Inhibition of Free Radical Polymerizations by Azodibenzoyl: a Degradative Chain Transfer in Competition with a Simple Reaction

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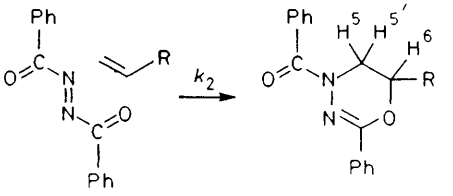
Summary The cycloaddition of azodibenzoyl to a selection of monomers with electron-rich vinyl groups has been shown to compete with its efficient radical-induced decomposition when it is present in systems in which the polymerization of the monomers by a free radical mechanism is initiated.

OVER the years, exhaustive studies of azo compounds as initiators of free radical polymerization have been made. It is now well recognized that amongst this class the most efficient initiators are aliphatic azo compounds, and that although aromatic azo compounds are radical sources, the parent compound is almost invariably an agent for degradative chain transfer, the product of this reaction being thought to be a stable hydrazyl radical.[1] If the polymerizing monomer is substituted with an electron-withdrawing group, the effect is simply to retard the polymerization, but if the substituent is electron-repelling, the reactivity is sufficiently increased as to inhibit the polymerization. Although these conclusions are well founded,

in this paper we report evidence that the reaction scheme for the polymerization of a range of monomers in the presence of azodibenzoyl (AZDB) (i) cannot be explained solely in terms of degradative chain transfer, and (ii) that this process is itself complex.

AZDB in benzene solution does not thermally decompose to give radicals at a significant rate at < 350 K.[2] We have found that in benzene solution in the presence of a monomer with a donor substituent, although polymerization is not evident, the originally orange solutions turn yellow even at 323 K. Product isolation followed by C, H, and N analysis and i.r. and n.m.r. spectroscopy (see Table) have established that the monomers and AZDB undergo an inverse Diels–Alder cycloaddition to form 6-substituted 2-phenyl-4-benzoyl-4*H*-5,6-dihydro-1,3,4-oxadiazines according to equation (1), at rates that correlate with the extent to which the vinyl group of the monomer is electron-rich.



(1)

When polymerization of the above monomers was initiated with azobisisobutyronitrile (AIBN) in the presence of AZDB in benzene solution at 323 K (at which temperature radical production from AZDB[2] is negligible compared to that from AIBN[3]), inhibition periods were observed, the duration of which (t_I) correlated with equation (2), based on the Scheme in which the monomer, AIBN, and AZDB are represented by M, C, and I, respectively, and primary radicals and initiated chains by R· and M·. Post-inhibition retardation was not observed.

$$\begin{aligned} \text{Cycloaddition} \quad & M + I \xrightarrow{k_2} \text{Product} \\ \text{Radical production} \quad & C \longrightarrow 2\,R\cdot \\ \text{Initiation} \quad & R\cdot + M \longrightarrow M\cdot \quad \text{Rate} = R_i \\ \text{Inhibition} \quad & M\cdot + I \longrightarrow \text{Products} \\ & k_2[M]t_I = \ln(1 + k_2\,[M][I]/R_i) \end{aligned} \qquad (2)$$

In the case of *N*-vinylcarbazole, for which it can be shown that $k_2[M][I] >> R_i$, k_2 and R_i have been evaluated from the slope and intercept of a plot of $\ln[I]$ *vs.* t_I. The rate constant thus obtained ($1{\cdot}14 \times 10^{-3}$ dm^3 mol^{-1} s^{-1}), although lower than that quoted in the Table, is nonetheless of comparable order. Apparent R_i values for the other monomers have been calculated from the values of k_2 quoted in the Table. They are all markedly greater than the more likely accurate rates of initiation obtained using diphenylpicrylhydrazyl as the inhibitor (4 fold, 5 fold, and 12 fold for styrene, vinyl acetate, and *N*-vinylcarbazole, respectively). The only explanation of this observation would seem to be that the products of the inhibition reaction include a radical (probably benzoyl) which is capable of reinitiating the polymerization, *i.e.* that the AZDB is consumed in the propagation step of a chain reaction. If that is the case, then it is difficult to visualise a stable hydrazyl radical being formed, and preliminary e.s.r. studies have in fact indicated that no such species is retained within these systems.

TABLE. I.r., n.m.r., and rate data for the cycloaddition (1)

R	k_2[a]/ dm^3 mol^{-1} s^{-1}	N.m.r. δ p.p.m. H^5	$H^{5'}$	H^6	ν I.r. cm^{-1} (Nujol) $\nu_{C=O}$	$\nu_{C=N}$
Carbazol-9-yl	$1{\cdot}9 \times 10^{-3}$	3·70	4·80	6·20	1648	1638
p-$MeOC_6H_4$	$7{\cdot}1 \times 10^{-4}$	3·66	4·68	5·52	—	1640
Ph	$5{\cdot}7 \times 10^{-5}$	3·70	4·76	5·64	1640	1618
$MeCO_2$[b]	—	3·10	4·34	6·28	—	—

[a] Obtained spectrophotometrically. [b] Vinyl acetate reacts very slowly at 323 K.

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