether, methylene dichloride, methanol, and acetonitrile).

Though a range of temperatures was employed from ambient up to those approaching the boiling points of the systems, with the exception of MMA, none yielded any polymeric product that could be attributed to initiation arising from the presence of DBDZ. Nonetheless, even at quite low temperatures, the originally orange solutions turned pale yellow in a time significantly shorter than that taken to effect a similar discolouration in an equivalent solution that contained no monomer; MMA again was the exception. From the rates of discolouration it was clear that the order of reactivity of the various systems was NVC > PMS > STY > VA.

Liquid chromatographic analyses of the products of the reactions of equimolar quantities (0.5 mol dm^{-3}) of DBDZ and the monomers in benzene solution at 323 K were accomplished on a μ-Porasil column with benzene as the mobile phase. Other than those that could be attributed to residual reactants, only single peaks were observed. The products were subsequently isolated by evaporative crystallization and purified by recrystallization from benzene.

The analytical parameters of the various products are summarized in Table 1 together with the corresponding detail (where relevant) for the monomers from which they are derived.

Firl and Sommer[6,7] have previously reported the $[4 + 2]_\pi$ cycloaddition of phenyl vinyl ether to carboxydiazenes. The elemental analyses in Table 1 have been calculated assuming that a like reaction (Scheme 1) yielding 6-substituted 4-benzoyl-2-phenyl-5,6-dihydro-4*H*-1,3,4-oxadiazines is occurring in these systems.

The i.r. spectra display bands characteristic of the C=O, C=N, and C–O–C linkages. The n.m.r. spectra display three quartets in the region δ 3.5—6.5. These are the same quartets as can be attributed to the adjacent methine and methylene protons in the n.m.r. spectra of the monomers, but shifted to higher field. Geminal coupling has increased and vicinal coupling decreased

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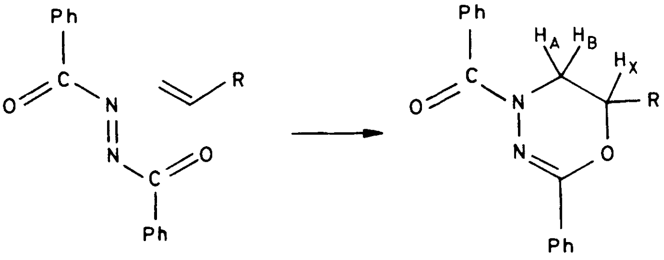
† This compound is frequently described in the literature as azodibenzoyl. The latter name (which is in fact of a diradical) is incorrect and will not be used here.

Table 1. Analytical data for the products of the reaction of DBDZ with *N*-vinylcarbazole, *p*-methoxystyrene, styrene, and vinyl acetate

	I.r. ν/cm^{-1}			^{1}H N.m.r.							Elemental analyses					
					δ^a			J/Hz			% Calc.			% Found		
Compound	C=O	C=N	C–O–C	Solvent	H_X	H_A	H_B	AB	AX	BX	C	H	N	C	H	N
NVC monomer				C_6D_6	6.7	5.1	4.6	1	15	9						
NVC adduct	1 645	1 635	1 295	C_6D_6	6.2	4.8	3.7	13	3	9	77.9	4.9	9.7	77.6	4.7	9.3
PMS monomer					6.6	5.5	5.0	1	18	11						
PMS adduct	1 640		1 250	C_6D_6		4.7	3.1	13		9	74.2	5.4	7.5	74.6	5.2	7.3
			1 080	$(CD_3)_2CO$	5.6	4.7	3.7	13	3	8						
STY monomer					6.6	5.6	5.1	1	18	11						
STY adduct	1 640	1 617	1 275	C_6D_6		4.7	3.2	13	3	9	77.2	5.3	8.2	76.8	5.1	7.6
			1 090	$(CD_3)_2CO$	5.6	4.7	3.7	13	3	8						
VA monomer					7.3	4.7	4.3	14	3	3						
VA adduct[b]				C_6D_6	6.3	4.3	3.1	1	14	6						

[a] Standard $(CH_3)_4Si$. [b] The vinyl acetate system proved to be far less tractable than the others. The n.m.r. data are from an imperfectly purified sample.



Scheme 1. R = $C_{12}H_8N$, $MeOC_6H_4$, Ph, or $MeCO_2$

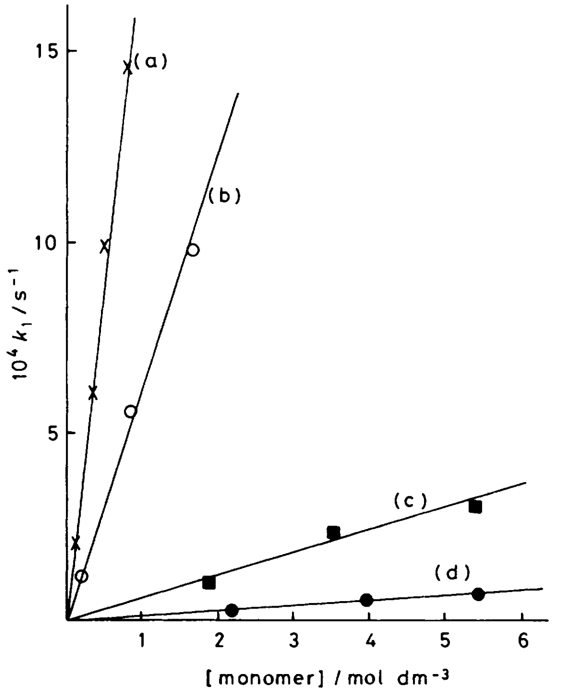


Figure 1. Variation of the first-order rate constants for the cycloaddition of vinyl monomers and DBDZ in benzene solution at 323 K: (a) *N*-vinylcarbazole; (b) *p*-methoxystyrene; (c) styrene; (d) vinyl acetate

markedly; these changes are entirely consistent with the opening of the olefinic double bond attendant upon ring formation involving the attached carbon atoms. Furthermore, within the bounds of experimental error, the integrated n.m.r. spectra are in agreement with the proposed structures.

Kinetics of the Cycloaddition.—The reactions of the various monomers with DBDZ in benzene solution at 323 K were followed spectrophotometrically at 470 nm. At this wavelength the monomers are transparent but DBDZ has an absorption maximum (ε 47 dm^3 mol^{-1} cm^{-1}). In each case a series of solutions was prepared with initial DBDZ concentration of 0.2 mol dm^{-3}, but with a range of initial monomer concentrations all in considerable excess of that value.

In accordance with a pseudo-first-order rate law, linear plots of ln(absorbance) *versus* time obtained. Figure 1 depicts the variation of the apparent first-order rate constant with monomer concentration, and Table 2 lists the second-order rate constants derived from the slopes of these plots. For the purpose of correlation, the parameter *e* of the *Q*/*e* scheme of Alfrey and Price[8] is included as a measure of the polarity of the various vinyl groups.

Polymerizations in the Presence of DBDZ.—(1) *Monomers with electron-rich vinyl groups.* Although the emphasis so far has been on the cycloaddition of DBDZ to the monomers, a second pattern of behaviour is apparent. DBDZ is a known initiator of the polymerization of monomers such as MMA and acrylonitrile which have electron-deficient vinyl groups, yet even at temperatures at which nitrogen elimination and benzoyl radical production from DBDZ is significant, no polymerization of monomers with electron-rich vinyl groups is observed. It follows that either DBDZ or the cycloaddition product is an inhibitor of these polymerizations. A preliminary experiment to distinguish these possibilities involved the initiation of the polymerization of NVC by azobisisobutyronitrile (AIBN) in both the presence and the absence of DBDZ as follows.

A solution of NVC (0.5 mol dm^{-3}) and AIBN (0.04 mol dm^{-3}) in benzene was divided into two equal parts, to one of which a few crystals of DBDZ were added. Both solutions were deaerated before thermoregulation at 323 K. Before the complete disappearance of the DBDZ was evident through colour change, a few ml of each solution were added dropwise to stirred methanol. A white precipitate of poly-NVC was produced only from the solution that did not contain DBDZ. The same test was performed after the DBDZ had been consumed. Poly-NVC was then evident in both solutions.

Figure 2 shows the gel permeation chromatogram of the NVC system before and after the end of the inhibition period. The peak eluted after 21.2 min is that of the cycloaddition product; the broad peak centred at 18.3 min is that of the

Table 2. Second-order rate constants for the cycloadditon of DBDZ and vinyl monomers in benzene solution at 323 K

Monomer	k_2/dm^3 mol^{-3} s^{-1}	e
NVC	1.92×10^{-3}	−1.40
PMS	7.1×10^{-4}	−1.11
STY	5.7×10^{-5}	−0.80
VA	1.3×10^{-5}	−0.22
MMA		+0.40

Table 3. Rates (R_p) and average degrees of polymerization (DP) for samples of PMMA prepared in benzene solution at 323 K; initial concentrations [AIBN] = 0.01 mol dm^{-3}, [MMA] = 2.3 mol dm^{-3}

10^3[DBDZ] mol dm^{-3}	10^5 R_p mol dm^{-3} s^{-1}	DP
0	3.52	985
0.3	3.30	979
0.7	3.04	947
1.0	2.90	937
2.0	2.40	830
3.0	2.10	780
5.0	1.60	685

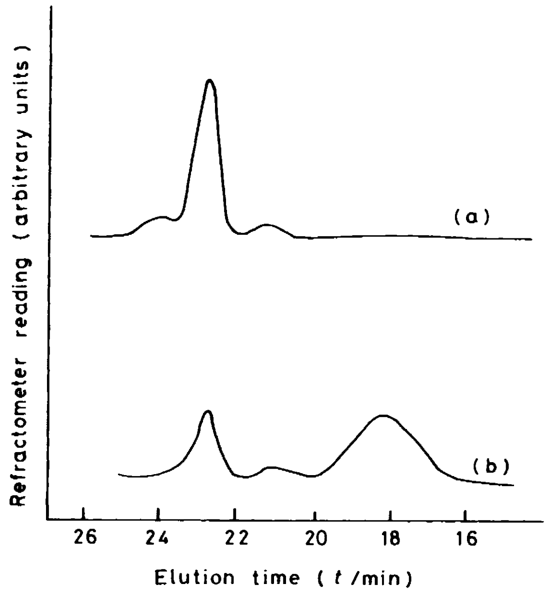


Figure 2. Gel permeation chromatograms obtained during the reaction of the AIBN–DBDZ–NVC system in benzene solution at 323 K: (a) before and, (b) after the consumption of DBDZ. Initial concentrations: NVC, 0.5; DBDZ, 3 × 10^{-3}; AIBN, 0.04 mol dm^{-3}

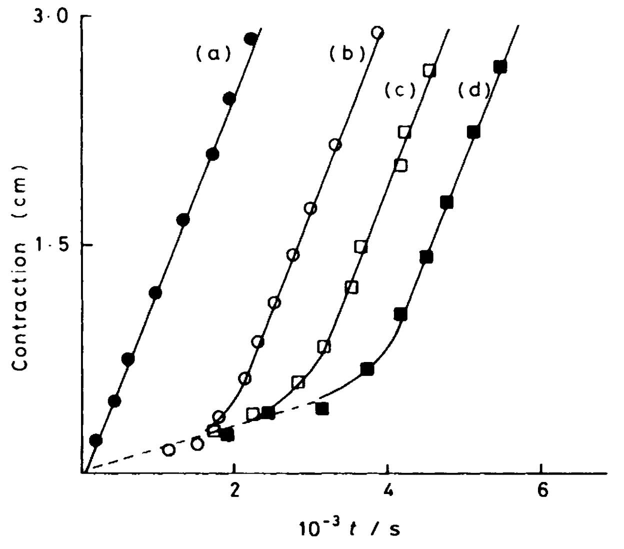


Figure 3. Contraction against time curves for the AIBN (0.04 mol dm^{-3}) initiated polymerizations of NVC (0.5 mol dm^{-3}) in the presence of DBDZ in benzene solution at 323 K. DBDZ concentrations (mol dm^{-3}): (a) 0; (b) 10^{-3}; (c) 3 × 10^{-3}; (d) 6 × 10^{-3}

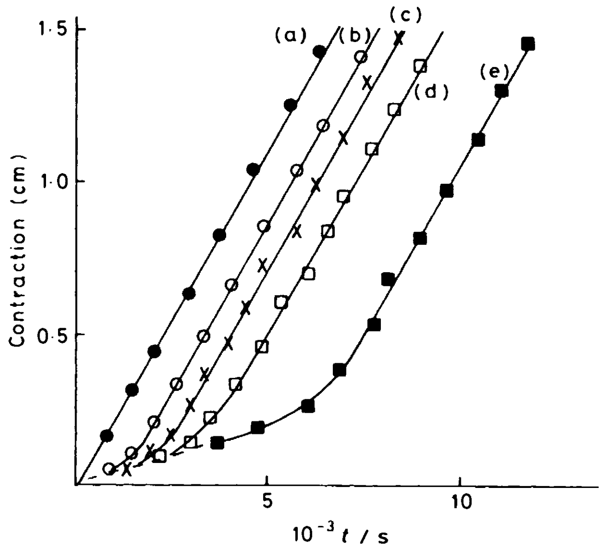


Figure 4. Contraction against time curves for the AIBN (0.01 mol dm^{-3}) initiated polymerizations of styrene (2.9 mol dm^{-3}) in the presence of DBDZ in benzene solution at 323 K. DBDZ concentrations (mol dm^{-3}): (a) 0; (b) 5 × 10^{-5}; (c) 10^{-4}; (d) 2 × 10^{-4}; (e) 6.6 × 10^{-4}

polymer. It is thus clear that polymerization can occur in the presence of this product, and, as will be evidenced by contraction–time curves, it does so at a rate identical with that of the unhibited polymerization.

Figures 3—5 show the dilatometric contraction–time curves for solutions prepared at the same monomer and AIBN concentrations, but over a range of DBDZ concentrations that were markedly less than those of the initiator.* Contraction attributable to the cycloaddition reaction is evidenced by the plots tending away from lines of positive slope rather than from the time axes. Consequently, the times corresponding to the points of intersection of the extrapolations of the two linear portions of each plot are taken to represent the inhibition times.

Figure 6 depicts the variations of the inhibition periods with DBDZ concentration. Unlike the equivalent plots (Figure 7) obtained using diphenylpicrylhydrazyl (DPPH) as an inhibitor of the polymerizations, they are not linear.

(2) *Methyl methacrylate.* Polymerizations of MMA initiated by AIBN at 323 K in benzene solution were found to be retarded by DBDZ. Figure 8 shows representative contraction–time plots for a series of solutions at the same initial monomer

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* Data for the polymerization of PMS are not presented as it was found that the rates of polymerization that obtained led to rates of contraction that were similar to those due to cycloaddition. That polymerization did occur, however, was confirmed by gel permeation chromatography.

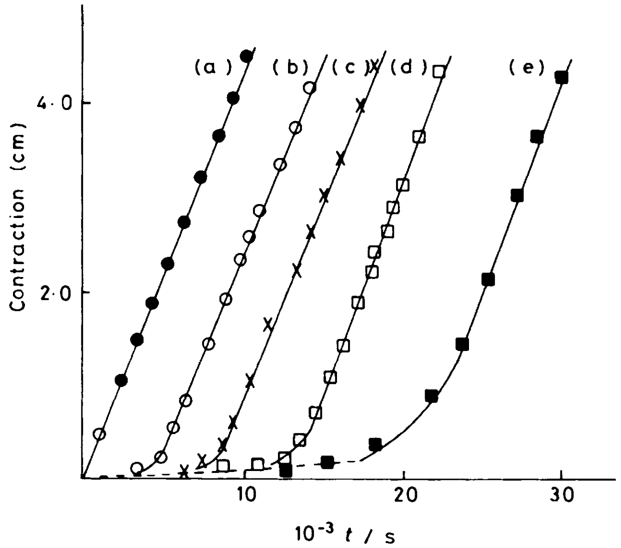


Figure 5. Contraction against time curves for the AIBN (0.01 mol dm^{-3}) initiated polymerizations of vinyl acetate (3.4 mol dm^{-3}) in the presence of DBDZ in benzene solution at 323 K. DBDZ concentrations (mol dm^{-3}): (a) 0; (b) 9×10^{-5}; (c) 1.8×10^{-4}; (d) 3.1×10^{-4}; (e) 6.3×10^{-4}

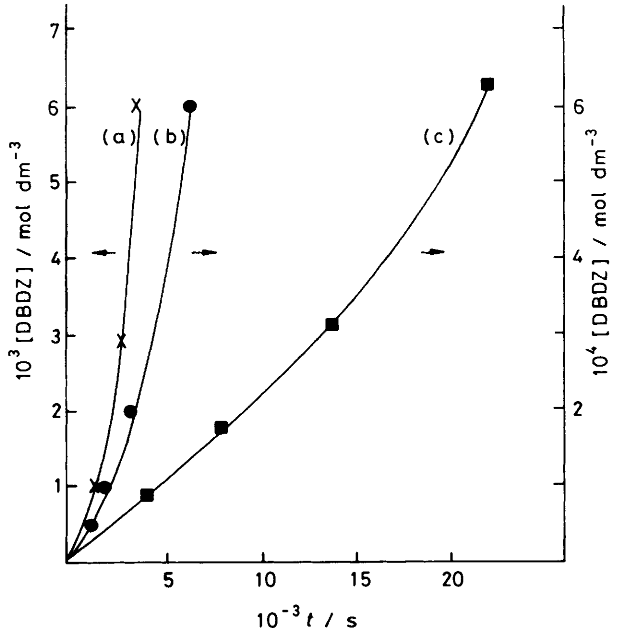


Figure 6. Variation of inhibition periods with DBDZ concentration for the AIBN-initiated, DBDZ-inhibited polymerizations of vinyl monomers in benzene solution at 323 K: (a) NVC; (b) styrene; (c) vinyl acetate

and initiator concentrations but with a range of DBDZ concentrations. Polymerizations were allowed to proceed for 3 h, after which the products were precipitated in methanol, collected, and dried. Initial rates of polymerization were calculated from the slopes of the contraction–time plots and the yields at the terminal contraction. Estimates of the number average molecular weights of the isolated polymers were obtained from their gel permeation chromatograms. The corresponding average degrees of polymerization and the rate data are recorded in Table 3.

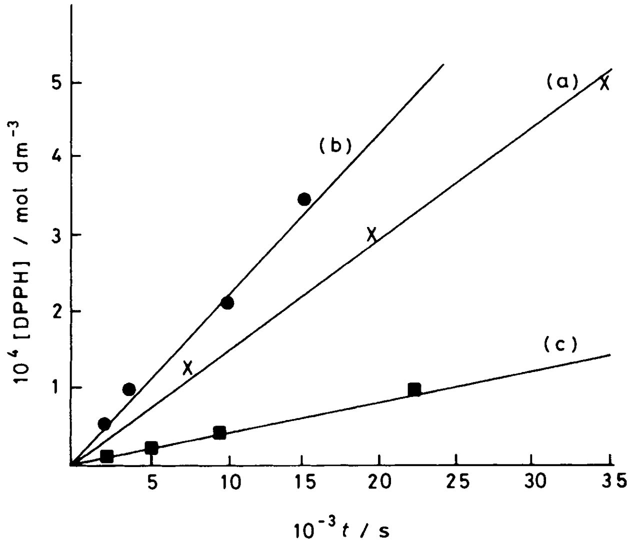


Figure 7. Variation of inhibition periods with DPPH concentration for the AIBN-initiated, DPPH-inhibited polymerizations of vinyl monomers in benzene solution at 323 K: monomer and initiator concentrations are as defined in Figures 3—5: (a) NVC; (b) styrene; (c) vinyl acetate

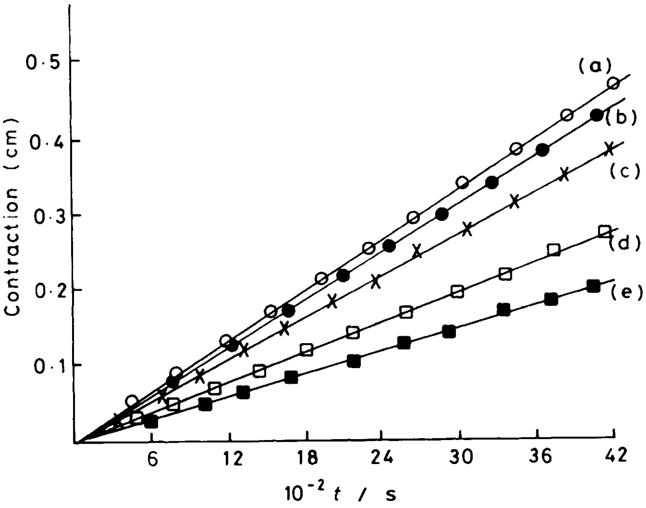


Figure 8. Contraction against time curves for the AIBN (0.01 mol dm^{-3})-initiated, DBDZ-retarded polymerization of methyl methacrylate (2.3 mol dm^{-3}) in benzene solution at 323 K. DBDZ concentrations (mol dm^{-3}): (a) 0; (b) 3×10^{-4}; (c) 10^{-3}; (d) 3×10^{-3}; (e) 5×10^{-3}

Discussion

It is evident that DBDZ reacts by cycloaddition to monomers with electron-rich vinyl groups whilst simultaneously inhibiting their polymerization. The parameters *e* of the *Q*/*e* scheme of Alfrey and Price for rationalizing copolymerization reactivity ratios are a measure of the polarity of the vinyl group. Table 3 shows that there is a good correlation of the *e* value and the rate constants of the cycloaddition reactions, and therefore with the 'inhibiting efficiency' of DBDZ. The more negative the *e* value of the monomer, the less efficient is DBDZ as an inhibitor of its polymerization. In all cases the inhibition periods are far shorter than when DPPH is used as the inhibitor. However, the following kinetic analysis shows that the cycloaddition reaction alone is not sufficient to explain the high rates of consumption of DBDZ in these systems.

Kinetics of the Inhibited Polymerizations.—With the initiator (AIBN) represented by C, DBDZ by I, monomer by M, primary radicals by $R^{\bullet}$ and initiated chains by $M^{\bullet}$, a simple mechanism of an inhibited polymerization competing with cycloaddition can be written (Scheme 2).*

Cycloaddition $$M + I \xrightarrow{k_2} MI \qquad (1)$$

Cycloaddition $$C \xrightarrow{k_c} 2R^{\bullet} \qquad (2)$$

Initiation $$R^{\bullet} + M \longrightarrow M^{\bullet} \qquad (3)$$

Inhibition $$M^{\bullet} + I \xrightarrow{k_i} MI^{\bullet} \qquad (4)$$

Scheme 2.

By assuming steady-state concentrations of $R^{\bullet}$ and $M^{\bullet}$ throughout the inhibition period, equation (i) follows, where f is

$$-d[I]/dt = 2fk_c[C] + k_2[M][I] \qquad (i)$$

the initiator efficiency.

Since $[C] \gg [I]$, the rate of initiation is sensibly constant over the inhibition period ($0 < t < t_i$), so equation (i) is readily integrated. Subsequent rearrangement gives (ii).

$$(\exp k_2\,[M]t_i - 1)\,[C]/k_2[M] = [I]/2fk_c \qquad (ii)$$

The values of k_2 in Table 2 allow the evaluation of the left-hand side of equation (ii). Figure 9 shows the plots of the experimental data in the linear form thus indicated. The slopes of the plots are the reciprocals of $2fk_c$. By substituting the known value[9] for the rate constant for decomposition of AIBN at 323 K, $k_c = 2.085 \times 10^{-6}\ s^{-1}$, $f = 0.5$ is determined for the VA polymerization, and $f = 1.35$ for both styrene and NVC polymerizations. Efficiencies of initiation greater than unity are clearly impossible and the more likely values of 0.14 (VA), 0.58 (STY), and 0.10 (NVC) determined from the slopes of the plots of Figure 7 suggest that all are on the high side. It follows that the rate of consumption of DBDZ through the radical path is greater than is represented in Scheme. 2.

By analogy with the behaviours of benzoquinone and chloranil in the polymerization of styrene,[10] it is conceivable that DBDZ might take part in short-chain copolymerizations with the monomers in accordance with Scheme 3; termination arises only through the competitive reaction which leads to a hydrazyl radical ($MI^{\bullet}$ of Scheme 2). As a comonomer DBDZ can be likened to an electron-deficient diene, and as such it would have polar properties opposed to those of monomers with electron-rich vinyl groups. In terms of the Alfrey–Price rationalization this would be manifest as a high *Q* value and a positive *e* value and even at the low concentrations of DBDZ in these systems, a high tendency towards alternation and a correspondingly high rate of consumption of DBDZ would obtain in copolymerization.

By extending Scheme 2 by including the propagation reactions (5) and (6), and assuming steady-state conditions for

$$M^{\bullet} + I \xrightarrow{k_t} I^{\bullet} \qquad (5)$$

$$I^{\bullet} + M \longrightarrow M^{\bullet} \qquad (6)$$

all radical species, equation (iii) is obtained.

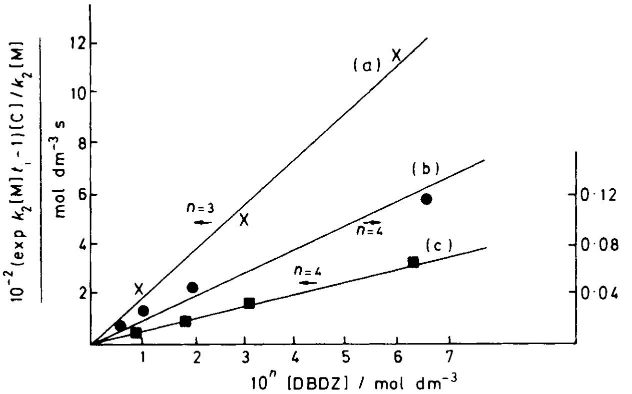
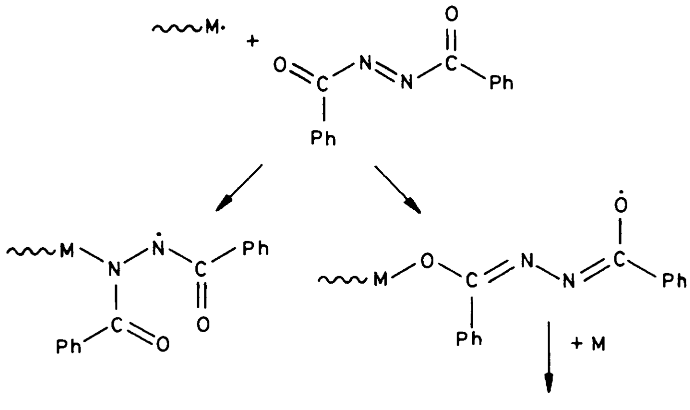


Figure 9. Linear correlations of inhibition periods with DBDZ concentrations for the AIBN-initiated, DBDZ-inhibited polymerizations of viny monomers in benzene solution at 323 K: (a) NVC (n = 3); (b) styrene (n = 4); (c) vinyl acetate (n = 4)



Scheme 3.

$$-d[I]/dt = 2fk_c[C](k_t + k_i)/k_t + k_2[M][I] \qquad (iii)$$

By writing $f' = k_i/(k_t + k_i)$, the fraction of radicals $M^{\bullet}$ which react with DBDZ to form a stable species rather than one which can further propagate, it is seen that (iii) is the same as (i) with f replaced by f/f'. The slopes of the plots of Figure 9 then give $f'/2k_c$, so by using the values of f determined from the DPPH-inhibited polymerizations, estimates of 0.28, 0.43, and 0.07 for f' are obtained for VA, styrene, and NVC, respectively.

The foregoing is presented as only one possible rationalization of inhibition periods of anomalously short duration. From what little is known about the reactions of radicals with DBDZ,[3,11] it is probably an oversimplification, but discussion of the nature of these reactions and their role in the inhibition processes is more appropriate to the second paper in this series.

Kinetics of the Retarded Polymerizations.—Bevington and Stamper have already presented a treatment of the kinetics and mechanism of the initiation of the polymerization of MMA by DBDZ at 363 K. They recognized that degradative transfer to initiator is pronounced in the system. The present work using AIBN as the initiator of the polymerization at the much lower temperature of 323 K confines DBDZ to its role as a chain-transfer agent, thus simplifying the kinetic analysis.

If we represent propagating radicals containing *i* monomer units by $M_i^{\bullet}$ and otherwise use the notation established for

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* At 323 K radical formation from DBDZ is negligible compared with that from AIBN.

Scheme 2, the mechanism of Scheme 4 can be written for a retarded radical polymerization. $M_iI^\bullet$ is again presumed to be a hydrazyl radical and therefore stable towards the re-initiation of polymerization.

Radical product $\quad C \xrightarrow{k_c} 2R^\bullet \qquad (7)$

Initiation $\quad R^\bullet + M \longrightarrow M_i^\bullet \qquad (8)$

Propagation $\quad M_i^\bullet + M \xrightarrow{k_p} M_{i+1} \qquad (9)$

Termination $\quad M_i^\bullet + M_j^\bullet \xrightarrow{k_t} \text{polymer} \qquad (10)$

Degradative transfer $\quad M_i^\bullet + I \xrightarrow{k_{tr}} M_iI^\bullet \qquad (11)$

Scheme 4.

If we assume stationary-state conditions for the propagating radicals, and write $[M^\bullet]$ for the total concentration, it follows that the rate of initiation (R_i) is given by equation (iv). If the

$$R_i = k_t[M^\bullet]^2 + k_{tr}[M^\bullet][I] \qquad \text{(iv)}$$

kinetic chains are sufficiently long, the consumption of monomer in the initiation reaction can be neglected in comparison with that in the propagation reaction and the rate of polymerization can be defined by equation (v). Substituting $[M^\bullet]$ as defined by (v) into equation (iv) leads to equation (vi).

$$R_p = -d[M]/dt = k_p[M][M^\bullet] \qquad \text{(v)}$$

$$k_t(R_p/k_p[M])^2 + k_{tr}(R_p/k_p[M])[I] - R_i = 0 \qquad \text{(vi)}$$

At constant R_i and [M], therefore, a plot of R_p^2 *versus* $R_p[I]$ should be linear with slope of $-k_{tr}k_p[M]/k_t$ and intercept $k_p^2[M]^2R_i/k_t$.

The experimental data are plotted accordingly in Figure 10. Substituting the known values[12] of k_p and k_t (410 dm^3 s^{-1} and 1.2 × 107 dm^3 mol^{-1} s^{-1}, respectively) and the appropriate values of [M] and [C], gives k_{tr} = 159 dm^3 mol^{-1} s^{-1} and R_i = 1.67 × 10^6 mol dm^{-3} s^{-1}. This rate of initiation corresponds to an initiator efficiency of 0.4, which is well within the range of values reported by others and so there is no reason to suspect that DBDZ is consumed in a radical copolymerization or another chain process in a similar manner to the inhibited polymerizations. This is not unacceptable, for with MMA and DBDZ having like polar properties, if DBDZ were a comonomer, at the concentrations employed its incorporation in the product would at best be occasional.

The average degrees of polymerization (*DP*) can also be related to the kinetic parameters. If we allow for the possibility of chain transfer to all species present, *DP* is given by equation (vii), where *x* refers to monomer, solvent, and initiator in turn,

$$\overline{DP}^{-1} = \frac{-(k_{tc} + 2k_{td})[M^\bullet]^2 + k_{tr}[M^\bullet][I] + \sum_x k_{xtr}[M^\bullet][X]}{k_p[M^\bullet][M]} \qquad \text{(vii)}$$

and k_{tc} and k_{td} are the rate constants for termination by combination and disproportionation, respectively. Substituting for $[M^\bullet]$ as defined by equation (v) and rearranging leads to equation (viii), where $\Delta = DP^{-1} - (k_{tc} + 2k_{td})R_p/k_p^2[M]^2$.

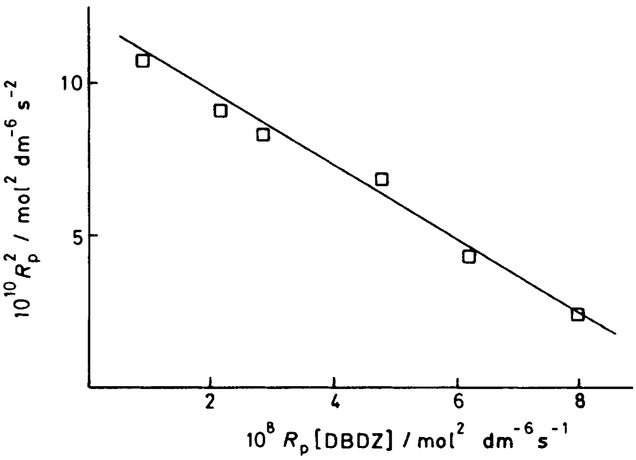

Figure 10. Linear correlations of rate data with DBDZ concentrations for the AIBN-initiated, DBDZ-retarded polymerization of methyl methacrylate in benzene solution at 323 K

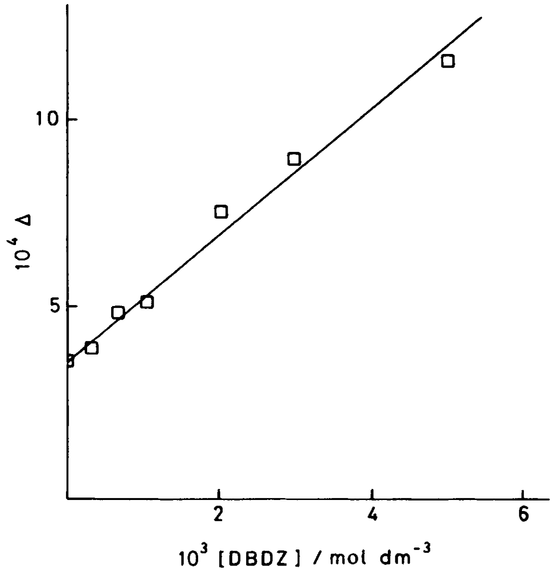

Figure 11. Linear correlations of rate and degree of polymerization data with DBDZ concentrations for the AIBN-initiated, DBDZ-retarded polymerization of methyl methacrylate in benzene solution at 323 K

$$\Delta = (k_{tr}[I] + \sum_x k_{xtr}[X])/k_p[M] \qquad \text{(viii)}$$

Values of Δ are readily calculated using k_{tc} = 7.25 × 10^6 dm^3 mol^{-1} s^{-1} as evaluated by Shulz *et al.*[12] The resulting plot of Δ *versus* [I] shown in Figure 11 is linear with a slope corresponding to k_{tr} = 158 dm^3 mol^{-1} s^{-1}; a value which is in remarkable agreement with that obtained from rate measurements alone. Benzoquinone and DPPH are respectively about 10 times and 5 000 times more reactive at the same temperature.[13]

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