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Iodoform as a transfer agent in radical polymerizations

C. A. Barson
School of Chemistry, University of Birmingham, Birmingham B15 2TT, UK

and J. C. Bevington* and B. J. Hunt
School of Physics and Chemistry, The University, Lancaster LA1 4YA, UK
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Iodoform has been examined as a reactive transfer agent in the radical polymerizations at 60°C of styrene and methyl methacrylate using azobisisobutyronitrile as initiator. The transfer constants have been determined by a procedure depending upon the determination of the initiator fragments incorporated as end-groups in the polymers. The polymerizations are retarded by iodoform; this effect is largely caused by an impurity, most probably elemental iodine, which is generated in the polymerizing systems by decomposition of the transfer agent. It is deduced that the transfer constants for iodoform with styrene and methyl methacrylate are ca. 10 and 3, respectively. Copyright © 1996 Elsevier Science Ltd.

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INTRODUCTION

A consideration of bond strengths suggests that alkyl iodides should be rather reactive as transfer agents in radical polymerizations and that they would be considerably more effective than the corresponding bromides or chlorides. A very extensive collection of information on transfer constants for many types of substances in the polymerizations of various monomers can be found in ref. 1, but the latter has few references to alkyl iodides. The data for iodomethane, iodoethane and 2-iodopropane with ethylene, 1-iodobutane and diiodomethane with styrene, and iodomethane and 1-iodobutane with vinyl acetate, confirm the high reactivities of such iodo compounds.

This paper reports the first part of a study of organic iodo compounds used as transfer agents in radical polymerizations, and is concerned with triiodomethane (iodoform) (IOD) with styrene (STY) and methyl methacrylate (MMA). The work makes use of a new procedure for the examination of transfer in radical polymerizations[2,3]; this involves the determination of the number of initiator fragments in the average molecule in a sample of polymer prepared in the presence of the substance under consideration. The required analyses for the end-groups were made possible by using ^{14}C-labelled azobisisobutyronitrile (AIBN) as the initiator for polymerizations at 60°C; measurements of the average molecular weights of the polymers were made by size exclusion chromatography.

The use of a compound such as IOD as a transfer agent may be of interest as a means of producing polymers with iodine-containing end-groups which are likely to be highly reactive. There is interest[4,5] also in the

use of multi-functional transfer agents and IOD could certainly be regarded as such an agent. Complications may, however, arise when organic compounds of iodine are used as additives in radical polymerizations because of their instability; it is significant that suppliers of these substances describe most of them as containing stabilizers. It appears that IOD, for example, readily becomes contaminated with elemental iodine, a substance which has profound effects on polymerizations.

Although this paper is concerned primarily with IOD, a few experiments were performed by using bromoform, chloroform and deuterochloroform as transfer agents.

EXPERIMENTAL

The general experimental procedures have been described previously[2]. IOD (Aldrich) was recrystallized from methanol; bromoform (Aldrich) and deuterochloroform (Aldrich) were used as received; chloroform (Merck) was distilled after washing with water and drying with $CaCl_2$; the transfer agents were stored in the dark. Polymerizations with benzene as diluent were performed anaerobically at 60°C and were monitored by dilatometry; conversions of monomer were less than 10%. Polymers were recovered by precipitation in methanol, purified by three further precipitations and then dried in vacuum. The ^{14}C-activities were measured by scintillation counting of the solutions. The molecular weights of the polymers were determined by size exclusion chromatography, using samples which had been subjected to the full purification procedure.

RESULTS AND DISCUSSION

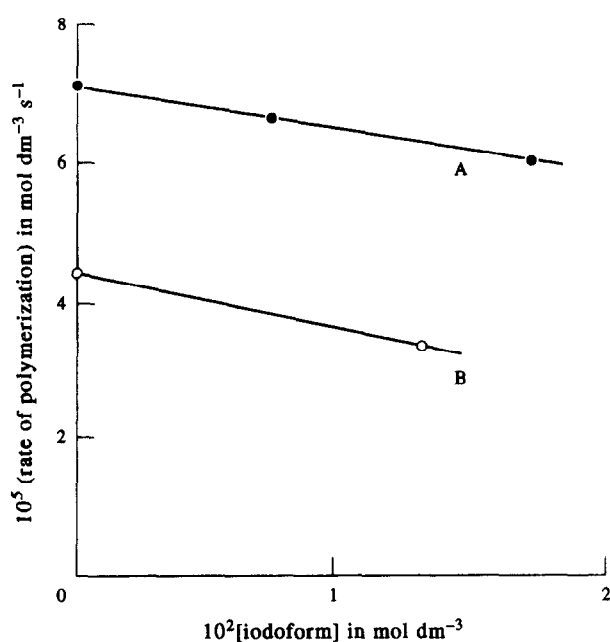When IOD was present in systems which also contained

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Figure 1 Effects of iodoform on rates of polymerization, subsequent to inhibition, for MMA and STY at 60°C using AIBN as initiator. Initial concentrations: (A) [AIBN] 0.77×10^{-2} mol dm^{-3}, [MMA] 2.78 mol dm^{-3}; (B) [AIBN] 1.15×10^{-2} mol dm^{-3}, [STY] 5.30 mol dm^{-3}

AIBN and either STY or MMA, there was inhibition of polymerization, but the subsequent reactions proceeded at steady rates, although retarded to an extent depending upon the initial concentration of IOD (see *Figure 1*). In a typical case in which the initial values of [AIBN], [IOD] and [MMA] were 0.77×10^{-2}, 0.76×10^{-2} and 2.78 mol dm^{-3}, respectively, inhibition lasted ca. 40 min, but the inhibition period was not really reproducible, although the extent of the subsequent retardation was reproducible. When bromoform replaced IOD, there was no inhibition or retardation. Chloroform or deuterochloroform at concentrations in the region of 2.7 mol dm^{-3} in systems which also contained MMA, benzene and AIBN produced neither inhibition nor retardation. It was confirmed that iodine at concentrations such as 1.5×10^{-4} mol dm^{-3} caused inhibition of the polymerizations of STY and MMA and that the subsequent reactions were not retarded. Dilute oxygen-free solutions of IOD in benzene, having concentrations

in the region of 10^{-2} mol dm^{-3}, rapidly darkened on standing at room temperature.

The occurrence of inhibition followed by retardation for the systems containing IOD is consistent with the view that inhibition is caused by small amounts of a reactive impurity, most probably elemental iodine, accumulating in the transfer agent during storage and the preparation of the reaction mixtures. Variations in the length of the inhibition period could readily be ascribed to different periods of storage of the transfer agent, and therefore different extents of contamination. The subsequent retardation could be attributed to the degradative nature of the transfer, i.e. inefficient reinitiation by the radical, presumably $\cdot CHI_2$, formed from IOD; it must also be supposed that retardation is caused by an impurity which is continuously generated from the transfer agent at the working temperature.

Table 1 refers to experiments involving ^{14}C-AIBN, in each case at a concentration near 0.7×10^{-2} mol dm^{-3}. The number of monomeric units in a polymer for each incorporated initiator fragment ($\bar{\nu}$) was obtained from the ^{14}C-activity of the polymer (a_p) and that of the initiator (a_i); for polySTY this is given by $82a_i/104a_p$ and for polyMMA by $82a_i/100a_p$. The average number of initiator fragments per polymer molecule (n) was determined as $\overline{DP}_n/\bar{\nu}$. The transfer constant (k_f/k_p) was calculated by the use of the following equation:

$$\frac{k_f[\text{transfer agent}]}{k_p[\text{monomer}]} = \frac{2 - 2n + nf}{2n\bar{\nu}} \qquad (1)$$

by taking f (the fraction of the number of interactions of polymer radicals occurring by combination) as 0.7 for STY and 0.1 for MMA[2], and by assuming that transfers to monomer and diluent can be neglected in these systems. Equation (1) is expected to be valid when the transfer is not degradative and every radical produced from the transfer agent subsequently reacts with monomer to initiate the growth of another polymer molecule. This limitation means that the transfer constants quoted in *Table 1* for IOD may require further consideration.

The transfer constants found from experiments (1) and (2) are considerably less than those from experiments (3) and (4), while that found from experiment (5) is much smaller than that from experiment (6). For both MMA and STY, it is believed that the most reliable values of the transfer constants are those found from systems in which

Table 1 Polymerization experiments involving haloforms

No.	[additive][a]	[monomer][b]	^{14}C-activity of polymer[c] (Bq g^{-1})	$\bar{\nu}$	$\overline{DP}_n$	$\overline{DP}_w/\overline{DP}_n$	n	k_f/k_p
1	1.75 i	2.78 m	173	1554	328	1.24	0.21	0.39
2	0.63 i	2.78 m	182	1482	316	1.28	0.21	1.13
3	0.133 i	2.55 m	300	897	364	1.40	0.41	3.18
4	0.018 i	2.55 m	265	1016	878	1.75	0.86	2.95
5	0.59 i	2.65 s	1215	213	82	1.75	0.38	4.08
6	0.039 i	2.73 s	1103	235	231	1.97	0.98	10.10
7	2.65 b	2.78 s	1027	259	267	1.78	1.03	0.13
8	1.44 b	3.97 s	885	293	375	1.74	1.28	0.12
9	263 c	1.97 m	290	929	900	1.69	0.97	6.6×10^{-5}
10	275 d	2.01 m	283	950	920	1.68	0.97	6.3×10^{-5}

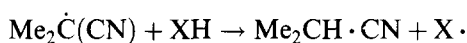[a] All values $\times 10^2$: i, iodoform; b, bromoform; c, chloroform; d, deuterochloroform
[b] m, methyl methacrylate; s, styrene
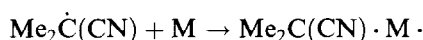[c] Activity of ^{14}C-AIBN $= 32.83 \times 10^4$ Bq g^{-1}

the concentration of IOD was particularly low; k_f/k_p is therefore thought to be ca. 3 for MMA and ca. 10 for STY. This conclusion has been reached by consideration of certain effects which could arise to greater extents when higher concentrations of IOD are used. The first point concerns the values of $\overline{DP}_w/\overline{DP}_n$ found for the various polymers.

The polydispersities for polymers (1), (2) and (3) are low, suggesting that there had been some fractionation during the recovery and purification of the polymers, probably because of loss of those polymer molecules which were rather small. An effect of this type has been demonstrated when polyMMA is precipitated in methanol[6]. The polydispersity is rather small for polymer (5) considering that transfer was quite prominent in the polymerization; it is possible that some of the smallest polySTY molecules were lost from the sample during precipitation in methanol, although it has been shown[6] that such losses are much less significant than in the case of polyMMA. Loss of polymer molecules can have little effect on n since $\overline{DP}_n$ and $\bar{\nu}$ are measured for samples of the same material; $\bar{\nu}$, however, would be overestimated because the lost molecules would be rich in end-groups derived from AIBN. The result of the losses would be to give values of k_f/k_p which are too small.

Primary radical transfer is a process which could interfere with the determination of transfer constants by the application of equation (1), especially for higher concentrations of IOD. The process would arise if a radical from the labelled initiator reacts with the transfer agent instead of adding to the monomer; as a result, the polymer would contain fewer initiator fragments than would be expected. On the basis of a competition between primary radical transfer and 'normal' initiation, according to the following scheme:

$$Me_2\dot{C}(CN) + XH \rightarrow Me_2CH \cdot CN + X \cdot$$

$$\text{rate constant} = k'$$

$$Me_2\dot{C}(CN) + M \rightarrow Me_2C(CN) \cdot M \cdot$$

$$\text{rate constant} = k''$$

where XH and M represent the transfer agent and the monomer, respectively, it is found that:

$$\frac{\text{Number of radicals engaging in primary radical transfer}}{\text{Number of radicals engaging in initiation}}$$

$$= \frac{k'[XH]}{k''[M]}$$

The possible significance of primary radical transfer was discussed for fluorene as a transfer agent during polymerizations of STY and MMA[3]. Its occurrence would lead to an overestimate of $\bar{\nu}$ when that quantity is found from the content of initiator fragments in the polymer. Any effect would become greater as the concentration of transfer agent is raised, with this being more evident when using MMA instead of STY, because k'' for STY is about twice k'' for MMA[7,8].

A third factor to be considered is the likelihood that IOD undergoes some decomposition during the polymerization. The significant product is most probably elemental iodine, which can be regarded as causing

retardation according to the following scheme:

$$P_n \cdot + I_2 \rightarrow P_n \cdot I + I \cdot$$

$$P_n \cdot + I \cdot \rightarrow P_n \cdot I$$
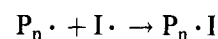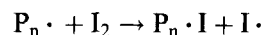
These processes would affect the value of n and so interfere with the determination of the transfer constant by means of equation (1). The production of iodine and therefore the interference would be greater when [IOD] is comparatively high.

The transfer constants for systems involving IOD need revision upwards if the reinitiation stage in the transfer process is inefficient, i.e. if the transfer is degradative. To allow for this effect, equation (1) has been modified[3] to give the following:

$$\frac{k_f[\text{transfer agent}]}{k_p[\text{monomer}]} = \frac{2 - 2n + nf}{2n\bar{\nu}(f - fe + e)} \quad (2)$$

for a system in which the radicals derived from the transfer agent either reinitiate by reacting with monomer or terminate another growing radical. In equation (2), e represents the fraction of the 'transfer' radicals engaging in reinitiation. The quantities f and e have highest possible values of unity and so $(f - fe + e)$ can never exceed unity. Comparison of equations (1) and (2) shows that k_f/k_p is underestimated if equation (1) is applied, when equation (2) should really be used.

The retardation associated with IOD is slight for the polymerizations of STY and MMA, and is due, in part at least, to an impurity formed by slight decomposition of the transfer agent during the polymerization; it is likely therefore that e is not much less than unity. For MMA at $60°C$, f has been taken as 0.1, and if e is then taken as 0.8, the transfer constant already quoted would need to be increased by a factor of 1.2 to allow for the inefficiency of reinitiation. In the case of STY, when taking f as 0.7 and e as 0.8, the correcting factor for k_f/k_p is even smaller, i.e. 1.06.

It must be supposed that fairly high reactivity in transfer is possessed by the $-CHI_2$ and $-I$ end-groups which are likely to be produced when IOD acts as a transfer agent. It can be deduced therefore that the effective value of [transfer agent]/[monomer] does not decrease as much as might be expected from the preferential consumption of transfer agent in a system in which k_f/k_p is appreciably greater than unity.

Table 1 also contains the results of a few experiments with transfer agents other than IOD. The value of k_f/k_p for bromoform with STY is, as expected, considerably smaller than that for IOD when using this monomer. The transfer constant for chloroform with MMA is even smaller, but the present value is similar to a previously reported value[9] of 4.54×10^{-5}. There is very little difference between the present results for chloroform and deuterochloroform, suggesting that the reaction between a polyMMA radical and chloroform is principally one of chlorine abstraction rather than hydrogen abstraction, otherwise an isotope effect would have caused the deuterated substance to be much less reactive. It should be noted that these present results for chloroform and deuterochloroform with MMA must be subject to some uncertainty because the values of n for polymers (9) and (10) are only a little less than the value of 1.05 expected for polymers prepared under similar conditions but in the absence of transfer agent. Quite substantial

changes in n for polymers (9) and (10) would be required to give values of k_f/k_p differing to the extent which might be expected if the transfer process were influenced by a primary isotope effect; thus, if n were 1.00 for polymer (10) and the other quantities were all unaltered, k_f/k_p would become 4.0×10^{-5}, a value which is still ca. 60% of the value of k_f/k_p found for chloroform with MMA.

Walling[10] commented on reactions of simple hydrocarbon radicals with chloroform; for these systems, it appears that hydrogen abstraction is favoured over chlorine abstraction. It is clear, however, that there is a delicate balance between control by resonance stabilization of the product radical (favouring production of $\cdot CCl_3$ rather than $\cdot CHCl_2$), and the effects of bond strengths which would lead to abstraction of chlorine to give $\cdot CHCl_2$. It may be that the nature of the abstracting radical has a large influence on the course of reaction.

REFERENCES

1   Berger, K. C. and Brandrup, G. in 'Polymer Handbook' (Eds. J. Brandrup and E. H. Immergut), 3rd Edn, Wiley, New York, 1989, p. II-94
2   Barson, C. A., Bevington, J. C. and Hunt, B. J. *J. Polym. Sci. Polym. Chem. Edn* 1995, **33**, 863
3   Barson, C. A., Bevington, J. C. and Hunt, B. J. *J. Polym. Sci. Polym. Chem. Edn* 1996, **34**, 227
4   Ullisch, B. and Burchard, W. *Makromol. Chem.* 1977, **178**, 1427
5   Yuan, C. M. and Di Silvestro, G. *Macromol. Chem. Phys.* 1995, **196**, 2905
6   Barson, C. A., Bevington, J. C. and Hunt, B. J. *Eur. Polym. J.* in the press
7   Bevington, J. C., Huckerby, T. N. and Hutton, N. W. E. *J. Polym. Chem. Polym. Chem. Edn* 1982, **20**, 2655
8   Héberger, K. and Fischer, H. *Int. J. Chem. Kinet.* 1993, **25**, 249
9   Chadha, R. N., Shukla, J. S. and Misra, G. S. *Trans. Faraday Soc.* 1957, **53**, 240
10   Walling, C. 'Free Radicals in Solution', Wiley, New York, 1957, p. 255