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PREPARATION AND THERMAL DECOMPOSITION OF POLYACRYLAMIDE AND ITS DERIVATIVES BY PLASMA-INITIATED POLYMERIZATION

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Abstract

Polyacrylamide (PAM), poly(N,N-dimethylacrylamide) (PDMA) and poly(N,N-diethylacrylamide) (PDEA) were synthesized by plasma-initiated polymerization. Both wet and dry polymers were prepared. The states of the water absorbed in the wet and dry samples were studied directly by means of TG, and the stabilities of the dry polymers in the process of thermal treatment were investigated by FT-IR. The activation energy of release of the bonded water was calculated by the Kissinger method. The water absorbed in the polymers was found to be in two states, i.e. weakly-bonded water and bonded water, and the absorbed water content varied with the monomer concentration, the plasma duration time and the type of polymer.

Keywords: acrylamide, FT-IR, N,N-dialkylacrylamide, plasma-initiated polymerization, TG

Introduction

In recent years, chemists have been paying increasing attention to the synthesis of a vinyl super water-absorbent resin. It can be obtained by bulk polymerization, solution polymerization, and inverse emulsion and suspension polymerization. Plasma-initiated polymerization has been reported by Osada *et al.* [1, 2]. The reaction of polymerization is initiated by substances formed in the plasma of a low-pressure glow discharge [1–3].

In the present paper, the plasma-initiated formation of polyacrylamide (PAM), poly(N,N-dimethylacrylamide) (PDMA) and poly(N,N-diethylacrylamide) (PDEA) is described. The effects of the monomer concentration and the plasma duration on the water-absorbent ability of PAM were studied by means of thermogravimetry (TG), and the stability of PAM in the course of thermal decomposition was investigated by FT-IR. The activation energies of the PAM polymers were evaluated by the Kissinger method [4]. The results demonstrated that the water absorbed in PAM, PDMA and PDEA display not only two different states [5] and the content exhibits

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saturability, but the proportion of water absorbed in the polymers appears to decrease with increasing alkyl chain length. This conclusion provides a basis for the application of PAM, PDMA and PDEA in medicine and chemical engineering.

Experimental

Preparation of polymers

Acrylamide was recrystallized three times from $CHCl_3$, N,N-dimethylacrylamide (DMA) and N,N-diethylacrylamide (DEA) were prepared and purified according to literature procedures [6].

The polymer samples (PAM, PDMA and PDEA) were made by plasma-initiated polymerization. A prescribed amount of acrylamide was dissolved in water at a prescribed concentration. The solution of PAM was irradiated at a radiation frequency after degassing under liquid N_2 three times, with a prescribed radiation time in a special glass vial. A glow discharge plasma was generated above the solvent in the vial. Next, the reactant was placed in a constant temperature bath for some time. Finally, the polymer was obtained by breaking the vial.

Table 1 The polymerization parameters

No.	Polymers	Concentration/ %	Plasma polymerization time/s	Polymerization temperature/°C	Post-poly merization time/h
1	PAM	30	60	25	24
2	PAM	40	60		
3	PAM	50	60		
4	PAM	50	30		
5	PAM	50	15		
6	PDMA	50	30		
7	PDEA	50	30		

The wet samples of PAM were obtained by torrefaction of the polymer under environmental temperature in the air. The dry sample was obtained by drying the wet sample in an oven at 25°C. The polymers synthesized under different conditions are presented in Table 1.

Apparatus

The carbon, hydrogen and nitrogen analyses were made with a Carlo-Erba model 1110 elemental analyser.

The IR spectra were recorded in NaCl plus a liquid film on a Muttson Alpha Centauri IR spectrometer.

Thermal decomposition studies of all the polymers were performed on a Perkin Elmer Delta series TG-7 in pure nitrogen flowing at a rate of 20 ml min^{-1}. The samples were heated at 5, 10, 15 and 20°C min^{-1} from 25 to 500°C, with a sample mass of about 40 mg.

Results and discussion

Elemental analyses

The results of elemental analyses, listed in Table 2, indicate that the measured values are smaller than the calculated values. This might be due to ammonolysis during the process of plasma-initiated polymerization.

Table 2 The data of elemental analysis

Polymers		PAM	PDMA	PDEA
C/%	theory	50.7000	60.6100	66.1401
	measured	49.5811	60.0908	65.8916
H/%	theory	7.0402	9.0904	10.2403
	measured	6.9895	8.995	10.0215
N/%	theory	19.7203	14.1408	11.0200
	measured	17.9324	13.9216	10.5732

Infrared spectra

Figure 1 shows the IR spectra of the PAM polymers at different temperatures in the course of thermal decomposition: a – at 25°C, b – at 250°C and c – at 300°C.

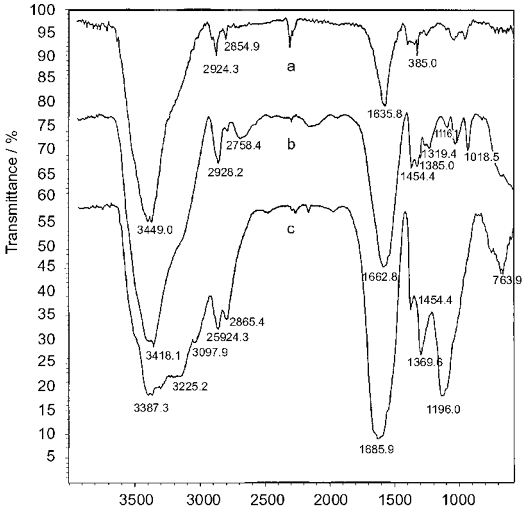

Fig. 1 The FT-IR spectra of PAM in the process of thermal decomposition; a – at 25°C; b – at 250°C; c – at 300°C

Table 3 Thermal decomposition data for polymers studied at $\beta=5^\circ C\ min^{-1}$

Polymers		MC[a]/ mass%	PDT[b]/ s	Stage I		Stage II		Stage III		Energy/ kJ mol^{-1}
				Temp./°C	Mass loss/%	Temp./°C	Mass loss/%	Temp./°C	Mass loss/%	
PAM 1#	wet	30	60	30–126	88.6	126–348	3.8	348–489	5.6	152.46
	dry			30–255.2	11.3	255–372.5	36.1	372.5–542	52.5	
PAM 2#	wet	40	60	30–134	91.4	134–350	3.4	350–450	4.9	144.39
	dry			30–263.8	12.6	263.8–379.7	33.4	379.7–550	53.9	
PAM 3#	wet	50	60	30–140	93.4	140–346	2.6	346–446	3.8	141.83
	dry			30–262.3	12.5	262.3–377.7	32.6	377.7–546	54.8	
PAM 4#	wet	50	30	30–138	99.2	–		–		–
	dry			30–226.7	8.25	266.7–376.5	34.3	376.5–556	57.4	
PAM 5#	wet	50	15	30–146	81.8	146–372	4.5	372–480	11.9	141.54
	dry			30–273.7	9.25	273.7–374.3	36.2	374.3–538	54.6	
PDMA	wet	50	30	30–158	97.8	–		–		–
	dry			30–254	12.4	254–406	64.9	406–500	11.8	
PDEA	wet	50	30	30–152	87.9	152–378	4.9	378–500	5.2	152.32
	dry			30–262	4.6	262–408	71.8	408–500	11.4	

[a] Monomer concentration
[b] Plasma duration time (s)

From a comparison of (a) with (b) and (c), the polymers exhibited strong $CONH_2$ stretching vibration absorptions at about 3400 and 1640 cm^{-1}, and no special absorption of C≡N at 2240 cm^{-1}. This suggested that the lost water molecules were absorbed in the cross-linked net of PAM before 300°C [7, 8], but not the inner condensation of $CONH_2$. Figures 1(a) and (b) reveal a medium C–O–C stretching vibration absorption at ~1200 cm^{-1}, and CH_2 and CH_3 absorptions at ~1380, 1450, 2800 and 2900 cm^{-1} [9], indicating that the PAM was partly oxidized during the loss of absorbed water molecules [10]. This is in accordance with the above results.

Thermal analyses

The temperature range of mass loss and the percentage mass loss measured at β=5°C min^{-1}, together with the activation energy values found for loss of the bonded water by the Kissinger method, are presented in Table 3. Some TG curves are shown in Figs 2–4.

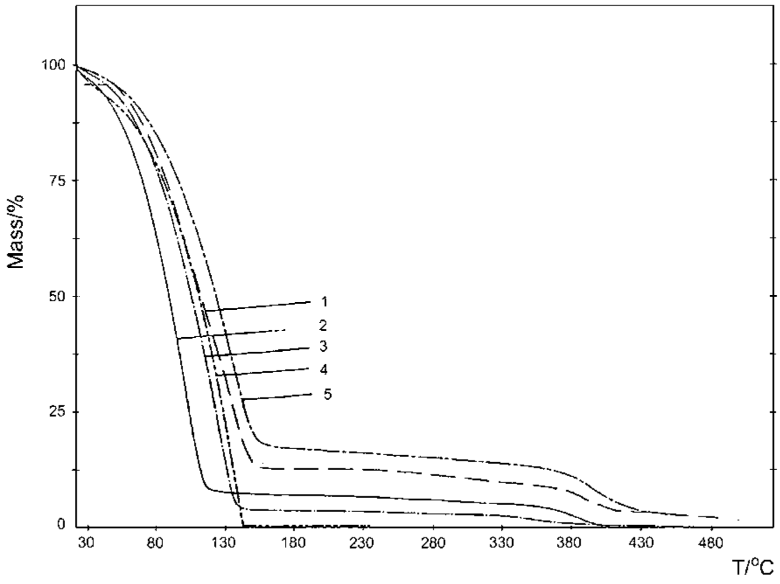

Fig. 2 The TG curves for 1# – 5# of wet PAM; 1 – 1#; 2 – 2#; 3 – 3#; 4 – 4#; 5 – 5#

The TG curves for all samples, except for wet 4# of PAM and PDMA, exhibit three steps. The first step corresponds to the removal of weakly-bond water molecules, followed by the step involving the release of the bonded water molecules, while the final step corresponds to the thermal decomposition of the polymers. The TG curves for the wet 4# of PAM and PDMA display only one step. This is probably due to a higher ratio of weakly-bonded water absorbed and relatively low contents of bonded water and polymers, which leads to difficulty in measuring the percentages of bonded water and polymers.

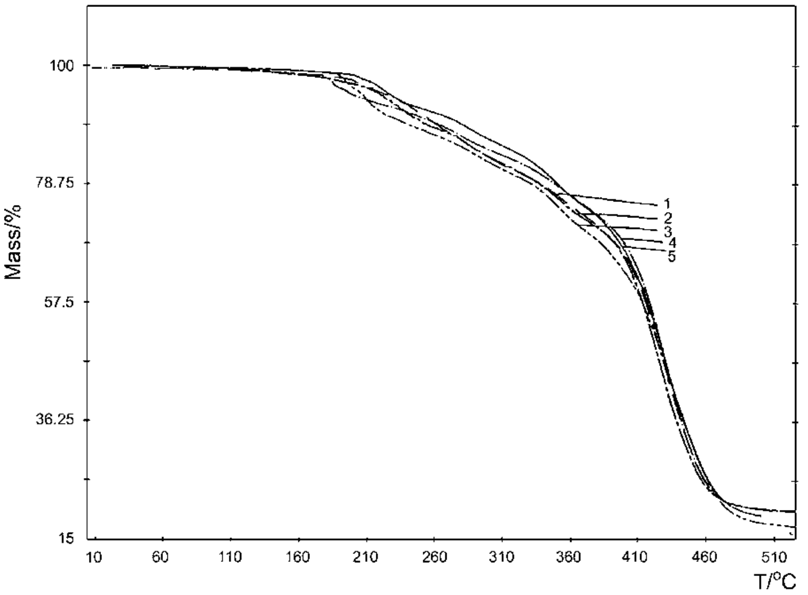

Fig. 3 The TG curves for 1# – 5# of dry PAM; 1 – 1#; 2 – 2#; 3 – 3#; 4 – 4#; 5 – 5#

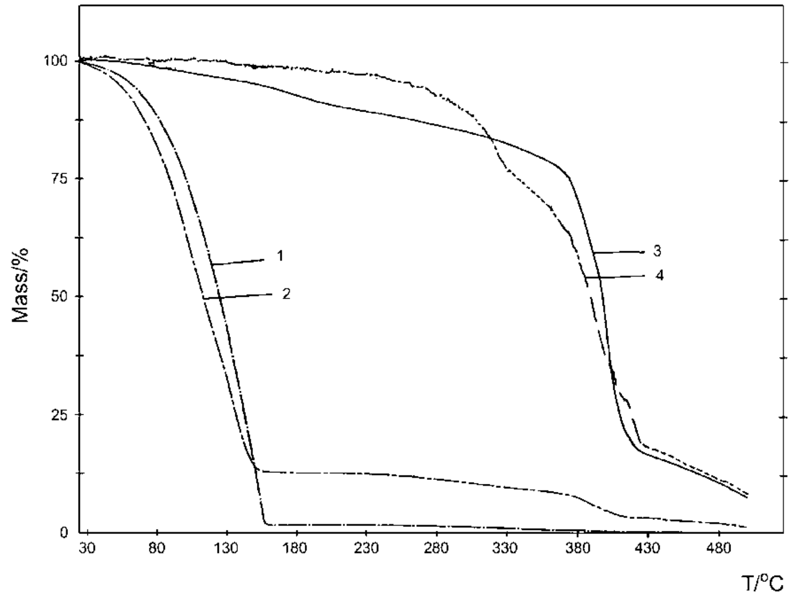

Fig. 4 The TG curves for wet and dry of PDMA and PDEA 1 – wet PDMA; 2 – wet PDEA; 3 – dry PDMA; 4 – dry PDEA

As seen from Table 3, the measured percentage mass loss increases with increasing monomer concentration in the PAM. This may be caused by an increase in the cross-linked polymer. When the plasma duration time (PDT) was less than 30 s, the percentage mass loss relating to water increases with increasing time. Over 30 s, the percentage of water lost dropped. This trend suggests that there is an optimum PDT during the polymerization.

It is interesting to note that the percentage of water absorbed decreases with increasing alkyl chain length, and the activation energy for loss of the bonded water decreases with increase in the mass of bonded water, which indicates that the ability to absorb water decreases with decreasing hydrophilicity of the polymers.

Conclusions

1. The water absorbed in PAM, PDMA and PDEA displays two different states weakly-bonded water and bonded water.

2. The thermal decomposition scheme for the studied polymers involves first the release of the weakly-bonded water, followed by immediate release of the bonded water, and finally the polymers decompose.

3. The mass of water absorbed increases with increasing monomer concentration, it first increases and then decreases with increase of the plasma duration, and it decreases with increase in length of the alkyl chain.

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References

1 Y. Osada, A. T. Bell and M. Shen, J. Polym. Sci. Polym. Lett. Ed., 16 (1978) 309.
2 Y. Osada, M. Takase and T. Iryama, J. Polym., 15 (1) (1983) 81.
3 T. Zhen, Gao fen zi tong bao, 2 (1993) 91.
4 H. E. Kissinger, Anal. Chem., 29 (1957) 1702.
5 S. Jun and Z. Liu, Polymeric Materials Science and Engineering, 13 (1997) 35.
6 N. Fan, Dictionary of Organic Synthesis, Elsevier, Beijing, China.
7 C. Panattoni, R. Graziani, B. Z. Bangoli and G. Bombieri, Inorg. Chem., 8 (1969) 320.
8 J. G. Allpress and A. N. Hambly, Aust. J. Chem., 12 (1959) 569.
9 Z. R. Lu, J. P. Sun, L. Yang and H. Z. Wang, Thermochim. Acta, 255 (1995) 281.
10 L. M. Minsk, J. Polym. Sci., Polym. Chem. Edition, 1974, p.133.