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Yinghai Liu[a]; Junbo Li[a]; Lanying Yang[a]; Zengqian Shi[a]
[a] College of Chemistry and Environmental Science, Hebei University, Baoding, P.R. China

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NOTE

Study on Kinetics of Acrylamide Polymerization Initiated by Potassium Ditelluratocuprate (III) in Alkaline Medium

Yinghai Liu,* Junbo Li, Lanying Yang, and Zengqian Shi

College of Chemistry and Environmental Science, Hebei University,
Baoding, P.R. China

ABSTRACT

A novel initiator, potassium ditelluratocuprate (III) (DTC) was employed to initiate homopolymerization of acrylamide (AM) in aqueous alkaline medium. The results indicate that the equation of the polymerization rate (R_p) is as follows: $R_p = k[\text{AM}]^{1.63}[\text{DTC}]^{0.61}$ and that the overall activation energy of AM polymerization is 26.0 kJ/mol, the polymer molecular weight decreases with the increasing DTC and increases with the increasing AM. The effects of various reaction conditions on the polymerization rate were also studied. The initiation mechanism was proposed and verified by Fourier transform infrared (FTIR) and ^{1}H nuclear magnetic resonance (^{1}H NMR).

Key Words: Ditelluratocuprate (III); Acrylamide; Redox initiation; Polymerization.

INTRODUCTION

Nowadays, supernormal valence transition-metals receive considerable attention and the feasibility of their applications to radical polymerization appeals to more researchers.

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*Correspondence: Yinghai Liu, College of Chemistry and Environmental Science, Hebei University, Baoding 071002, P.R. China; E-mail: lijunbo027884214@163.com.

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Some of radical copolymerizations were carried out in the aqueous solution initiated with ceric ammonium nitrate,[1–6] potassium persulfate,[7–10] ferric ion-hydrogen peroxide,[11] or copper (II).[12] Of these methods, the chain transfer reaction is the most ordinary process for engendering graft polymers. Generally speaking, grafting efficiency of these initiators is very low. Although ceric ammonium nitrate is an excellent initiator, it is expensive and the copolymerization which it initiated must be implemented in the acidic medium. Therefore, to find new supernormal valence transition-metals as oxidant and low weight organic compounds or polymer as reductant for the redox system which initiates the radical homopolymerization and grafting copolymerization reaction is the important content of the research on radical polymerization.

During recent years, we have obtained some achievements on the polymerization and graft copolymerization of vinyl monomer initiated by supernormal valence transition-metals, such as diperiodatocuprate (III),[13–15] diperiodatoargentate (III),[16,17] and diperiodatonickelate (IV).[18–21] It has been demonstrated that Cu(III) is an efficient initiator, but only the orthoperiodate was used as complexing agents. Whether ditelluratocuprate (III) (DTC) can be employed to initiate the free radical polymerization has not been reported as yet.

There is much literature for strong oxidative behaviors of DTC, however, most of them were used in the oxidization of low molecular weight compounds in alkaline medium, such as aliphatic amines,[22] aryl alcohols,[23] aromatic aldehydes[24] in organic compounds and azide ion,[25] hypophosphite,[26] and nitrite ion[27] in inorganic, etc. Although some of them discovered free radical in their reports,[23,24] they haven't been studied further. In this paper, polymerization of acrylamide (AM) initiated by potassium DTC in alkaline medium has been carried out, DTC as oxidant and AM itself as reductant making up the redox system. The effects of monomer concentration, initiator concentration, temperature, and PH on R_p have been investigated. The overall activation energy and the equation of the polymerization rate have been worked out, and the initiation mechanism has been determined by Fourier transform infrared (FTIR) and ^{1}H NMR. Because of its low activation energy, the polymerization reaction can be carried out at room temperature and in an aqueous alkali medium. At the same time, we found in our latter work that DTC was able to perform grafting copolymerization reaction with nylon, cellulose, chitosan, casein, starch, and so on, which also contains the characteristic group (—CONHR) of weak reductibility, to afford the grafting products of high efficiency. We will carry out detailed research in the future papers. Accordingly, we can draw a conclusion that DTC is an effective initiator and the reaction conditions are superior to the those of other free radical initiator reactions.

EXPERIMENTAL

Materials

The stock solution of DTC $\{[Cu(H_2TeO_6)]^{5-}\}$ was prepared by the method given by Chandra and Yadava.[28] The concentration of DTC was obtained by its absorption at $\lambda = 405\,nm$[29] using a Shimadzu UV-265 Spectrophotometer (Japan). Acrylamide, a product of the reagent factory of Beijing chemical reagent stocking and providing station, was an analytical reagent. The other reagents were also of an analytical reagent.

Polymerization

A known amount of AM aqueous solution was added into the reaction vessel and was immersed in a water bath which was maintained at a definite temperature, and then the reaction vessel was deaerated by sparing with nitrogen for 5 min. A known calculated amount of DTC was filled under nitrogen and the time was noted. After polymerization for a given time and neutralized by an aqueous hydrochloric acid solution, the polyacrylamide (PAM) was precipitated out by adding an excess of methanol, washed repeatedly with methanol, and dried under vacuum at 60°C to a constant weight.

The molecular weight of the polymer were determined by viscosity measurement in a 0.1 M NaCl aqueous solution using a Ubbelohde viscometer and a Mark-Houwink relationship of the type:[30,31]

$$[\eta] = 9.33 \times 10^{-3}\,\mathrm{M}^{0.75}\,\mathrm{cm}^3/\mathrm{g}.$$

RESULTS AND DISCUSSION

Effects of the Different Factors on R_p

The homopolymerization of AM initiated by DTC in alkaline medium has been investigated at various concentrations of monomer, when the total volume, the concentration of the initiator [DTC], pH value, and the reaction temperature remained unchanged. The results are shown in Fig. 1. It can be seen that the R_p increases regularly with an increasing [AM], which was consistent with the general rule of free radical polymerization.

At the fixed [AM], [DTC], and pH value, the relationship between the temperature and R_p has been investigated and is shown in Fig. 2. It can be seen that the R_p increases with the rise in temperature, which was in agreement with the common rule of reaction.

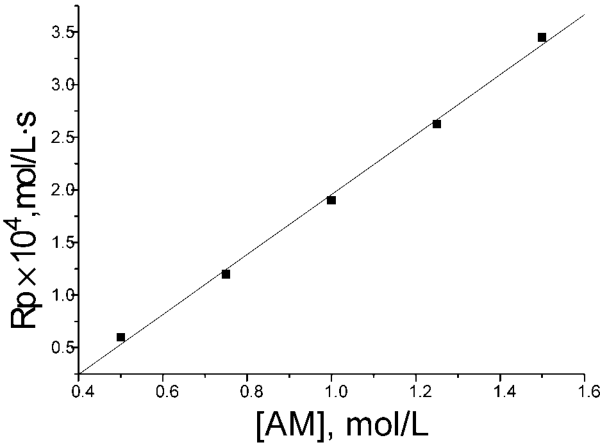


Figure 1. Variation of R_p with different [AM]. $[\mathrm{DTC}] = 1.4 \times 10^{-3}$ mol/L, $T = 298$ K, pH = 13.0.

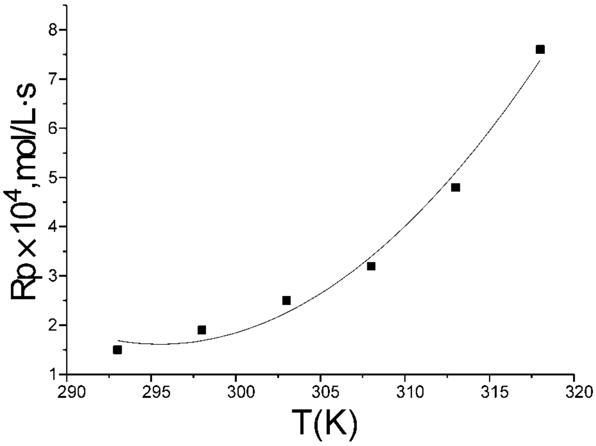


Figure 2. Variation of R_p with different temperature. [DTC] = 1.4×10^{-3} mol/L, [AM] = 1 mol/L, pH = 13.0.

When the other reaction conditions were invariable, the relationship between pH value and R_p is shown in Fig. 3, it is found that the R_p increases initially and then decreases with a further rise in pH value of the reaction system, which was in agreement with the rule of the polymerization initiated by redox systems of potassium diperiodatocuprate (III) and AM in our previous report.[1] The peak point of R_p appears in pH = 13. The probable reason is that under different pH value conditions, the type of DTC complex is different. Furthermore, the effective concentration of DTC involved in the initiation was different.

Figure 4 shows the effect of concentration of the initiator on R_p under the other conditions as being unchanged. It is seen that R_p increases with the increasing [DTC]

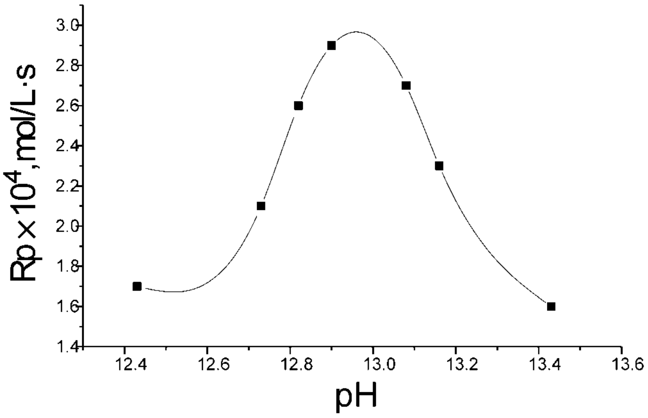


Figure 3. Variation of R_p with different pH value. [DTC] = 1.4×10^{-3} mol/L, [AM] = 1 mol/L, T = 298 K.

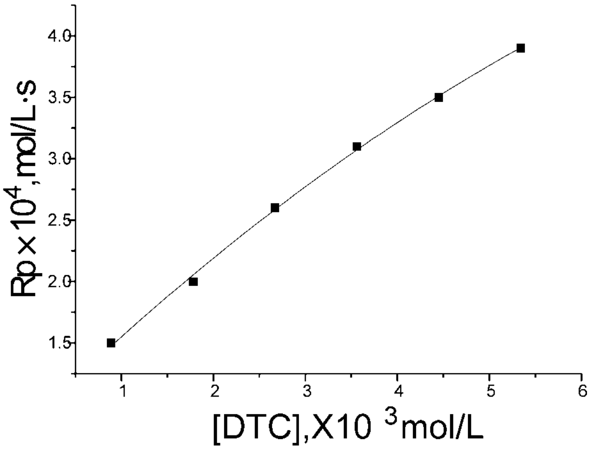


Figure 4. Variation of R_p with different [DTC]. [AM] = 1 mol/L, $T = 298$ K , pH = 13.0.

within a definite range. This is because DTC reacts with the characteristic group of AM (—CONH$_2$) directly and increasing radicals could be originated to initiate the polymerization of AM.

The Effect of [AM] and [DTC] on Molecular Weight of Polyacrylamide

Tables 1 and 2 indicate the relationship between the mean molecular weight ($\bar{M}$) of PAM and [AM], and [DTC]. From Tables 1 and 2, $\bar{M}$ rises with the increasing [AM] and declines with the increase of [DTC], which is consistent with the general rule of free radical polymerization.

Kinetics of Polymerization

Polymerization was also carried out under varying [AM], and the double logarithmic plot of R_p vs. [AM] was shown in Fig. 5 .The slope indicates that R_p is proportional to the 1.63 power of [AM]. At the same time, the double logarithmic of R_p vs. [DTC] was

Table 1. Verification of molecular weight of PAM.

[AM] (mol/L)	0.75	1.00	1.25	1.50	1.75	2.00
M ($\times 10^{-5}$)	1.3	2.0	2.7	3.6	5.0	6.8

Note: $T = 30°$C, solvent was 0.1 M NaCl aqueous solution, Ubbelohde viscometer.

Table 2. Verification of molecular weight of PAM.

[DTC] (10^{-3} mol/L)	0.89	1.78	2.67	3.56	4.45	5.34
M ($\times 10^{-5}$)	2.6	1.9	1.4	0.9	0.6	0.4

Note: $T = 30°C$, solvent was 0.1 M NaCl aqueous solution, Ubbelohde viscometer.

shown in Fig. 6. The slope also indicates that R_p is proportional to the 0.61 power of [DTC].

The equation of the polymerization rate is as follows:

$$R_p = k[\mathrm{AM}]^{1.63}[\mathrm{DTC}]^{0.61}$$

This equation included two contents. On the one hand, AM was employed, not only as the monomer taking part in the reaction of chain propagation, but the reductant participating in the reaction of initiation. On the other hand, the termination of the growing polymer chains would have both monoradiacal and biradiacal termination mechanism.

The effects of temperature on the R_p were investigated from 25°C to 45°C. From the Arrhenius plot (Fig. 7), the overall activation energy was calculated as 26.0 kJ/mol, which is lower than the overall activation energy of homopolymerization of AM initiated with potassium diperiodatocuprate (III).[1]

Discussion of the Initiation Mechanism

In order to test the nature of the polymerization, free radical inhibitors, ferric chloride, and *p*-dihydroxy benzene (1% mole of AM) were added to the reaction system separately,

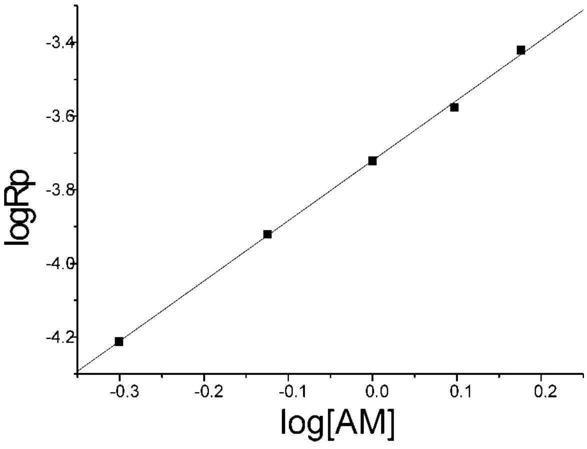


Figure 5. Double logarithmic plot of R_p vs. [AM]. $[\mathrm{DTC}] = 1.4 \times 10^{-3}$ mol/L, $T = 298$ K, pH = 13.0.

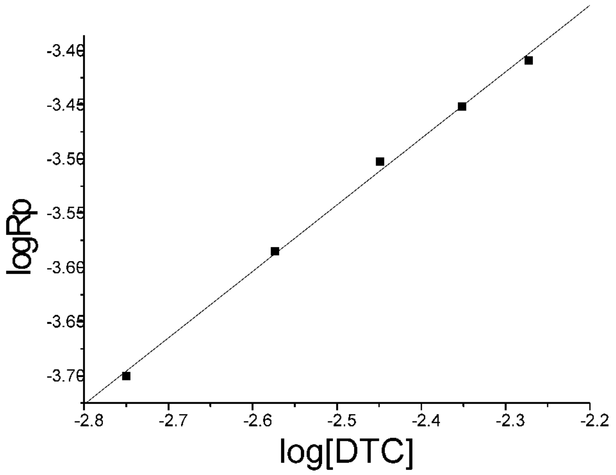


Figure 6. Double logarithmic plot of R_p vs. [DTC]. $[DTC] = 1.4 \times 10^{-3}$ mol/L, $T = 298$ K, pH = 13.0.

and no polymerization occurred. Thus, it may be concluded that the reaction appeared to have the characteristics of free radical polymerization.

The proof of initiation mechanism was $-\overset{|}{\mathrm{N}}\mathrm{H}$ obtained from the FTIR spectrum and ^{1}H NMR spectrum of poly(methyl methacrylate) (PMMA) were shown in Figs. 8 and 9. Poly(methyl methacrylate) was synthesized initiated by the redox system of DTC and formamide. The reason is that it is difficult to identify and $-\mathrm{NH_2}$ in the structure of PAM at FTIR $>\mathrm{C{=}O}$ spectrum. It can be seen from the Fig. 8 that the characteristic absorption of —CONHR appears at the range from 1551–1650 cm^{-1} corresponding to

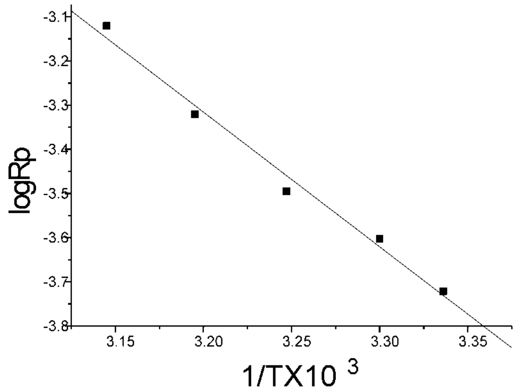


Figure 7. Arrhenius plot relative to the R_p. $[DTC] = 1.4 \times 10^{-3}$ mol/L, [AM] = 1 mol/L, pH = 13.0.

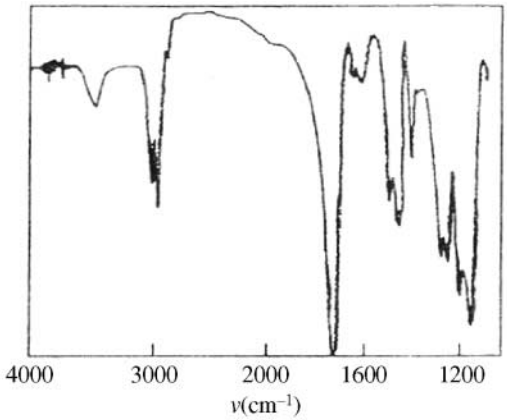


Figure 8. Infrared spectrum of PMMA.

the stretching of and the vibration of N—H. However, the FTIR spectrum of PMMA initiated by AIBN hardly showed the peaks of characteristic absorption clearly within that range. The peak at 3450 cm^{-1} is attributed to the stretching absorption of N—H. This illustrates the existence of the —CONHR.

The ^{1}H NMR spectrum of the PMMA, initiated by the redox system of DTC and formamide, is shown in Fig. 9. The signal at 4.6 ppm is due to the proton of —CONHR. However, the same signal does not exist in the ^{1}H NMR spectrum of PMMA initiated by AIBN. Therefore, the conclusion can be given that DTC takes part in the initiation reaction. First, the nitrogen of amide group transfers one electron to Cu(III) and forms the free radical cationic, which is likely to lose the proton H in alkaline medium to turn into

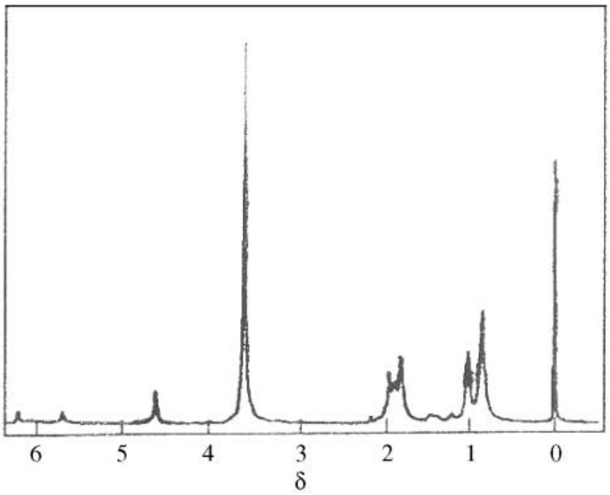
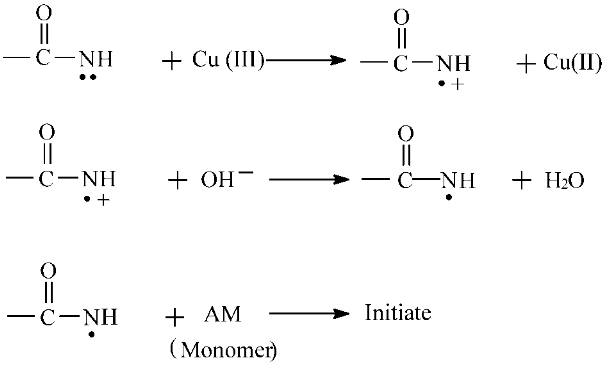


Figure 9. ^{1}H NMR spectrum of PMMA in $CDCl_3$.

the free radical initiating the polymerization reaction. The initiation mechanism belongs to a single-electron-transfer mechanism and is shown as follows:



CONCLUSION

It was the first time that DTC was employed to initiate homopolymerization of AM in an aqueous alkaline medium. The proof of initiation was obtained from FTIR spectrum and ^{1}H NMR spectrum tests. Under our experimental conditions, the effects of the different factors on R_p, and the effects of [AM] and [DTC] on mean molecular weight of PAM have been investigated. All of these were in accord with the general rule of free radical polymerization. At the same time, kinetics of polymerization was also studied. Because of its low activation energy, the polymerization reaction can be carried out at room temperature and in aqueous alkali medium, which is superior to the conditions of the other free radical initiator reaction.

ACKNOWLEDGMENT

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