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Plasma-Initiated Polymerization of (2-Methacryloyloxyethyl) Thrimethyl Ammonium Chloride

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Plasma-initiated polymerization of (2-methacryloyloxyethyl) thrimethyl ammonium chloride (MTAC)) was studied. The effects of discharge time and discharge power on temperature in a tubular-type reactor chamber were accurately tested by on-line thermocouple, and the equation relating discharge time, discharge power and temperature in the tubular-type reactor chamber was derived. The results indicated that temperature played a very important role in controlling the solubility of Poly(MTAC) in water. For $T \geq 130°$, Poly(MTAC) was cross-linked, and the highest rate of absorbing water of Poly(MTAC) was 15 $g{\cdot}g^{-1}$. For $T < 130°$, Poly(MTAC) was linear, and the highest intrinsic viscosity of Poly(MTAC) was 420.2 $cm^3{\cdot}g^{-1}$. The polymerization condition of linear Poly(MTAC) was optimized as follows: discharge time 60 s and discharge power 60 W.

Key Words: Plasma-initiated polymerization, temperature, discharge time, discharge power.

Introduction

In plasma-initiated polymerization, the water-soluble monomer is initiated in a solid directly or dissolved in an aqueous solution, and then initiated by plasma with different time and power.[1] The final product is usually water soluble or cross-linked. There has been considerable interest in the homopolymerization and copolymerization of cationic vinyl monomers because the cationic polyelectrolyte obtained has a wide range of applications in water treatment, soil conditioning, antistatic treatment of textiles, etc.[2] The radiation-initiated copolymerization of (2-methacryloyloxyethyl) thrimethyl ammonium chloride (MTAC) with acrylamide in aqueous solution has been studied before, and chemical-initiated emulsion copolymerization has also been described in some papers.[2–5] In the present study, we investigate the use of plasma-initiated polymerization of MTAC in aqueous solution to prepare a pure cationic polyelectrolyte. It is found that in this way we can easily produce a homopolymer with a much higher intrinsic viscosity compared to that prepared from a free-radical initiator. Although the influence of discharge time and discharge power on

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plasma-initiated polymerization has also been discussed in some papers,[6−8] so far the effect of the temperature in a tubular-type reactor chamber on polymerization has not been reported. Therefore, the key point of this paper is to investigate the influence of temperature in a tubular-type reactor chamber on polymerization and thus contribute to a broadening of the applications of plasma.

Experimental

Materials and apparatus

MTAC (80% solution, Xing Yu Chemicals Co. Ltd) was used without further purification and was kept below 5°, and the chemical structure of MTAC is shown in Figure 1. GR grade ethanol was used as received. A tubular-type reactor chamber (Φ20 × 200 mm) and 2 parallel electrodes (30 × 200 mm) were constructed in-house. The glow discharge frequency was 13.56 MHz. The vacuum meter (Model Fzh-2B) and vacuum pump (Model K-150A) were manufactured by Bei Yi Co. Ltd.

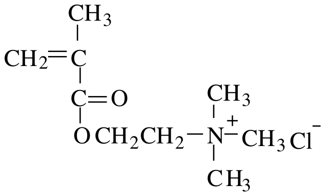

Figure 1. The chemical structure of MTAC.

2.2 Preparation of cationic polyelectrolyte

One gram of MTAC solid monomer was added to the tubular-type reactor chamber specially designed for the plasma-initiated polymerization. Figure 2 shows a schematic diagram for the overall process. MTAC solid monomer was added to the tubular-type reactor chamber, and nitrogen was also introduced into it for 30 min to remove oxygen, and then a vacuum was applied to the chamber by a vacuum pump to keep the pressure at 133 Pa. The plasma was ignited at a frequency of 13.56 MHz, and then discharge power was loaded directly to the tubular reactor chamber for several seconds, while the temperature of the system was accurately measured with an on-line thermocouple. After the initiating process, 3 g of distilled water was added to the tubular-type reactor chamber to dissolve MTAC monomer, and it was kept at a constant temperature of 50 ± 0.5° for 5 h post-polymerization.

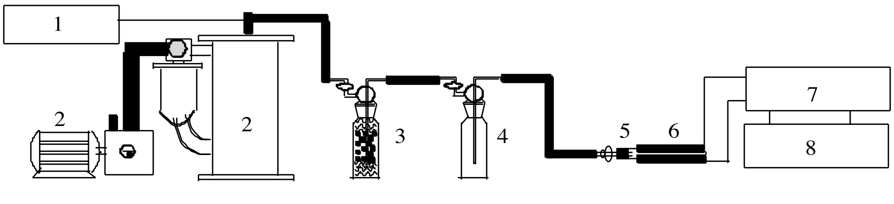

Figure 2. Schematic diagram of experimental apparatus. 1. vacuometer, 2. vacuum pump, 3. dryer, 4. bumper, 5. tubular type reactor chamber, 6. electrode, 7. radio-power supply, 8. matching power supply.

Intrinsic viscosity measurement

Eighty percent MTAC-water solution can be easily dissolved in ethanol, and it can form a homogeneous solution with water in any proportion; however, the dried Poly(MTAC) can be only dissolved in ethanol with a very small solubility of 0.01625 g (30°). Therefore, the polymerized gel (about 0.7 g) was precipitated in a large quantity of ethanol (100 g) to remove the residual monomer, and Poly(MTAC) with a highest conversion of 74.5% was obtained after being dried in vacuum. The intrinsic viscosity of the polymer was determined in aqueous 1 N NaCl by Ubbelode capillary viscometer at 30°.

Results and discussion

Effect of temperature

To study the temperature effect on polymerization, the discharge time was varied from 0 to 400 s, and the discharge power was varied from 10 to 80 W. In this experimental condition, the temperature in the tubular-type reactor chamber was varied from 20 to 220°. Figure 3 shows the effects of discharge time and discharge power on temperature in the tubular-type reactor chamber as measured by on-line thermocouple. It can be seen that the temperature increased with an increase in discharge power and discharge time, and we also concluded that temperature is a main factor that can influence polymer solubility in water in plasma-initiated polymerization. In distribution *a*, for $T \geq 130$ °C°ross-linked Poly(MTAC) was obtained, and the highest capability of absorbing water was 15 g·g^{-1}. In distribution *b*, for $T < 130°$, linear Poly(MTAC) was generated, and the highest intrinsic viscosity of Poly(MTAC) was 420.2 cm^3·g^{-1}. Since in this plasma-initiated polymerization system the monomer was competitive both in cross-link polymerization and in linear polymerization, an increase in the temperature might be due to cross-link polymerization playing a more important role than linear polymerization. This was because the higher discharge power and longer discharge time generate exorbitant electron energy, which could be due to electrons bumping from the plasma, resulting in increased side-reactions between polymer chains, leading to cross-linking. Furthermore, it was found that the influence of discharge time and discharge power on temperature accorded with the following regression equation, which was fitted by experimental data:

$$T = 15.935942 + 0.279195t + 0.200020P - 0.000595t^2 + 0.004284tP + 0.005297P^2$$

where T is temperature (°C°t and P are discharge time (s) and discharge power (W), and$t$ is varied from 0 to 400 s, and P is varied from 10 to 80 W.

IR spectra analysis

IR spectra were run on a FIR spectrometer in 400-4000 cm^{-1} waves using a KBr disk. It was shown that the absorption at 2921 and 2850 cm^{-1} was assigned to C-H stretching of CH_2 moieties. The absorption near 1733 cm^{-1} was assigned to $C-O-C=O$ stretching, and the absorption near 3340 and 3190 cm^{-1} was assigned to N-H stretching of NH_4 moieties, and there was no C=C characteristic, and so it was confirmed that the product was the Poly(MTAC).

Reaction conditions

Based on the experimental for obtaining the linear polymer, the reaction conditions were as follows: monomer mass fraction 25%, post-polymerization temperature 50 ± 0.5 °C°nd post-polymerization time 5 h.

Discharge time effects on intrinsic viscosity of Poly(MTAC) and monomer conversion

The effects of discharge time on intrinsic viscosity of the Poly(MTAC) and monomer conversion are shown in Figure 4. It was found that $[C] \propto\propto^{-1}$ (where $C$is monomer conversion). Since the monomer polymerization follows the radical mechanism,[1] this result suggests that the termination reaction of polymer radicals was slightly depressed at 60 s because of the decrease in their mobility at a higher viscosity. It is also found in Figure 4 that an increase in discharge time increased the intrinsic viscosity of the Poly(MTAC) in 0-60 s, and the monomer conversion could reach up to 83.3% at 60 s. However, this effect was slight when the discharge time was over 60 s. This was because the active seeds generated by plasma were saturated at 60 s, and so it can be negligible for polymerization if the discharge time is prolonged.

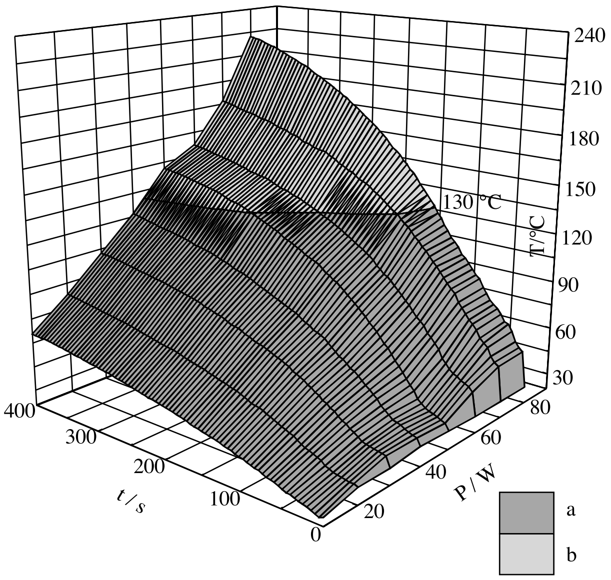

Figure 3. The effects of discharge time and discharge power on temperature in 133 Pa a: distribution of linear Poly(MTAC); b: distribution of cross-linked Poly(MTAC).

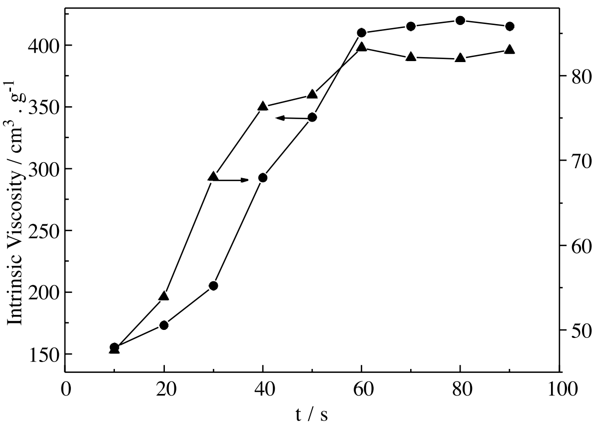

Figure 4. The effects of discharge time on intrinsic viscosity of Poly(MTAC) and conversion. Post-polymerization time 5 h, post-polymerization temperature 50 ± 0.5°, discharge power 60 W, MTAC mass fraction 0.25.

Discharge power effects on intrinsic viscosity of Poly(MTAC) and monomer conversion

The effects of discharge power on intrinsic viscosity of Poly(MTAC) and monomer conversion are shown in Figure 5. The monomer conversion increased with the increase in discharge power up to 60 W. Beyond 60 W, the monomer conversion increased slightly. The intrinsic viscosity of Poly(MTAC) exhibited a similar trend in 0-60 W, but beyond 60 W it decreased with the increase in discharge power. In this paper, plasma-initiated polymerization involved 2 essentially different procedures. The first procedure was the initiated reaction, such as the π bond opened in C=C by the bombardment from electrons and ions generated by plasma. The second procedure was the post-polymerization. The former procedure was more important in polymerization, for an increase in discharge power could enhance the electrons' energy, leading to an increase in initiating efficiency in the range 0-60 W. However, beyond 60 W, the exorbitant electron energy decreased the efficiency of plasma. Therefore, the intrinsic viscosity of Poly(MTAC) did not increase with increasing discharge power, but showed the maximum value of intrinsic viscosity of Poly(MTAC) 420.2 $cm^3 \cdot g^{-1}$ at 60 W. This was attributed to the amount of electrons with appropriate energy. It was also confirmed by the following theory: the energy distributing of electrons accords with the Maxwell-Boltzmann distribution, and the average energy of electron was calculated from the following equation (1):

$$Te = \frac{q}{k} \bullet 0.30 \bullet \sqrt{\frac{Mm}{Me}} \bullet \lambda el \bullet \frac{E}{P} \tag{1}$$

where Te is an average energy of electron (eV), and q is electron charge, and k is the Boltzmann constant. Mm and Me are molecule and electron mass. λ_{el} is the electron mean free path in 0 °C° 133 Pa (cm), and E is the electric field intensity (V/cm), and P is the pressure (Torr).

For nitrogen plasma, the average energy of electron can be calculated as follows (2):

$$Te = 1.68\frac{E}{P} \tag{2}$$

It could be concluded that the average energy of electron was affected by E/P. In this paper, the parallel electrode distance was 4 cm, and the tubular type reactor chamber pressure was 133 Pa (1 Torr), and the discharge voltage was 20-30 V; therefore, the average energy of electron Te varied from 8.4 to 12.6 eV. The energy Ee of π bond opening in C=C was approximately 9 eV. Ee lay in the scope of Te. Therefore, the optimal discharge power was 60 W. This result also confirmed the feasibility of plasma-initiated polymerization theoretically.

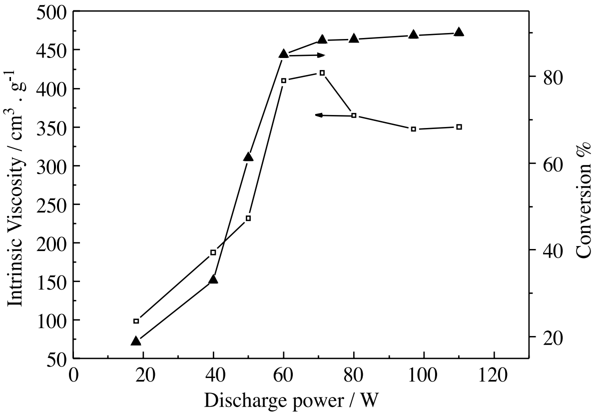

Figure 5. The effects of discharge power on intrinsic viscosity of Poly(MTAC) and conversion.

Post-polymerization time 5 h, post-polymerization temperature 50 ± 0.5 °C°TAC mass fraction 0.25, discharge time 60 s.

Conclusions

The plasma-initiated polymerization technique was used to prepare cationic polyelectrolyte. First, Poly(MTAC) was successfully confirmed by ATR-FTIR. Second, the effect of temperature on polymerization was studied. The temperature increased with an increase in discharge power and discharge time. It was also concluded that temperature was a main factor that could influence polymer soluble properties in water in plasma-initiated polymerization.

For $T \geq 130°$, Poly(MTAC) was cross-linked, and the highest rate of absorbing water was 15 $g{\cdot}g^{-1}$. For $T < 130°$, Poly(MTAC) was linear, and the highest intrinsic viscosity was 420.2 $cm^3{\cdot}g^{-1}$. Third, the polymerization condition of linear Poly(MTAC) was optimized as follows: discharge time 60 s and discharge power 60 W. An increase in discharge time increased the monomer conversion and the intrinsic viscosity of Poly(MTAC) in 0-60 s; however, this effect was slight when the discharge time was over 60 s, and the monomer conversion could reach up to 83.3%. The effects of discharge power on the monomer conversion and the intrinsic viscosity of Poly(MTAC) exhibited a similar trend in 0-60 W, but beyond 60 W the latter decreased with the increase in discharge power.

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