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Polymer Vol. 36 No. 12, pp. 2491–2492, 1995
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0032-3861/95/$10.00+0.00

Initiation in high-conversion radical polymerizations: comments on some recent papers

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(Received 18 October 1994)

Recent papers by Takenaka, Johnson and Kamide (*Polymer* 1994, **35**, 3899, 3908) include some claims about the efficiency of azobisisobutyronitrile as an initiator of certain radical polymerizations. It was suggested that the efficiency factor is unity up to high conversions and then decreases quite markedly and abruptly. It is now shown that the treatment is probably in error, and that the conclusions may be untenable.

(Keywords: high-conversion polymerizations; azobisisobutyronitrile; initiator efficiency)

Two recent papers by Takenaka, Johnson and Kamide deal with some aspects of high-conversion radical polymerizations. One contribution[1] is concerned with homopolymerizations of acrylonitrile (AN) and methyl acrylate; in the other[2], copolymerization of these monomers is considered. In all cases, azobisisobutyronitrile (AIBN) was the source of initiating radicals. The authors reach some conclusions on the efficiency of the initiator but they are contrary to established views based on direct and sound experimental evidence. They conclude that, for the polymerization of AN in dimethylsulfoxide (DMSO) at 60°C, the efficiency (f) of initiation is unity up to quite an advanced stage in the polymerization, and then falls quite abruptly. The present note calls attention to what seem to be failings in the arguments advanced by Takenaka *et al.*; the remarks refer to the case of AN but they are applicable in the main to the other systems also.

Takenaka *et al.* base their determination of f upon equation (5) of their first paper[1]; however, this equation is faulty because it is dimensionally unbalanced. Equation (5) is used in conjunction with Figure 5 assuming particular values for k_p^2/k_t and k_d, where k_p and k_t are rate constants for propagation and termination, respectively, in the polymerization, and k_d is the rate constant for the dissociation of the initiator. The precise values of these quantities must be open to question, despite the claims of the authors, and it is probable that they change significantly as the nature of the medium changes quite drastically as the polymerization proceeds to conversions in the region of 80%; it is unlikely that changes in k_p^2/k_t are neutralized by those in k_d. The slope of the line in Figure 5 is taken as proportional to $f^{1/2}$; the scatter of the experimental points is such that it would be quite reasonable to take f as 0.7 instead of unity in the early stages, with pronounced decrease at higher conversions.

In order to account for a value of 1.0 for f, Takenaka *et al.* express the view that dissociation of AIBN first yields a 2-cyano-2-propyl radical and a diazenyl radical, and that the latter subsequently dissociates to give a second cyanopropyl radical. A paper by Pryor and Smith[3] is cited in support of this scheme but actually those authors found no evidence for a two-stage dissociation of AIBN, although there were indications of such a process for some other azo compounds not commonly used as initiators of polymerization. Takenaka *et al.* interpret their conclusion that f is unity as showing that initiation occurs before formation of a geminate pair of cyanopropyl radicals which might undergo cage interaction, so leading to wastage from the point of view of initiation. This idea must imply that half the initiation processes involve diazenyl radicals, leading to end-groups $(CH_3)_2C(CN){\cdot}N{:}N{-}$, as well as those represented as $(CH_3)_2C(CN){-}$ arising from the cyanopropyl radicals. This situation must be rejected in view of the abundant evidence that polymers, including polyAN, contain only one type of end-group derived from AIBN[4–6]. Comparisons of the reactivities of monomers towards the initiating radicals derived from AIBN show that AN does not exhibit exceptional behaviour[6], a conclusion reinforced by recent direct measurements[7] of the rate constants for the reactions of the radicals with monomers.

Takenaka *et al.* present a ^{13}C n.m.r. spectrum for a system containing partially polymerized AN, AIBN and d_6-DMSO. Signals from unreacted monomer, polymer and undecomposed initiator are readily identified but it is not possible to see signals originating from products, such as tetramethylsuccinodinitrile (TMSDN), which would be formed from 'wasted' initiator. Moad *et al.*[8] showed that, for the case of styrene with AIBN in d_8-toluene, 'waste' products could be detected but it was necessary to use ^{13}C-enriched initiator to enhance the signals, and the products were detected only in the later stages of polymerization, beyond about 65% conversion. At that point, the efficiency of initiation was decreasing and there was of course an accumulation of the 'waste' products formed at earlier stages. Takenaka *et al.* assume that the failure to detect 'waste' products supports the

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view that all the radicals formed from AIBN are used in initiation except when the conversion is high; it is much more likely that the failure is due to there being only very small amounts of the products in the system. It appears that the n.m.r. spectrum which is displayed was recorded when about 20% of the monomer had polymerized and of course the initiator was not isotopically enriched. If *f* were actually about 0.7, the number of radicals converted to products such as TMSDN could not exceed about half the number of initiator fragments incorporated as end-groups. It is not possible to comment on end-group signals in the published spectrum because they are covered by signals from the much more abundant monomeric units in the polymer; the end-group signals could be detected only by using ^{13}C initiator and by applying difference spectroscopy[6].

^{14}C-labelled AIBN was used some time ago in a study of the initiation of the polymerization of AN in dimethylformamide[9]. Examination of the polymer formed at low conversion showed that the efficiency of initiation was about 0.5; isotope dilution analysis confirmed that 'waste' products such as TMSDN were present in the system at the expected levels. There is no compelling reason why the situation should be completely different when using DMSO as diluent. It should also be noted that essentially the same chemical reactions occur at low and high conversions; any differences in overall behaviour must be associated with changes in the concentrations of reactants, and in the viscosity and nature of the medium. It is also necessary to consider that transfer to polymer must become more pronounced at high conversions, leading to an increased possibility of structural branching.

Whatever the merits of the approaches adopted by Takenaka *et al.* for investigation of the important subject of high-conversion polymerizations, it must be concluded that their statements about efficiency of initiation for AIBN should be treated with great caution unless more convincing evidence is produced to support them.

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