Kinetics of the Benzoyl Peroxide and Azobis-isobutyronitrile Initiated Thermal Polymerizations of *N*-Vinylcarbazole in Solution

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Summary Whereas the azobis-isobutyronitrile thermally initiated polymerization of *N*-vinylcarbazole in solution obeys the usual rate law for a free-radical polymerization, the rate law for the benzoyl peroxide initiated polymerization is found to have a monomer exponent of two and an initiator exponent of one; a partial charge-transfer mechanism of the polymerization is proposed.

IN recent years there has been renewed interest in the polymerization of *N*-vinylcarbazole (vcz), and in particular in mechanisms of the initiation reaction. Polymerizations by halogens[1-3], various substituted quinones,[1,2,4-6] tetranitromethane,[2-6] and trichloroacetonitrile and other organic electrophiles[1,2] have been described, as have polymerizations by salts of metals.[7] The initiation of such polymerizations has been attributed to the thermal[1,4,6] or photolytic[8] excitation of a charge-transfer complex formed between a monomer molecule and an initiator molecule, the exact nature of which remains the subject of some controversy. On the other hand, thermal polymerizations by free-radical initiators such as benzoyl peroxide and azobis-isobutyronitrile (azbn) have also been observed.[9] The effect of organic base retarders and inhibitors such as aniline, dimethylaniline, and trimethylamine on such polymerizations has led to the conclusion that they proceed by a free-radical mechanism. We now report kinetic evidence that although this assumption may be justified in the case of initiation by azbn, it is most probably erroneous for that of initiation by benzoyl peroxide.

Polymerizations of solutions (deaereated by repeated freeze–pump–thaw cycles to a static pressure of 10^{-5} Torr) of vcz in aromatic hydrocarbon solvents were carried out in sealed dilatometers over ten-fold ranges of monomer concentration $[M]$ (constant initiator concentration) and initiator concentration [I] (constant monomer concentration). Rates of polymerization (R_p) were obtained from the initial slopes of the contraction-time curves, from which log R_p *vs.* log $[M]$ and log R_p *vs.* log [I] plots were obtained. The contraction coefficients for the systems were obtained from measurements of the densities of standard solutions of the monomer and of the polymer.

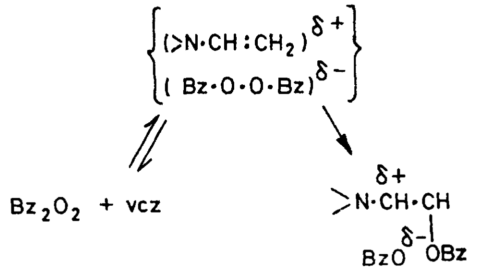
The azbn initiated polymerization at 50 °C was noticeably more rapid than that of the benzoyl peroxide-initiated polymerization at 60 °C, and whereas the former obeyed the usual rate law for a free-radical polymerization ($R_p = 7{\cdot}5 \times 10^{-5}\,[M][I]^{0{\cdot}5}$ mol l^{-1} s^{-1} at 50 °C), the latter obeyed a rate law more usually associated with polymerization by an ionic mechanism ($R_p = 10^{-4}\,[M]^2\,[I]$ mol l^{-1} s^{-1} at 60 °C). No sensible free radical mechanism can be advanced to explain this observation, though if it is assumed that vcz and benzoyl peroxide form a donor-acceptor complex of the kind proposed by Scott *et al.*[1] then the following mechanism of the polymerization is consistent with the kinetic expression [equations (1)—(3)].

$$\text{Initiation: } Bz_2O_2 + vcz \rightleftharpoons (Bz_2O_2.vcz) \rightarrow BzOvcz^{\delta+}OBz^{\delta-} \qquad (1)$$

$$\text{Propagation: } BzOvcz^{\delta+}OBz^{\delta-} + nvcz \rightarrow BzO(vcz)^{\delta+}_{n+1}OBz^{\delta-} \qquad (2)$$

$$\text{Termination: } BzO(vcz)^{\delta+}_{n+1}OBz^{\delta-} \rightarrow Bzo(vcz)_{n+1}PBz \qquad (3)$$

A preliminary investigation of the spectra of solutions of vcz and benzoyl peroxide in cyclohexane indicates the possible formation of a charge-transfer complex in that the presence of the peroxide enhances the u.v. absorption spectrum of vcz in accordance with similar observations by Ellinger[4] on other acceptor–vcz systems. Further support for the proposed mechanism of the polymerization comes from the observed charge-transfer interaction between *NN*-dimethylaniline and benzoyl peroxide,[10] the formation of such complexes between other known acceptors and aromatic amines being well recognized. In addition, the benzoyl peroxide–*NN*-dimethylaniline system is known to initiate a more rapid polymerization than benzoyl peroxide alone.[11] Such polymerizations have been explained in terms of initiation by a cation radical derived from the amine by single electron transfer to a benzoyl peroxide molecule, with the concomitant formation of a benzoyloxy-radical and a benzoate ion. That total electron transfer should occur in the vcz–benzoyl peroxide system in aromatic hydrocarbon solvents is unlikely. The ionization would not be favoured in a medium of such low dielectric constant, and vcz, being a weaker base than dimethylaniline, would be a poorer donor. It is therefore proposed that benzoyl peroxide as a thermal initiator behaves atypically in this system in that the polymerization proceeds by a partial charge-transfer rather than by a free-radical mechanism, the initiation reaction being the thermal excitation (leading to rearrangement) of a complex formed between benzoyl peroxide and vcz as in equation (4).



(4)

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