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COMMENTS ON RECENT PAPERS CONCERNING TRANSFER IN RADICAL POLYMERIZATIONS

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NOTE

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Accounts have been given [1, 2] of a new method for determination of transfer constants for additives in radical polymerizations promoted by an appropriate initiator; a potentially valuable modification of the method has been proposed and examined by Kapfenstein and Davis [3]. The procedures, both original and modified, depend upon the use of an initiator for which transfer to initiator is negligible and which functions entirely by the attachment of a well defined fragment to a molecule of monomer; for most systems, azobisisobutyronitrile (AIBN) is suitable giving rise to end-groups $(CH_3)_2C(CN)$-. It is necessary to know the number-average kinetic chain length (ν) in a polymerization; this quantity is given by the number of monomeric units for each initiator fragment incorporated in the resulting polymer, as found by end-group analysis.

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Low conversion systems are used so that there can be only very slight interference from copolymerization of methacrylonitrile which might be formed from "wasted" initiator [4]. Knowledge of the number (n) of the initiator fragments in the average polymer molecule is also required; n can be found by considering the results of the end-group analysis and the number-average molecular weight of the polymer as found by, for example, size exclusion chromatography (SEC). For a case involving a transfer agent effective enough for transfers to monomer and diluent to be neglected, Equation 1 is used to calculate the transfer constant.

$$\frac{k_f[T]}{k_p[M]} = \frac{2 - 2n + nf}{2n\nu} \qquad (1)$$

where [T] and [M] are the concentrations in the polymerizing system of transfer agent and monomer respectively, k_f/k_p is the required transfer constant, f is the fraction of the normal termination processes occurring by combination, and n and ν are as defined already. Equation 1 is applicable when there is efficient re-initiation during transfer; in principle, it can be used not only for conventional transfer agents but also for those which function by the addition/fragmentation mechanism. An equation more elaborate than (1) is needed when re-initiation is inefficient and transfer is accompanied by appreciable retardation [5].

The analyses for incorporated initiator fragments can be performed satisfactorily by using AIBN labelled with carbon-14 and comparing the specific activity of the initiator with that of the derived polymer; the method is well established and reliable. It has been demonstrated [6] that it is possible to adopt an alternative procedure utilizing AIBN enriched with carbon-13, followed by examination of the ^{13}C-NMR spectrum of the resulting polymer; the spectrum however must be recorded under stringently controlled conditions and the sensitivity of the end-group analysis is greatly inferior to that easily achievable when using ^{14}C-AIBN.

The method has been applied to various systems but generally the experiments were not planned to allow the transfer constants to be determined also by the classical Mayo method; this limitation did not fully apply however to cyano-derivatives of propene as transfer agents in the radical polymerizations of methyl methacrylate (MMA) and styrene (STY) at 60°C [7]. It was shown that 1-cyano-1-propene (crotononitrile (CRN) and 3-cyano-1-propene (allyl cyanide) (ALC) at moderate concentrations cause negligible retardation of the polymerizations so that Equation 1 could be applied. The derived values of k_f/k_p are $1{\cdot}4 \times 10^{-4}$

(CRN/MMA), $3{\cdot}5 \times 10^{-4}$ (CRN/STY), $5{\cdot}6 \times 10^{-4}$ (ALC/MMA) and $2{\cdot}7 \times 10^{-3}$ (ALC/STY); the last of these transfer constants was wrongly printed as $2{\cdot}7 \times 10^{-4}$ at one point in the publication. The values obtained by the Mayo method for the three cases for which it could be applied were $1{\cdot}0 \times 10^{-4}$ (CRN/MMA), $5{\cdot}3 \times 10^{-4}$ (ALC/MMA) and $3{\cdot}8 \times 10^{-3}$ (ALC/STY); the results are of limited accuracy and may involve uncertainties of up to ±25% but, on that basis, it appears that the transfer constants obtained by the two procedures are in reasonable agreement.

Kapfenstein and Davis [3] reported a study of 2-methyl-2-propanethiol as a transfer agent during the polymerization of MMA at 60°C in toluene, comparing methods for determining the transfer constant. They obtained consistent and acceptable results by application of the Mayo method and by using a treatment based on the distribution of chain lengths in a polymer [8]. It was shown later that the two procedures are essentially equivalent [9]. An attempt was made [3] to modify the new method referred to in the preceding paragraphs although it was mistakenly described as involving the use of a radioactive initiator in conjunction with NMR spectroscopy. Matrix-assisted-laser-desorption-ionization (MALDI) mass spectrometry was used in an attempt to determine both n and ν and so to avoid the regulatory controls which are associated with the use of ^{14}C-AIBN.

Unfortunately, the transfer constants found using MALDI spectra were widely scattered and inconsistent with those found by other methods. Further, there are statements in the paper which give cause for concern; the first of them is " . . . . to minimize problems with non-quantative response in the MALDI analyses, the spectra were compared with results from SEC. Only those MALDI spectra which gave a good match were used for the subsequent analysis". There is also some discussion on page 2406 of Reference [3] about three types of molecules in the polymer, differing in their end-groups; it includes the statement that n and ν have the same values for all three species at the same degree of polymerization. The meaning is obscure in view of the fact that n and ν, as used in Equation 1, refer to values averaged over the whole polymer. The paper includes no details of the calculations and it is not possible to perform checks by reference to the single printed MALDI spectrum. There is no doubt that these spectra can be valuable in many connections including studies of end-groups and, when properly applied, provide information on topics such as the balance between combination and disproportionation in certain termination processes [10]. It is equally clear that there is ample justification for the conclusion reached by Kapfenstein and Davis [3] that "further developments in MALDI instrumentation and methods are required before reliable kinetic data can be extracted from MALDI spectra".

A point can be made about a possible extension of the method for finding transfer constants by application of ^{14}C-AIBN for end-group analyses. The work originated with an assessment of the relative importances of combination and disproportionation during the polymerizations of STY and MMA [11]; f and n, as already defined, are related thus:

$$f = 2(n - 1)/n$$

The most recent and refined results were reported in 1996 [2]. The procedure is inapplicable for those monomers which engage in radical polymerizations for which transfer reactions of various types are prominent. There is still a scarcity of reliable information on the termination processes in many of these cases but Equation 1 may provide a means for solving the problems. Suppose that the transfer constant for a particular agent is known for a certain monomer, perhaps by application of the Mayo method. Further study involving analyses for end-groups derived from the initiator could allow use of Equation 1 with k_f/k_p known and f as the quantity to be determined. If and when work with ^{14}C-AIBN can be resumed, this possibility will be explored. In the meantime, attention is being paid to an alternative procedure involving initiators containing fluorine; the sensitivity achievable with ^{19}F-NMR is such that the necessary analyses for initiator fragments are feasible even for polymers of quite high molecular weight [12]. The use of fluorinated initiators would mean that radioactive materials could be avoided.

CONCLUSION

Acceptable values for transfer constants in radical polymerizations can be obtained by a procedure involving analyses of polymers for end-groups derived from an initiator such as azobisisobutyronitrile. The analyses can be performed with the required sensitivity and accuracy by making use of initiator labelled with carbon-14. The method could be adapted to deal with the combination/disproportionation problem. An unsuccessful attempt has been made by Australian workers to apply MALDI mass spectrometry of polymers for the characterization necessary to determine transfer constants, so dispensing with the use of ^{14}C-labelled materials. It appears that it was recognized that the failure was not due to faults in the principles of the method but was caused by inadequacies of experimental aspects. At this stage, it is concluded that the use of radioactive initiator cannot easily be avoided although it is possible that satisfactory results might be obtained from studies by ^{19}F-NMR of polymers made using a fluorine-containing initiator.

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