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Polymerization of acrylamide initiated by the redox system Ce(IV)-4,4'-azobis (4-cyano pentanol)

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SUMMARY

Acrylamide was polymerized by ceric ion Ce(IV)-4,4'-azobis(4-cyano pentanol)(ACP) redox pair in aqueous nitric acid under nitrogen atmosphere. The rate of polymerization is proportional to $[M]^2$,[ACP] and $[Ce(IV)]^{-1}$. Termination mechanism which was exclusively linear offered one azo group per polymeric chain. The obtained polyacrylamide can be used as a water soluble initiator for vinyl polymerization.

INTRODUCTION

Synthesis of block copolymers has recently attracted a revitalized interest in connection with the demand of novel materials possessing specific physical properties. Beside the various synthetic methods, polymeric azo initiators have been succesfully used for the synthesis of block copolymers via a radical mechanism (1). They can be prepared from low molar-mass azo initiators by means of condensation (2-5), cationic (6-8) and anionic polymerization (9,10) processes without any loss of the azo function.

It is well known that certain ceric salts such as the nitrate and sulfate form very effective redox systems in the presence of organic reducing agents such as alcohols (11),aldehydes (12),and amines (13). Application of this technique to polymers with pendant reducing groups, namely alcholic hydroxyl groups, provides a versatile method for graft polymerization of suitable monomers (14).

In the present work, cerium ion was used in conjuction with 4,4'-azobis (4-cyano pentanol) (ACP) to initiate a polymerization of acrylamide (AAm). The resulting polymer possesses central thermosensitive azo function,

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EXPERIMENTAL

Materials :

Acrylamide (AAm)(Fluka) was recrystallized from ethylacetate, ceric ammonium nitrate (Aldrich) was used without further purification. 4,4'-azobis (4-cyano pentanol)(ACP) was synthesized according to the described procedure(15).

Polymerization by the Redox System :

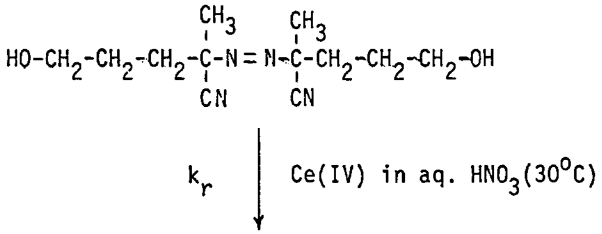
Schlenk tubes of aqueous solutions of AAm containing given amount of ACP were degassed and purged with nitrogen in three cycles. Appropriate solutions of ceric ammonium nitrate in 1N nitric acid was then added. The polymerization experiments were conducted with stirring in the dark at 30°C. PAAm formed was precipitated from the solution into ten-fold excess acetone.

Emulsion Polymerization :

PAAm obtained by the method described above was dissolved in water containing a given amount of sodium dodecyl benzene sulphonate, NaH_2PO_4 and styrene (St). Polymerization of styrene was induced by heating of the nitrogen-purged solution at 60°C with stirring. Homo polystyrene (PSt) and PAAm were separated by extracting with toluene and water, respectively.

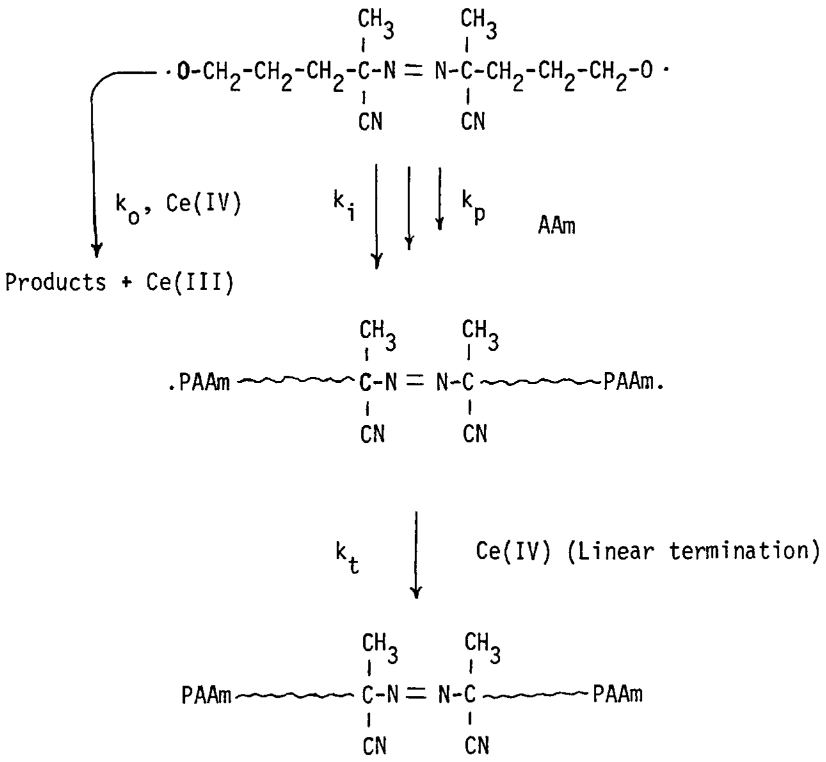
RESULTS and DISCUSSION

The polymerization of AAm was carried out by a redox system consisting of ceric ions and an azo-initiator having alcoholic hydroxyl groups according to the following reactions.



$$HO\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}\underset{CN}{\overset{CH_3}{C}}\text{-}N{=}N\text{-}\underset{CN}{\overset{CH_3}{C}}\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}OH$$

$$k_r \Big\downarrow \; Ce(IV)\text{ in aq. }HNO_3(30^{o}C)$$



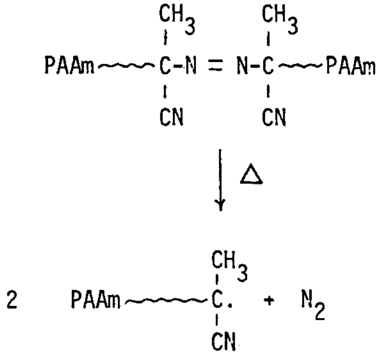
Applying the steady state assumption to primary radicals and chain radicals, one can derive the following expressions for the rate of polymerization (R_p),

$$R_p = \frac{k_p k_r \ [ACP] \ [M]^2}{k_t([M] + k_o/k_i \, [Ce(IV)])}$$

It is seen from this expression R_p is proportional to [ACP], $[M]^2$ and $[Ce\ (IV)]^{-1}$. These relationships were experimentally established for the ACP-Ce(IV) system. (Figures 1-3)

Figure 1. shows the dependence of R_p on [ACP] . Based on the insignificant polymerization in the absence of the reducing agent,it is concluded that polymerization of AAm is initiated by the redox system consisting of ceric ion and reducing groups on the azo initiator. Furthermore, R_p increased linearly with increasing alcohol concentration in the range of $0{,}22\text{-}5.94 \times 10^{-3}$ mol l^{-1} indicating the linear termination by Ce(IV). Similarly, the square dependence of R_p on monomer was observed in the concentration range of 0.2-0.45 mol l^{-1} (Figure 2). The $[M]^2$ dependence deviates from the linearity at high monomer concentrations. The rate was also proportional to [Ce(IV)] inversely (Figure 3). This finding eliminates the mutual termination and emphasizes the linear mode termination (16) as a major process.

This process leads to the formation of PAAm with an azo group in the main chain. PAAm functionalized in this way will decompose on heating and forms radicals in a similar way to the low-molar mass azo initiators.



$$\text{PAAm}\sim\sim\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CN}{|}}{C}}-N=N-\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CN}{|}}{C}}\sim\sim\text{PAAm} \xrightarrow{\Delta} 2\ \text{PAAm}\sim\sim\sim\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CN}{|}}{C}}\cdot + N_2$$

If the thermolysis is carried out in the presence of free radically polymerizable monomer, water soluble or in emulsion, the PAAm attached radical may initiate free radical polymerization to generate copolymers. As a crude demonstration, PAAm was used to initiate the emulsion polymerization of styrene. Experimental conditions and results are shown in Table 1.

In conclusion, these preliminary results clearly indicate the usefulness of ceric ion-azo initiator redox system for the preparation of water soluble polymers having appropriate initiating functionality for subsequent vinyl polymerization. Detailed studies on block-copolymerization by means of azo-linked PAAm are now in progress.

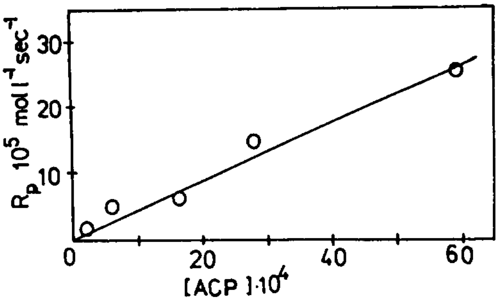


Fig.1 : Plot of R_p vs [ACP], [M]=0.386 mol.l^{-1}, [Ce(IV)]=3x10^{-4}mol l^{-1} in 1N HNO_3 at 30^{o}C.

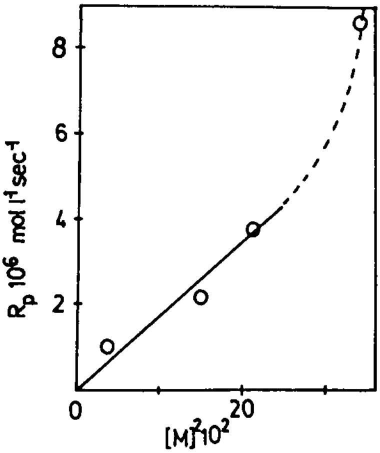


Fig.2 : Plot of R_p vs $[M]^2$, [Ce(IV)]= 3x10^{-4}mol l^{-1}, [ACP]= 1.98x10^{-3}mol l^{-1} [HNO_3]=1N at 30^{o}C.

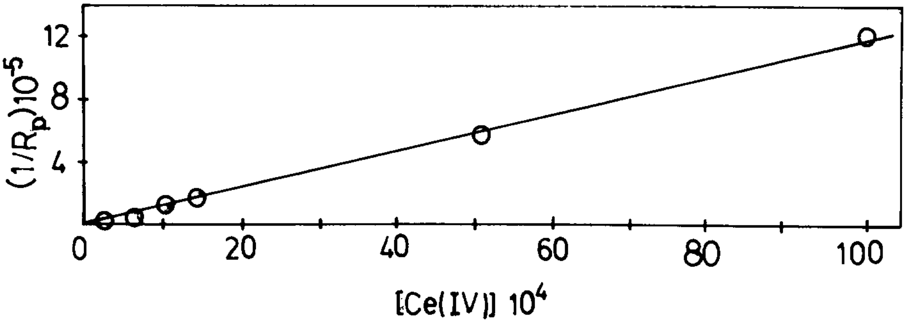


Fig.3 : Plot of $1/R_p$ vs [Ce(IV)] , [M]=0.579 mol l^{-1} , [ACP]=1.98x10^{-3}mol l^{-1}, [HNO_3]=1N at 30^{o}C.

Table 1. Emulsion Polymerization of Styrene Initiated by Polyacrylamide at 60^oC.

Polymeric initiator	, g	0.123
Styrene	, ml	10
Time	, h	6
SDBS, Emulsifier	, g	0.210
NaH_2PO_4	, g	0.010
Water	, ml	20
Conversion	, % St	3
Block copolymer	, % wt	7.1

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