

EFFECT OF RADIATION ON HIGH-CHARGE-DENSITY POLYDIALLY-DIMETHYL AMMONIUM CHLORIDE IN DILUTE AQUEOUS SOLUTION

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Abstract The effect of radiation on high-charge-density cationic polymer, polydiallyl-dimethyl ammonium chloride (polyDADMAC), in dilute aqueous solution was investigated. The irradiated samples were characterized in terms of reduced viscosity and electric conductivity. The crosslinking reaction of polyDADMAC chains occurs preferentially in the irradiated samples at a concentration of polyDADMAC higher than 1.3 g/100 mL that was induced indirectly by the OH radicals, one of the radiolysis products of water. In more dilute samples (less than 0.8 g/100 mL) the chain scission of macro radicals appears to be the main reaction. N_2O atmosphere enhances the crosslinking due to the extra OH radicals produced by reaction between N_2O and e_{aq}^- , another radiolysis products of water. Methanol and some mineral salts such as KCl, KBr inhibit the crosslinking to a certain extent. The mechanism of sensitization and inhibition is discussed in detail.

Keywords Poly diallyl-dimethylammonium chloride, Irradiation, Crosslink, Viscosity

INTRODUCTION

Water-soluble synthetic polyelectrolytes are of continuously growing interest due to their wide applications in industrial processes and technology^[1]. Among the various polyelectrolytes, polydiallyl-dimethylammonium chloride (polyDADMAC) is a very important and typical one. PolyDADMAC molecules possess a backbone of cyclic units and a charged quaternary ammonium group found in each chain unit provides the polymer with a high water solubility and solution properties corresponding to those of strong polyelectrolytes. ^{13}C -NMR structural measurements show that the parameters and characteristics of the structure could be influenced and regulated by the synthesis process, except the ring size and 6:1 ratio of *cis*- and *trans*- substitution of the main structure. The chain structure of polyDADMAC is shown in Fig. 1^[2].

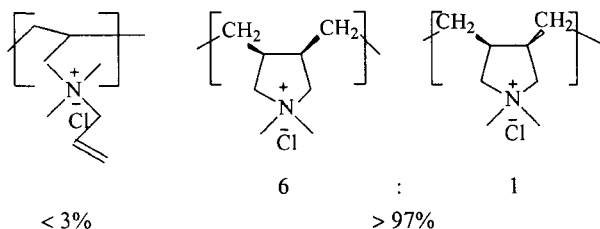


Fig. 1 Structural units of polyDADMAC through cyclopolymerization

Research interest in polyDADMAC has gradually increased not only because of its special structure but also due to its applications, such as in papermaking, wastewater treatment, mineral processing, food and medical

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Received September 6, 2002; Revised November 20, 2002; Accepted November 23, 2002

industry. A very concise review on it was published recently^[3]. Many aspects of polyDADMAC including its synthesis, chemical structure, and characteristics were investigated in detail, but the radiation effects on polyDADMAC in dilute aqueous solution which have some significance for its flocculation uses have not yet been reported. In this work, the mechanism of the radiation effect on polyDADMAC in dilute aqueous solution and influences of some additives were investigated.

EXPERIMENTAL

Materials

Diallyl-dimethylammonium chloride (DADMAC) in the form of 60 wt% aqueous solution was purchased from TCI Tokyo Kasei Kogyo Co. Ltd. Linear polyDADMAC was synthesized by radiation polymerization described in our previous paper^[4]. The weight-average molecular weight of the polymer was 2.61×10^5 as measured by the National Research Center of Standard Materials (China, Beijing). Deionized water was used in the preparation of polymer solutions. All the other reagents were used without further purification.

Method

Preparation and irradiation of polyDADMAC solutions

A certain amount of polyDADMAC (0.05–0.15 g) was completely dissolved in 10 mL water. Each 1.00 mL portion of the solution was poured into a glass tube which was sealed after passing N_2 for 20 min and then irradiated by γ -rays from the Co-60 source (Peking University). Irradiated sample was transferred into a 100 mL volumetric flask and diluted with deionized water up to the mark.

Viscosity measurement

The viscosity data provide a general criterion showing the change in molecular weight of each sample during irradiation. The reduced viscosity η_{sp}/c of the aqueous sample solution was measured at $25 \pm 0.1^\circ C$ by using a Ubbelohde viscometer.

Measurement of electric conductivity

The conductivity κ of the sample solution was measured at $25 \pm 0.1^\circ C$ by a digital electric Conductivity Detector (Model DDS-307, China) and was used to represent the change of molecular weight of polyDADMAC in aqueous solution before and after irradiation.

RESULTS AND DISCUSSION

Effect of Solution Concentration on Viscosity and Electric Conductivity

The relation between η_{sp}/c , κ and solution concentration was studied. It can be seen from Fig. 2 curve 1 that η_{sp}/c decreases as the concentration of polyDADMAC in dilute solutions increases. This phenomenon is contrary to the behavior of neutral polymers and it is quite common for polyelectrolytes^[5]. In dilute aqueous solution polyelectrolyte is in dissociated state, and the cations repel each other so the polyDADMAC chains become more extended, which is responsible for the increase of the reduced viscosity. However, the electric conductivity of solution increases with the concentration (see Fig. 2 curve 2) because of the simultaneous increase of both the charged groups and the concentration of polyDADMAC in solution.

Radiation Effect of Linear PolyDADMAC in Dilute Aqueous Solution

Due to the limited solubility, the concentration of polyDADMAC in water here was below 1.5% (5.85×10^{-5} mol/L) which belongs to dilute solution of polymer. From Fig. 3 it can be seen that for the samples of different concentrations of polyDADMAC their η_{sp}/c as a function of absorbed dose shows obvious differences. The η_{sp}/c values of 1.3% and 1.5% polyDADMAC samples showed no changes below 6 kGy and then increased rapidly with dose. In contrast, when the sample's concentration was as low as 0.8%, the η_{sp}/c values showed no obvious change up to an irradiation dose of 10 kGy. However, for a more dilute sample (0.5%), a slight decrease in η_{sp}/c was observed.

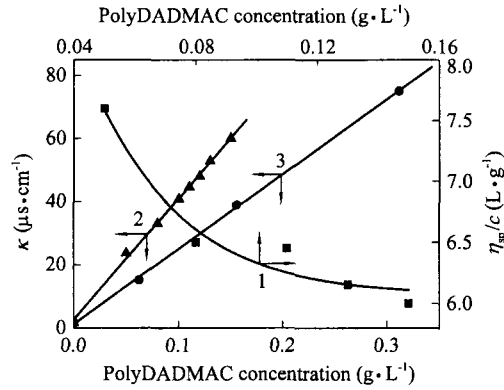


Fig. 2 η_{sp}/C and K as a function of concentration of polyDADMAC in dilute aqueous solutions
■ $M_w = 2.61 \times 10^5$; ▲ $M_w = 2.61 \times 10^5$; ● $M_w = 3.57 \times 10^5$

In this work, the concentration of polyDADMAC for some samples was kept constant during irradiation, so the η_{sp}/c value could be used to indicate the change of molecular weight of polyDADMAC during irradiation and an increase of η_{sp}/c means that the crosslinking reaction of molecular chains has taken place. The limiting concentration to induce crosslinking was about 1.3% at an irradiation dose of 10 kGy.

In dilute aqueous solution the radiation effect on polyDADMAC was induced indirectly by the products produced from water radiolysis, such as $\bullet OH$, $\bullet H$, H_2O_2 , H_2 , e_{aq}^- etc., mainly by oxidizable OH radicals. The macromolecular radicals of polyDADMAC were produced by hydrogen abstraction reaction between $\bullet OH$ and polyDADMAC molecules.



Where P and P• are the polyDADMAC molecules and macromolecular radicals respectively; and the crosslinking reaction occurs by bimolecular combination of the macro radicals.

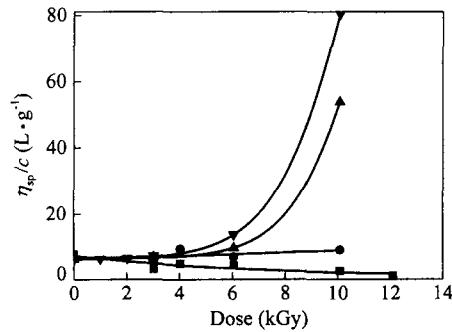


Fig. 3 η_{sp}/c as a function of dose
Dose rate: 33.6 Gy/min;
[polyDADMAC]: ▼ 1.5%; ▲ 1.3%; ● 0.8%;
■ 0.5%

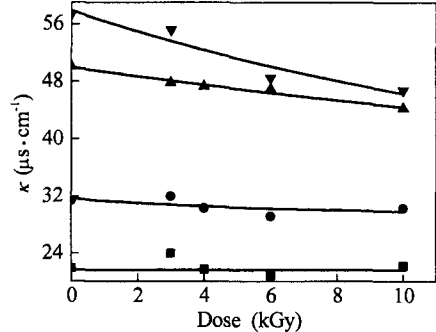


Fig. 4 Electric conductivity K as a function of dose
Dose rate: 33.6 Gy/min;
[polyDADMAC]: ▼ 1.5%; ▲ 1.3%; ● 0.8%;
■ 0.5%

In the case of more dilute solution, for instance, the concentration of polyDADMAC in aqueous solution is lower than 0.5%, the polyDADMAC backbone radicals become so dilute as to be terminated by coupling, so

chain scission reaction appears to be the main radiation effect on polyDADMAC. Figure 4 shows the results of electric conductivity measurements for the irradiated samples. Generally speaking, the electric conductivity of polyDADMAC in aqueous solution would be decreased with the extension of molecular chains of polyDADMAC due to molecular coiling. Comparing with curve 2 and curve 3 in Fig. 2, it can also be seen that the electric conductivities of polyDADMAC of low molecular weight are always higher than those of high molecular weight at the same concentration. So the results in Fig. 4 show that the electric conductivity decreases with the dose for the polyDADMAC samples of concentrations 1.3% and 1.5% indicate the increase of molecular weight in both samples and are consistent with the results of viscosity measurement in Fig. 3.

Influence of Gas Atmospheres on Radiation Effect of PolyDADMAC

Figure 5 shows the influence of different gas atmospheres on radiation effect of polyDADMAC in 0.8% and 1.5% aqueous solution. Under oxygen atmosphere, η_{sp}/c shows slightly decreasing tendency with increasing of dose. This is reasonable, because oxygen is a strong radical scavenger. Under N_2O atmosphere, however, η_{sp}/c increased sharply beyond 3–6 kGy for both polyDADMAC concentrations.

The susceptibility of N_2O to crosslinking of polyDADMAC is due to the reaction between N_2O and e_{aq}^- .



The extra OH radicals would induce more crosslinking of polyDADMAC molecules. The susceptibility of N_2O to crosslinking of polyDADMAC appeared more obviously in 0.8% and 1.5% solution (see Fig. 5).

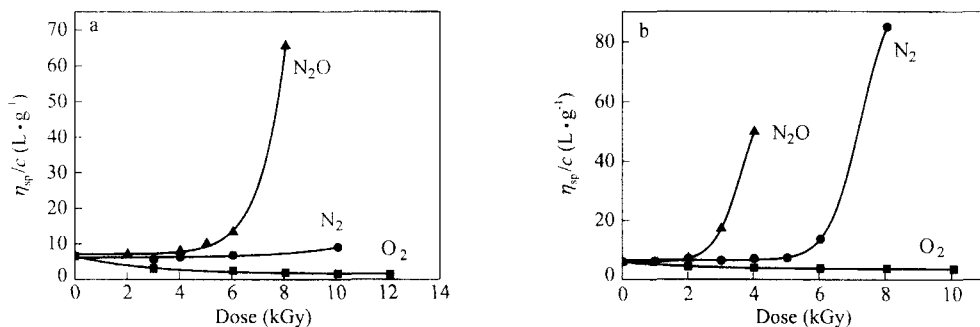


Fig. 5 Effect of radiation atmospheres on η_{sp}/c
a) 0.8% PolyDADMAC; b) 1.5% PolyDADMAC

Figure 6 shows the results of electric conductivity measurements for the respective samples. Under O_2 and N_2 atmospheres the results were reasonable as explained above, but under N_2O atmosphere below 6 kGy the responsive electric conductivities were higher than that under N_2 atmosphere. It seems to be strange, however if taking account of Eq. (4), in the mean time of giving extra OH radicals the OH^- anions produced as well which made the increase of electric conductivity of the system. When the crosslinking effect was rather high (above 6 kGy) the decrease of electric conductivity induced by increasing of molecular weight might exceed its increase by Eq. (4).

Effect of Methanol on PolyDADMAC Crosslinking

Methanol (MeOH) is also a kind of radical scavenger. In the presence of MeOH, the OH radicals in irradiated samples are consumed by chain transfer reaction with MeOH and produce $\cdot CH_2OH$ radicals which are reductive in nature and have no contribution to crosslinking. Figure 7 shows that at higher doses (such as about 6 kGy) the inhibition by MeOH becomes obvious. From Fig. 8 it can be seen that a small amount of MeOH in mixed solvents could inhibit radiation crosslinking completely at 6 kGy dosage.

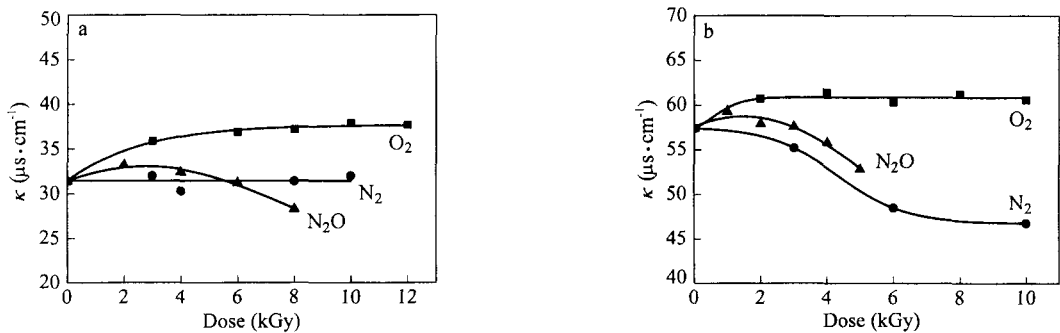


Fig. 6 Effect of radiation atmosphere on κ
a) 0.8% PolyDADMAC; b) 1.5% PolyDADMAC

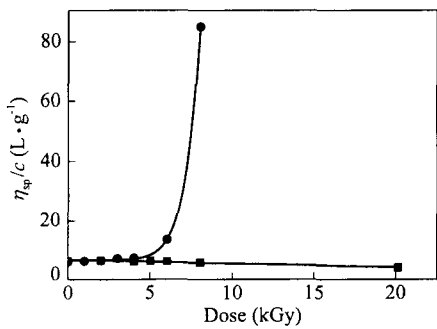


Fig. 7 η_{sp}/c as a function of dose in different solvents
Dose rate: 33.6 Gy/min; [polyDADMAC]: 1.5%
● Water; ■ MeOH

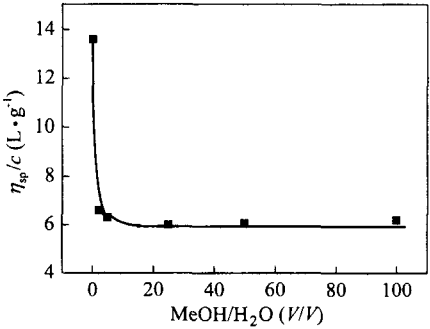


Fig. 8 Influence of MeOH on viscosity in mixed solvents of MeOH-H₂O
Dose: 6.0 kGy; Dose rate: 33.6 Gy/min;
[polyDADMAC]: 1.5%

Effect of Mineral Salts on the Viscosity of PolyDADMAC in Aqueous Solutions

The effect of mineral salts such as KCl, KBr on the viscosity of polyDADMAC in aqueous solution is investigated in this work, which has significance in flocculation applications. PolyDADMAC is a polyelectrolyte with quaternary ammonium group, and mineral anions Cl^- or Br^- which could neutralize polyDADMAC to form a more coiled state and decrease the viscosity of the polymer solution and also decrease the possibility of bimolecular combination of the backbone radicals. So when the concentration of Cl^- in the solution reaches 1 mol/L, the crosslinking tendency of polyDADMAC does not appear to be high, even at 30 kGy dosage (see Fig. 9).



Compared to KCl in the same 0.1 mol/L concentration, the inhibition of crosslinking by KBr in solution at increasing dose appears more obvious (see Fig. 10). The is because KBr is a scavenger of OH radicals apart from exerting a coiling effect on polyDADMAC molecules.

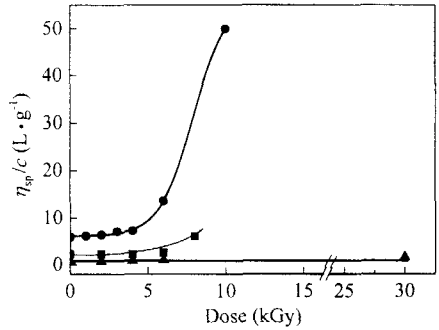


Fig. 9 The effect of KCl on viscosity at different doses
Dose rate: 33.6 Gy/min; [polyDADMAC]: 1.5%,
[KCl] (mol/L): ● 0; ■ 0.10; ▲ 1.00

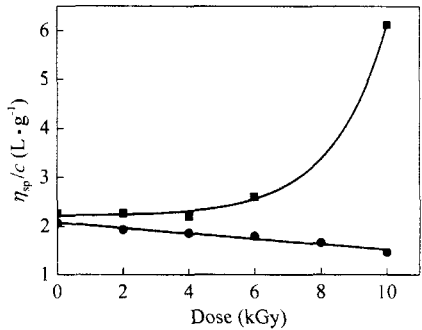


Fig. 10 η_{sp}/c as a function of dose in 0.1mol/L KCl and KBr solution
Dose rate: 33.6 Gy/min; [polyDADMAC]: 1.5%
■ KCl; ● KBr

CONCLUSION

The effect of radiation on polyDADMAC (a typical high-charge-density cationic polyelectrolyte) in dilute aqueous solution was investigated. If the concentration of polyDADMAC was higher than 1.3 g/100 mL and the absorbed dose was above 6 kGy, radiation crosslinking mainly occurred, while in more dilute solution (lower than 1.3 g/100 mL) chain scission of polyDADMAC could not be disregarded.

The radiation crosslinking of polyDADMAC in dilute aqueous solution is induced indirectly by OH radicals, which is one of the products of water radiolysis.

The radiation crosslinking is enhanced under N₂O atmosphere by the extra OH radicals produced by reaction between N₂O and e_{aq}⁻, which is another product of water radiolysis.

Methanol and some mineral salts, such as KCl, KBr inhibit the crosslinking to a certain extent.

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