

Photopolymerization of 2-(dimethylaminoethyl)methacrylate induced by diacetoxyiodobenzene and bis(trifluoroacetoxy)iodobenzene

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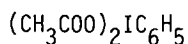
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Summary

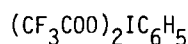
The title hypervalent iodine compounds are efficient photoinitiators for the polymerization of 2-(dimethylaminoethyl)methacrylate. The polymer is formed in daylight but faster under UV irradiation, with high conversion; its molecular weight $\langle M_n \rangle$ is 9×10^4 daltons. Copolymerization of this monomer with styrene occurs also under similar conditions at a high rate. A free radical mechanism is suggested for these polymerizations.

Introduction

Recently we have demonstrated the efficiency of diacetoxyiodobenzene (DAI) and bis(trifluoroacetoxy)iodobenzene (BTI) as photoinitiators in a number of cationic polymerizations (1).



DAI



BTI

Diaryliodonium salts constitute another class of hypervalent iodine compounds, which are excellent photoinitiators mainly for cationic polymerization (2,3) but also for free radical polymerization, in which case they serve as co-initiators (4-6). This dual reactivity has been attributed to their ability to serve as one-electron acceptors. It occurred to us that DAI and BTI might be useful photoinitiators for a monomer undergoing free radical polymerization and possessing a one-electron oxidisable group. For this purpose we have chosen 2-(dimethylaminoethyl)methacrylate (DMAEM), a monomer known to be polymerized by free radical or anionic mechanism (7), with the added advantage that its water-soluble polymer is a good surface tension modifier which has applications in medicine and industry (8,9). In this communication we present preliminary findings on the polymerization of DMAEM catalysed by either DAI or BTI and also by diphenyliodonium tetrafluoroborate.

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Experimental

Monomers and solvents were purified by conventional drying and distillation procedures. DAI, BTI and $(C_6H_5)_2I^+BF_4^-$, all of which are also commercial products, have been synthesised by standard methods (10). Polymerizations were carried out in glass tubes without special precautions under daylight and air atmosphere at room temperature for 24h. The initiator was first dissolved in the polymerization solvent (CH_2Cl_2 or benzene) and then the monomer was added to this solution so that the ratio (v/v) of DMAEM:solvent to be constant and equal to 3:7. In the case of photopolymerizations, the solution of polymerization prepared as above was placed in quartz tubes and irradiated at room temperature and air atmosphere for 24h at a distance of 10cm from the UV source (a Philips 400-W low-pressure mercury lamp). The polymer was precipitated by addition of hexane and dried to a constant weight. From this weight the yield (% conversion) and the rate of polymerization were calculated.

The intrinsic viscosity of the polymers, determined in 0.1N NaCl aqueous solution at 25°C with an Ubbelohde viscometer, was used for the calculation of the molecular weight $\langle M_n \rangle$ from the equation (7):

$$[\eta] = 6.14 \cdot 10^{-5} \langle M_n \rangle^{0.79}$$

I.r. spectra (in $CHCl_3$ solution) were recorded with a Perkin-Elmer 281-B spectrometer and 1H n.m.r. spectra (in $CDCl_3$) with a Varian A-60A instrument.

Results and Discussion

When a solution of DMAEM in benzene or methylenechloride is treated with either DAI or BTI a blue colour develops (broad absorption at ~600 nm) which after a few minutes turns yellow. With time, polymerization takes place the results of which appear in Table 1. It can be seen that DAI is a more efficient initiator than BTI and that for both compounds there is a maximum of concentration (3g/100 ml of solution) beyond which yields of polymer do not increase. These yields as well as the rate of polymerization are greater in CH_2Cl_2 than in benzene: for DAI the yields are approximately double in CH_2Cl_2 , whereas the rate of polymerization amounted to $4.8 \times 10^{-2}\%$ conversion/h in CH_2Cl_2 and $1.2 \times 10^{-2}\%$ conversion/h in benzene (both at a concentration of 0.5g DAI/100 ml of solution). By using diphenyliodonium tetrafluoroborate no colour change was observed and no polymerization took place under similar conditions.

It is noted that other acrylic esters such as methyl acrylate and

TABLE 1
Polymerization of DMAEM initiated by DAI and BTI

| Initiator (g/100ml solution) | Solvent | Yield (% conversion) |
|------------------------------|---------------------------------|----------------------|
| DAI (0.3) | CH ₂ Cl ₂ | 2.4 |
| | C ₆ H ₆ | 1.1 |
| DAI (0.5) | CH ₂ Cl ₂ | 8.5 |
| | C ₆ H ₆ | 4.2 |
| DAI (1.0) | CH ₂ Cl ₂ | 34.3 |
| | C ₆ H ₆ | 15.6 |
| DAI (3.0) | CH ₂ Cl ₂ | 55.6 |
| | C ₆ H ₆ | 30.2 |
| BTI (0.3) | CH ₂ Cl ₂ | 1.0 |
| | C ₆ H ₆ | 0.5 |
| BTI (0.5) | CH ₂ Cl ₂ | 1.6 |
| | C ₆ H ₆ | 1.1 |
| BTI (1.0) | CH ₂ Cl ₂ | 3.3 |
| | C ₆ H ₆ | 2.1 |
| BTI (3.0) | CH ₂ Cl ₂ | 9.7 |
| | C ₆ H ₆ | 6.5 |

methyl methacrylate were not polymerized by DAI or BTI under similar conditions.

The yields of poly-DMAEM induced by DAI or BTI decrease 10-fold in the dark, but increase considerably upon UV irradiation, as it is shown in Table 2, where polymerization rates (R_p) rather than yields have been tabulated. In photopolymerizations only DAI was used and in one instance, for comparison reasons, diphenyliodonium tetrafluoroborate. From Table 2 it is evident that DAI is a very efficient photoinitiator, since at the level of 0.5g/100 ml solution it accelerates the polymerization rate 200-fold, in comparison with the rate obtained without irradiation. Increasing concentrations of DAI from 0.2g to 1g increase linearly the polymerization rate, which is again greater in CH₂Cl₂ than in benzene. The photopolymerization proceeds also modestly without DAI, with a higher rate in benzene, whereas the addition of diphenyliodonium tetrafluoroborate has a considerable accelerating effect, nevertheless smaller than that of DAI.

TABLE 2
 Photopolymerization of DMAEM initiated by DAI and $(C_6H_5)_2I^+BF_4^-$

| Initiator (g/100ml solution) | Solvent | R_p (% conversion/h) |
|------------------------------|------------|------------------------|
| --- (0.0) | CH_2Cl_2 | 2.1 |
| | C_6H_6 | 2.6 |
| DAI (0.2) | CH_2Cl_2 | 6.1 |
| DAI (0.5) | CH_2Cl_2 | 9.3 |
| DAI (0.7) | CH_2Cl_2 | 10.7 |
| DAI (1.0) | CH_2Cl_2 | 14.5 |
| | C_6H_6 | 8.0 |
| $Ph_2I^+ BF_4^-$ (0.2) | CH_2Cl_2 | 4.0 |

From the data of Table 2, R_p was found to be proportional to the square root of the concentration of the initiator; this indicates that DAI initiates the polymerization of DMAEM by radical mechanism. The intrinsic viscosity of the poly-DMAEM thus obtained is 0.507 dl/g, corresponding to a $\langle M_n \rangle$ equal to 9×10^4 daltons. I.r. and 1H n.m.r. spectra of poly-DMAEM produced by the above methods were very similar with the spectra of poly-DMAEM produced by AIBN-initiation.

The polymerization of styrene (St) did not proceed to a considerable degree by UV-DAI. However mixtures of DMAEM and St afforded easily a copolymer. The composition of the copolymer, based on elemental analysis of nitrogen and the rate of copolymerization for various ratios of the monomers are shown together in Figure 1. The composition curve 1 (Fig. 1) which is a typical radical copolymerization curve, enhances the view that DAI initiates the polymerization of DMAEM by radical mechanism.

A comparison of present results with those obtained previously (1) in the photopolymerization of t-butyl vinyl ether induced by DAI and BTI reveals that the reactivity of these photoinitiators is reversed and an analogous reversal of polymer yield holds also for the solvent: best results for DMAEM are obtained by DAI in CH_2Cl_2 , whereas BTI in benzene were the most favorable conditions for the ether (1). Clearly, a different mechanism operates in these two cases. We suggest that the cationic mechanism which has been established for the polymerization of t-butyl vinyl ether has now changed to a free radical mechanism for the polymerization of DMAEM.

A partial sequence of steps likely to take place is the following, by analogy with mechanisms proposed for the non-photochemical arylation of ter-

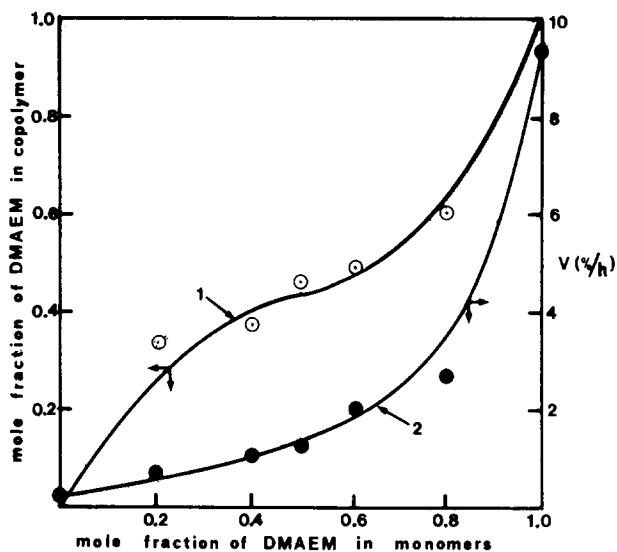
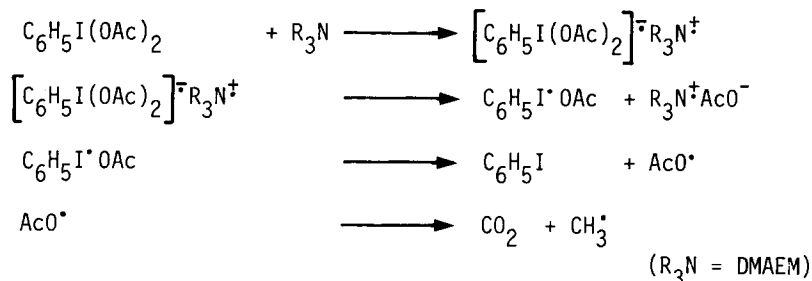
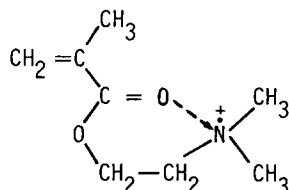


Figure 1. Copolymer composition (curve 1) and rate of copolymerization (curve 2) by variation of DMAEM-St composition.

tertiary amines by diaryliodonium salts (11) the photocatalysed step being possibly the second or third equation:



The radical cation $\text{R}_3\text{N}^\ddagger$ may be stabilised by intramolecular transfer of electron density from the methacrylate moiety and must be responsible for the blue color initially developed:



Apparently the presence of the Me_2N group is essential for the poly-

rization to occur. However, the above species is unlikely to participate in the polymerization to a significant degree, because it does not account for the high rate increase under photochemical conditions; besides it is produced by both DAI and BTI and yet the former is more efficient than the latter. More probably the iodine free radical, $C_6H_5I^{\bullet}OAc$ and its decomposition products, AcO^{\bullet} and CH_3^{\bullet} , make the greater contribution, serving as the true initiators. The enhanced reactivity in CH_2Cl_2 makes also likely its participation in the process of the polymerization, whereas trifluoroacetic acid released from BTI (1) must have an inhibiting effect related to its ability to protonate DMAEM. There is no doubt that the situation is very complicated and no detailed mechanism can be suggested. Further studies planned for the photopolymerization of various monomers promoted by hypervalent iodine compounds in general may help in elucidating to some degree their interaction.

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