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Aqueous polymerization of acrylamide initiated by 4,4′-azobis (4-cyano pentanol) and chain extension of polyacrylamide by means of ceric ion redox systems

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SUMMARY

The polymerization of acrylamide (AA) initiated by 4,4'-azobis (4 cyanopentanol) (ACP) was investigated in aqueous solution at 60°C. The molecular weight and the conversion depend on polymerization duration and initiator concentration. Polymerization of AA initiated by ACP yields polyacrylamide (PAA) with hydroxyl terminal groups. Redox polymerization of AA initiated by hydroxyl terminated PAA in conjuction with Ce(IV) provided increase in the molecular weight of the initial polymer.

INTRODUCTION

During the last two decades, the industrial use of acrylamide polymers has increased tremendously. The main uses of polyacrylamides involve water treatment, mining and paper manufacture. In some uses such as flocculation, the objective is to attain a very high molecular weight.

Without doubt, aqueous polymerization using conventional azo, peroxy or redox initiators is the chiepest and the most widely used way of producing such materials (1). However, the method is straight forward for low molecular weights, but very high molecular weight polymer forms gels that are difficult to deal with.

Ceric salts such as nitrate and sulphate have been used as effective initiators in combination with organic reducing agents such as alcohols (2), aldehydes (3), and amines (4). The generally accepted mechanism for initiation involves the formation of a free radical in the reductant groups by transfer of an electron. Application of this technique to polymers having pendant reducing groups, provides a versatile method for graft polymerization of suitable monomers (5). In preceding papers, we reported the use of Ceric ion Ce(IV) with low molar-mass(6) and polymeric azo initiators (7-8) having hydroxyl functions as redox pairs for the polymerization of acrylamide (AA) and methylmethacrylate (MMA). The resulting polymers possess central thermosensitive azo functions which can be used for subsequent vinyl polymerization to yield block copolymers.

In the present paper, we report the aqueos polymerization of AA initiated by 4,4'-azobis (4-cyano pentanol) (ACP) resulting in polymers with hydroxyl groups. Subsequently, chain extension of the obtained polyacrylamide (PAA) by ceric ion was investigated.

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EXPERIMENTAL

Materials :

Acrylamide (AA) (Fluka) was recrystallized from ethylacetate, ceric ammonium nitrate was used without further purification. 4,4-Azobis (4-cyano pentanol) (ACP) was synthesized according to described procedure (9).

Aqueous Polymerization of Acrylamide :

Aqueous solution of AA containing a known amount of ACP were purged with nitrogen in the usual manner and placed in a thermostat at 60°C. At the end of polymerization, the reaction mixtures were poured into ten-fold excess of acetone and the precipitated polymers were filtered and dried.

Polymerization by the Redox System :

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

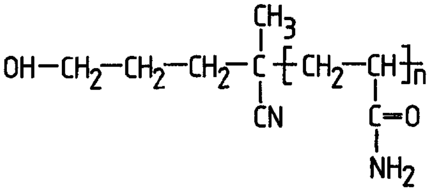
Molecular weights were determined from the solution viscosities at 30°C in water with the aid of the following equation (10).

$$[\eta] = 6.8\mathrm{x}10^{-4}\,\overline{Mn}^{0.66}\ .$$

RESULTS AND DISCUSSION

In the first part of paper, aqueous polymerization of AA carried out thermaly under the action of ACP is approached. The thermal polymerization was carried out at different durations, temperatures and initiator concentrations. Variations in monomer conversion and molecular weight of PAA as a function of these parameters were observed (Figures 1-4). From these figures, it can be seen that the conversion is directly proportional to the amount of initiator used and polymerization time up to the certain level and thereafter levels off, while the molecular weight decrease with increasing initiator concentration. These results indicate that polymerization of AA with ACP shows the general behaviour of this type of initiation (11).

AA polymerization by means of ACP is expected to yield PAA molecules with one hydroxyl groups per chain since chain termination is believed to be mainly by disproportionation (12, 13).



$$\mathrm{OH{-}CH_2{-}CH_2{-}CH_2{-}}\overset{\mathrm{CH_3}}{\underset{\mathrm{CN}}{\mathrm{C}}}\mathrm{{-}\!\left[CH_2{-}\underset{\underset{\underset{NH_2}{|}}{C{=}O}}{CH}\right]_n}$$

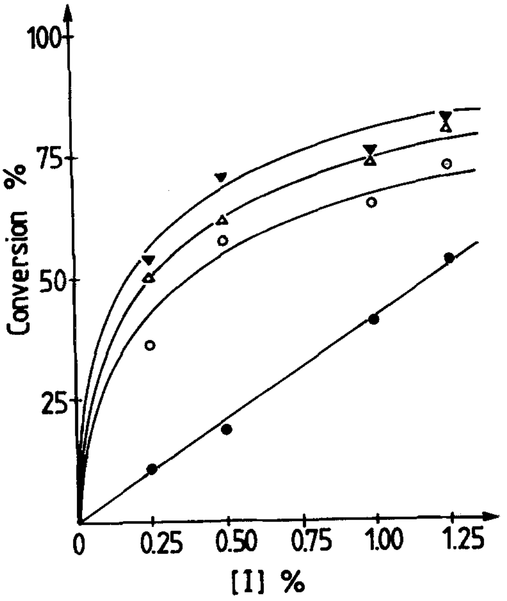


Fig. 1: Conversion-Initiator concentration relations for different polymerization durations in aqueous polymerization of acrylamide at 60°C

●:15 min; ○:30 min;
△:45 min; ▼:60 min
[Acrylamide]=2.71 mol.l^{-1}

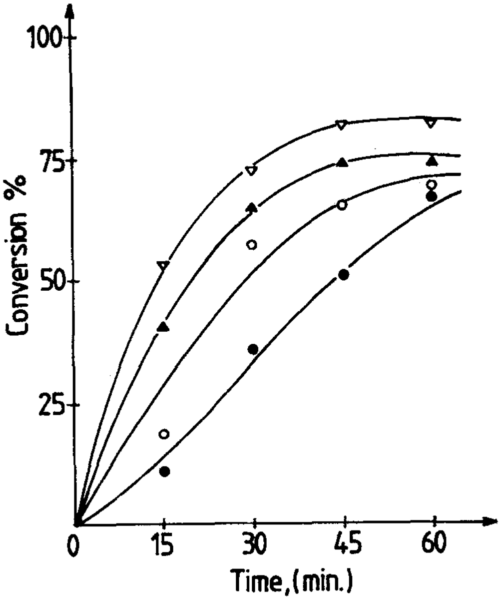


Fig. 2: Conversion-time relations for different initiator concentration in aqueous polymerization of acrylamide

●: [I]=0.25 %;○: [I]=0.5 %;
▲: [I]=1.0 %; ▽: [I]=1.25 %;
[Acrylamide]=2.71 mol.l^{-1}

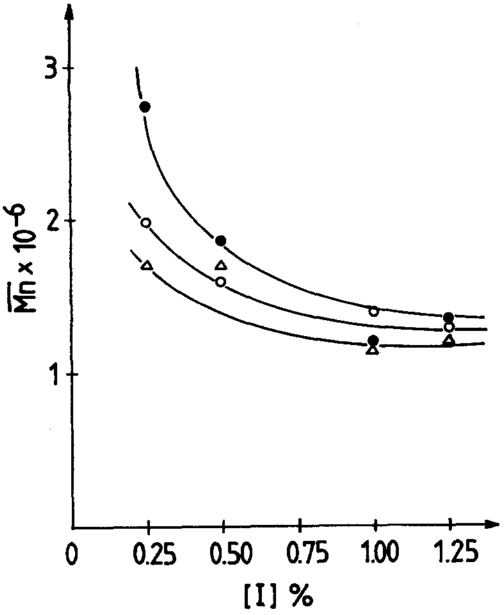


Fig. 3: Molecular weight-Initiator concentration relations for different polymerization durations in aqueous polymerization of acrylamide

●:15 min; ○:30 min;
△:45 min;
[Acrylamide]=2.71 mol.l^{-1}

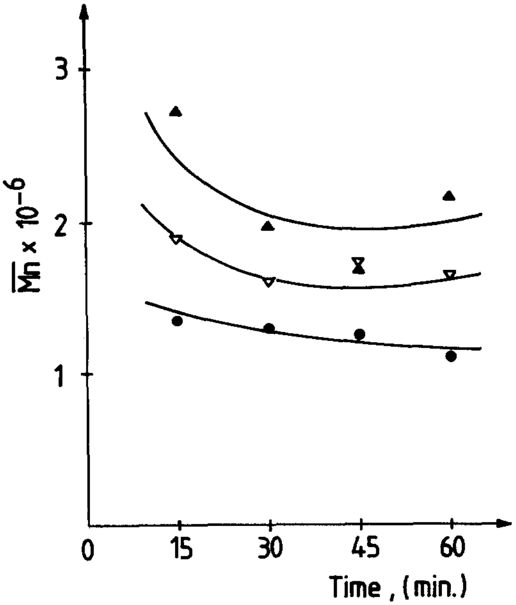


Fig. 4: Molecular weight-Polymerization time relations for different initiator concentrations in aqueous polymerization of acrylamide,

▲:[I]=0.25 %; ▽:[I]=0.5 %
●:[I]=1.25 %;
[Acrylamide]=2.71 mol.l^{-1}

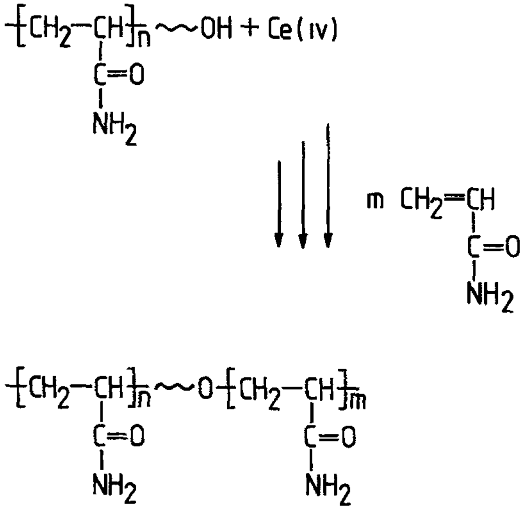
Table 1
Chain Extension of PAA by Redox Polymerization[a]

[PAA] (g/l)	[AA] (mol/l)	$10^{-5}\ \overline{M}_n$[b] Initialy	$10^{-5}\ \overline{M}_n$[b] After Polymerization	Increase in $\overline{M}_n$ (%)
6.3	1.6	6.39	19.73	208
6.3	0.8	6.39	13.16	105.8
5.9	0.6	7.82	10.92	39.6
5.9	0.4	7.82	8.35	6.8

[a] $[Ce(IV)] = 2.45$ mol.l^{-1} in all cases

[b] Values of $\overline{M}_n$ estimated from measurements of $[\eta]$ in water at 30°C

Whether or not the product polymer possesses one or two hydroxyl end groups depends mainly on the ratio of disproportionation to combination for particular polymerization. In either case, chain extension via redox polymerization of AA may be accomplished essentially as indicated below.



$$\left[CH_2-\underset{\underset{NH_2}{|}}{\underset{C=O}{|}}{CH}\right]_n\sim OH + Ce(IV) \xrightarrow{m\ CH_2=CH-C(=O)-NH_2} \left[CH_2-\underset{\underset{NH_2}{|}}{\underset{C=O}{|}}{CH}\right]_n\sim O-\left[CH_2-\underset{\underset{NH_2}{|}}{\underset{C=O}{|}}{CH}\right]_m$$

Typical results are given in Table 1. It is interesting to note that PAA with lower molecular weight appears to undergo chain extension more efficiently indicating the importance of the hydroxyl group concentration. The efficiency of the chain extension is affected also by the amount of monomer in the redox system.

A different sequence of the same procedure may also be used. As previously reported (6), polymerization of AA initiated by ACP-Ce(IV) redox system provided the formation of PAA with one (-N=N-) group per chain. Thermal decomposition of the azo linkage produces two polymeric radicals per chain, which gives rise to the chain extension in the presence of AA.

As a typical example, 0.15 g. of azo-linked PAA ($\overline{M}_n$=1679359) which was obtained as described previously (6), and AA [1.48 mol/l] was dissolved in 25 ml. of water and heated at 60^{o}C for 4 hours. The molar mass of the resulting polymer ($\overline{M}_n$=2133910) was higher than that of the initial polymer indicating addition of the monomer to the polymeric radical formed upon cleavage of the azo group.

These results indicate the efficiency and convenience of using ACP-Ce(IV) combined system to prepare high molecular weight PAA in aqueous solution via a two-step procedure which avoids the problems associated with aqueous gel.

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