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Low temperature initiation by methylene bis(diethyl malonate)–Ce(IV) redox system in organic solvents

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Abstract

Methylene bis(diethyl malonate)–cerium ammonium nitrate redox couple serves as initiator in triethyl phosphate for polymerization of methyl methacrylate at room temperature. High polymerization yield (>90%) can be attained at moderate concentration ratios (monomer/initiator ≅ 70:1) in 4 h reaction periods. Increasing molar ratio of methylene bis(diethyl malonate) to cerium salt causes to low molecular weights which implies possibility of its chain transfer effect through active methylene groups at the same time. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Low temperature redox polymerization of vinyl monomers is of importance especially for industrial view points. Besides its economical benefits suppression of side reactions such as branching is its additional advantage over common thermal initiation methods.

There are many possibilities for redox initiation in aqueous solutions. Fenton reagent (1), persulfate-various reductants such as metals, metal complexes, thiols and polyhydric phenols [1,2]. Cerium(IV)–alcohol [3] or -amino acids [4,5] and permanganate with oxalic acid [6] and ascorbic acid [7] redox couples are well-known low temperature radical initiators for polymerization of water soluble vinyl monomers. However redox initiation in organic solvents is not so much successful. Peroxide–tertiary amine [8] or hydroperoxide–cobalt octeate [9] systems reported are not applicable for all vinyl polymerizations. In fact redox reactions are more complicated than we thought and presumably water involves in some steps of the reactions.

In the present communication we have described redox initiation of methyl methacrylate (MMA) polymerization with cerium(IV) ammonium nitrate (CAN) and an active methylene compound, methylene bis(diethyl malonate) (MBD) in triethyl phosphate (TEP).

The cerium salt has appreciable solubility in TEP. MBD is an oily liquid and miscible with many organic solvents. In the study, the efficiency of initiation has been tested in polymerization of MMA at different combinations.

2. Experimental

The monomer, MMA was distilled before use. All the other chemicals were analytical grade chemicals. They were used as supplied (diethyl malonate (E. Merck), triethyl phosphate (E. Merck), cerium ammonium nitrate (Fluka)).

MBD was prepared by condensation of diethyl malonate with formaldehyde as described in the literature [10]. The product is a heavy viscous liquid.

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2.1. Polymerization reactions

In the redox polymerization of MMA, solution of CAN in TEP, MMA and MBD were mixed and the mixture was stirred at room temperature. A typical procedure is as follows: 13.68×10^{-4} mol CAN was dissolved in 10 ml TEP. The solution was added to 0.1 mol MMA in a two-necked flask equiped with reflux condenser and a nitrogen inlet. Under nitrogen atmosphere 15.52×10^{-4} mol of MBD was added to the mixture and stirred at room temperature. After a while, the reaction content was poured into 50 ml methanol. The white polymer precipitated was filtered and dried under vacuum at 40°C for 24 h.

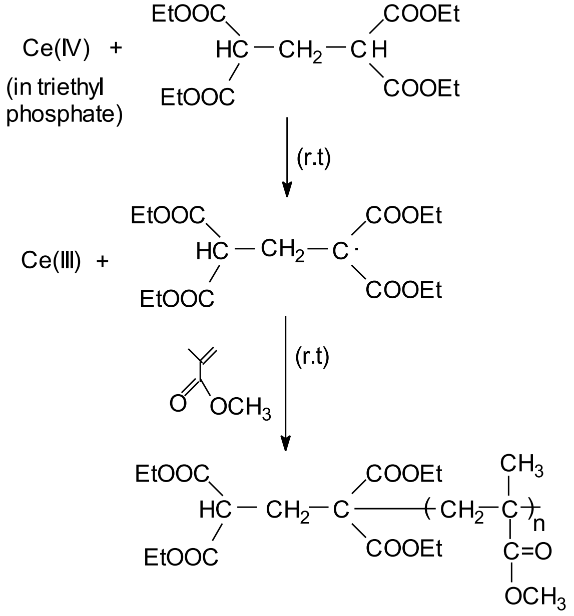
2.2. Polymer characterization

The polymer obtained was characterized by ^{1}H-NMR (using Bruker, 250 mHz), FT-IR (Mattson 1000) and viscosity measurements (Ubbelohde viscometer).

3. Results and discussion

CAN is a powerful oxidizing agent, but it is not soluble in organic solvents. Fortunately it dissolves appreciable amounts in triethyl phosphate. Although it is not soluble in methyl methacrylate, 0.75 g of it remains soluble in 20 g of MMA–TEP (1:1) mixture. In the case of low percentages of TEP (5%), an immediate precipitation of CAN is observed. Because of this fact, TEP was used as solvent in the redox initiation. As far as we know, the use of active methylene compounds has not been reported in the literature. We have observed that MBD acts as redox couple together with CAN dissolved in TEP and polymerization of MMA takes place in acceptable periods at room temperatures.

The polymerization of MMA can be depicted simply as shown in Scheme 1:



Scheme 1.

Here, MBD is believed to serve as reducing agent for Ce(IV). Active methylene group must be considered as the radical generating center initiating polymerization of MMA. Oxidation potential of Ce(IV) is known to be higher in acidic media. In the polymerization, hydrogen on the active methylene group can be considered as a weak proton source due to enolization of MBD. Electron transfer from enolate anion or from its carbanion tautomer by Ce(IV) seems to be most plausable mechanism for initiation of the polymerization. This mechanism has been evidenced by ^{1}H-NMR (Fig. 1) spectra of the polymer obtained by using a high initiator ratio (([initiator]/[monomer]) = 1/10), which represents MBD moieties as polymer end groups. Thus multiple signals around 4.1 ppm are due to methylenoxy protons of MBD. Integral ratio of these protons to those of methoxy proton signals at 3.6 ppm gives about 13 repeating units which corresponds to 1300 Da of molecular weight.

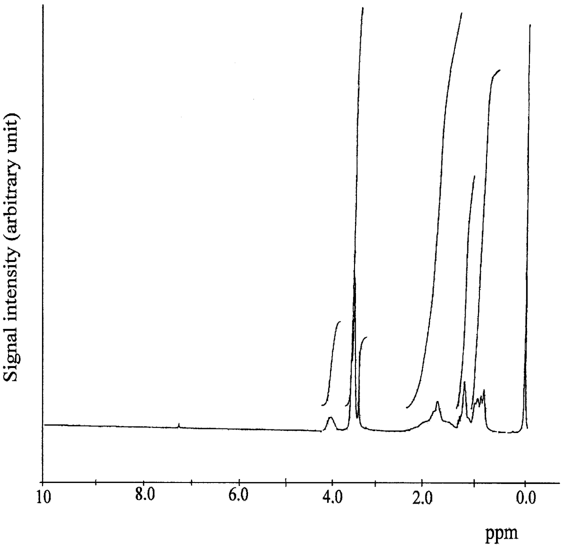


Fig. 1. ^{1}H-NMR Spectrum of the polymer obtained by using a high initiator ratio [initiator]/[monomer] = 1/10.

Diethyl malonate itself can be considered as reducing agent in the polymerization, However experiments indicate that when MBD is replaced with diethyl malonate no polymer is obtained in 10 h at the same reaction conditions, most probably because of less enolizability of the later.

Table 1
Polymerization yields and molecular weights in various $n_{\mathrm{MBD}}/n_{\mathrm{CAN}}$ ratios

$n_{\mathrm{MBD}}/n_{\mathrm{CAN}}$	Yield (%)	M_v[a]	Polymerization time (h)
1.14	92	52 500	4
2.28	60	21 550	3
4.56	31	19 650	2

MMA = 10 g (0.1 mol); TEP = 10 ml; $n_{\mathrm{CAN}} = 1.36 \times 10^{-3}$ mol.
[a] Viscosity-average molecular weight.

Table 2
The effect of mole ratios of the monomer to initiator on conversion yield and molecular weights of the polymer

$n_{\mathrm{CAN}}/n_{\mathrm{MMA}}$	Yield (%)	M_v[a]	Polymerization time (h)
0.0136	92	52 500	4
0.0068	45	52 800	4
0.0034	31	76 500	4

MMA = 10 g (0.1 mol); TEP = 10 ml; $n_{\mathrm{MBD}}/n_{\mathrm{CAN}} = 1.1$.
[a] Viscosity-average molecular weight.

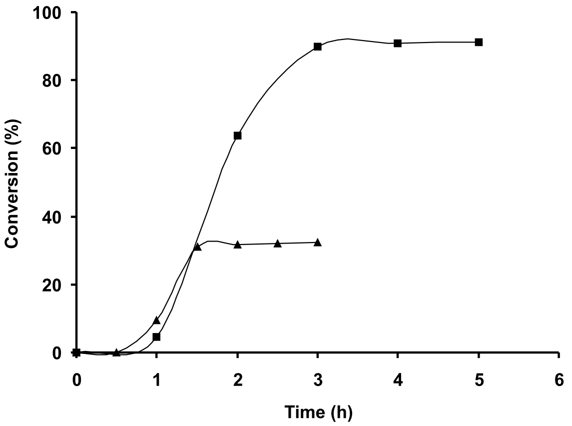


Fig. 2. The Time dependence of the polymerization yields with different MBD contents. MMA = 0.025 mol; TEP = 2.5 ml; Ce(IV)= 3.42×10^{-4} mol; MBD = 15.52×10^{-4} mol (■), 62.11×10^{-4} mol (▲).

In the case for MBD/CAN > 1 molar ratios, the molecular weight and polymerization yields are low (Table 1) which implies chain transfer and terminating effect of MBD.

Of course, the procedure worths to investigate in detail to find the polymerization parameters and limitations. However, these preliminary results show that the low temperature redox system presented seems to be promising for initiation in organic solvents.

Conversion–time plots of the polymerization with $n_{\mathrm{MBD}}/n_{\mathrm{CAN}} = 1.14$ ratios indicate that (Fig. 2) the polymerization is almost quantitative in about 90 min. Whereas increasing MBD ratio causes to substantial low polymerization yields (see lower curve in Fig. 2) This result can be ascribed to terminating effect of MBD at the same time. As it might be expected, increasing monomer ratios result in high molecular weight polymers but low polymerization yields for 4 h of reaction times (Table 2).

In conclusion, active methylene compounds can be used as a reducing agent in combination with cerium ammonium nitrate for polymerization of MMA in TEP solvent at room temperature.

Acknowledgements

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