Colloid Polym Sci (2009) 287:609–614
DOI 10.1007/s00396-009-2015-2

SHORT COMMUNICATION

The thermolysis behavior of Ag/PAMAMs nanocomposites

Zheng Peng · Jianmin Zhang · Xiuguo Sun · Jinhui Yang · Jianzhi Diao

Received: 7 November 2008 / Revised: 7 February 2009 / Accepted: 9 February 2009 / Published online: 6 March 2009

Abstract Ag/polyamidoamine (PAMAM) nanocomposites were produced by photoreduction of relevant metallic salts in different generations of PAMAM (PAMAMs) methanol solutions under room temperature and ambient pressure. The obtained Ag nanoparticles were quite uniform in size with a diameter of about 15 nm. Thermogravimetric analysis (TGA) results showed that the amount of Ag nanoparticles could well affect the thermal stability of PAMAMs. As the mass ratio of Ag nanoparticles to PAMAMs increased, the weight-losing ratios decreased. Meanwhile, TGA curves also indicated that the thermal behavior of Ag/PAMAMs was greatly different in the two stages of low (130~280 °C) and high temperature (280~450 °C) range; the loading of Ag nanoparticles mainly influences the thermal stability of PAMAMs in high temperature region (280~450 °C). Moreover, the multistage decomposition profile of derivative thermal gravimetry curves suggested that there might contain some intermediate Ag/PAMAMs type of composites.

Keywords PAMAMs · Ag nanoparticle · Thermolysis

Introduction

The properties of nano- or microscale sizes of metals are size-dependent and can be simply tuned by changing the dimension [1]. Recently, people found that polymer embedding represents a simple but effective way to use mesoscopic properties of nano-sized metals because polymer/metal nanoparticle composites are very useful for functional applications [2], of which silver polymer nanocomposites have a lot of novel properties and have many potential applications in the areas of heterogeneous catalysts, antibacterial agent and health-care products [3, 4], and so on. There are many polymer-embedding methods [5–8] to synthesize silver polymer nanocomposites, such as chemical reduction [9] and photoreduction [10–12].

High generations of dendritic polyamidoamines (PAMAMs) have a dramatic structure because they exhibit densely packed near-spherical topologies with many cavities in nanometer sizes [13], and the cavities can act as nanoscale templates to produce metal nanoparticles [14–17].

In this paper, Ag nanoparticles were successfully prepared by amino-terminated dendritic PAMAMs acting as monodispersed templates. And, the thermal behavior of Ag/PAMAMs nanocomposites was investigated by virtue of thermal gravimetry (TG)-derivative thermal gravimetry (DTG) techniques in detail.

Experimental

Materials

Ethylenediamine, methanol, and silver nitrate are analytically pure and used as received, while acrylic acid ester was used after being purified by distillation.

Z. Peng (✉) · J. Zhang · X. Sun · J. Yang · J. Diao
School of Material Science and Engineering,
Shijiazhuang Railway Institute,
Shijiazhuang 050043, People's Republic of China
e-mail: sjzpzh@sina.com

G1-G5 PAMAM was synthesized by the reaction to ethylenediamine with acrylic acid ester in methanol according to the literature [18].

Apparatus

The morphology of the Ag/PAMAMs nanocomposites were observed on a Hitachi Model H-800 transmission electron microscope. Samples for transmission electron microscopy (TEM) observation were prepared by ultrasonic dispersion in methanol for 30 min, followed by dipping copper 400-mesh carrier grids covered with carbon-coated Formvar films into the dispersions.

Thermogravimetric analysis (TGA) data for the PAMAMs and composites were taken on 851^{e} TGA/SDTA (Mettler-Toledo, Switzerland) at a heating rate of 10 °C/min in argon atmosphere.

Synthesis of Ag/PAMAM nanocomposites

Ag/PAMAMs nanocomposites were produced by photo-reduction of silver nitrate in PAMAM methanol solutions under room temperature and ambient pressure. Different amount of silver nitrate (gram mass, (a) 0 g; (b) 0.32 g; (c) 0.64 g; (d) 1.08 g; (e) 1.44 g; (f) 1.60 g) and PAMAMs (10.0 g) were dissolved in methanol (100 mL), respectively. These solutions were respectively put into four-necked flasks equipped with mechanical stirrer and nitrogen inlet, then the silver nitrate methanol solutions were slowly added into the flasks within 2 h.

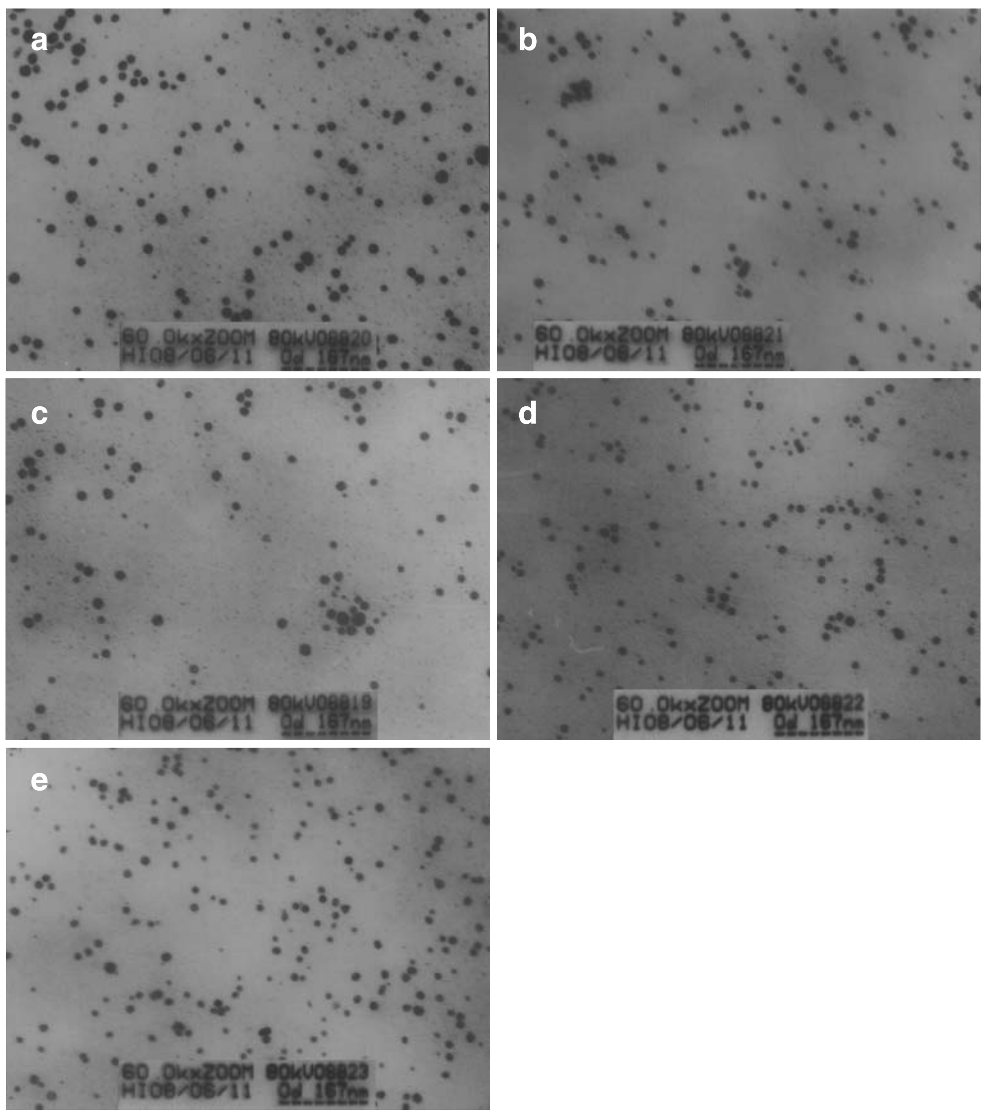

Fig. 1 TEM images of Ag/PAMAMs nanocomposites, the mass ratio of silver nanoparticles to: **a** G1; **b** G2; **c** G3; **d** G4; **e** G5 PAMAM is 1.0:10

The mixture was continuously stirred under a nitrogen atmosphere for 3 h; it was pale yellow. Later, the mixture was irradiated under ultraviolet light lamp (180 W) for 3 h; the color of mixtures became dark, and some dark suspension appeared. Subsequently, the mixed solutions were filtrated with a buchner filter after ultraviolet irradiation. It was found that the limpidity filter liquor did not turn turbid when the filter liquor was titrated by dilute hydrochloric acid., so silver nitrate in the solutions was considered to be completely photoreduced at the moment.

Whereafter, the mixtures were volatilized in rotary vacuum evaporator at 40 °Cfor 5 h. Then it was dried in a vacuum drying oven at 50 °C for 24 h. Finally, the brown products (the gram mass: (a) 10.00 g; (b) 10.20 g; (c) 10.40 g; (d) 10.60 g; (e) 10.80 g; (f) 11.00 g; in the series of

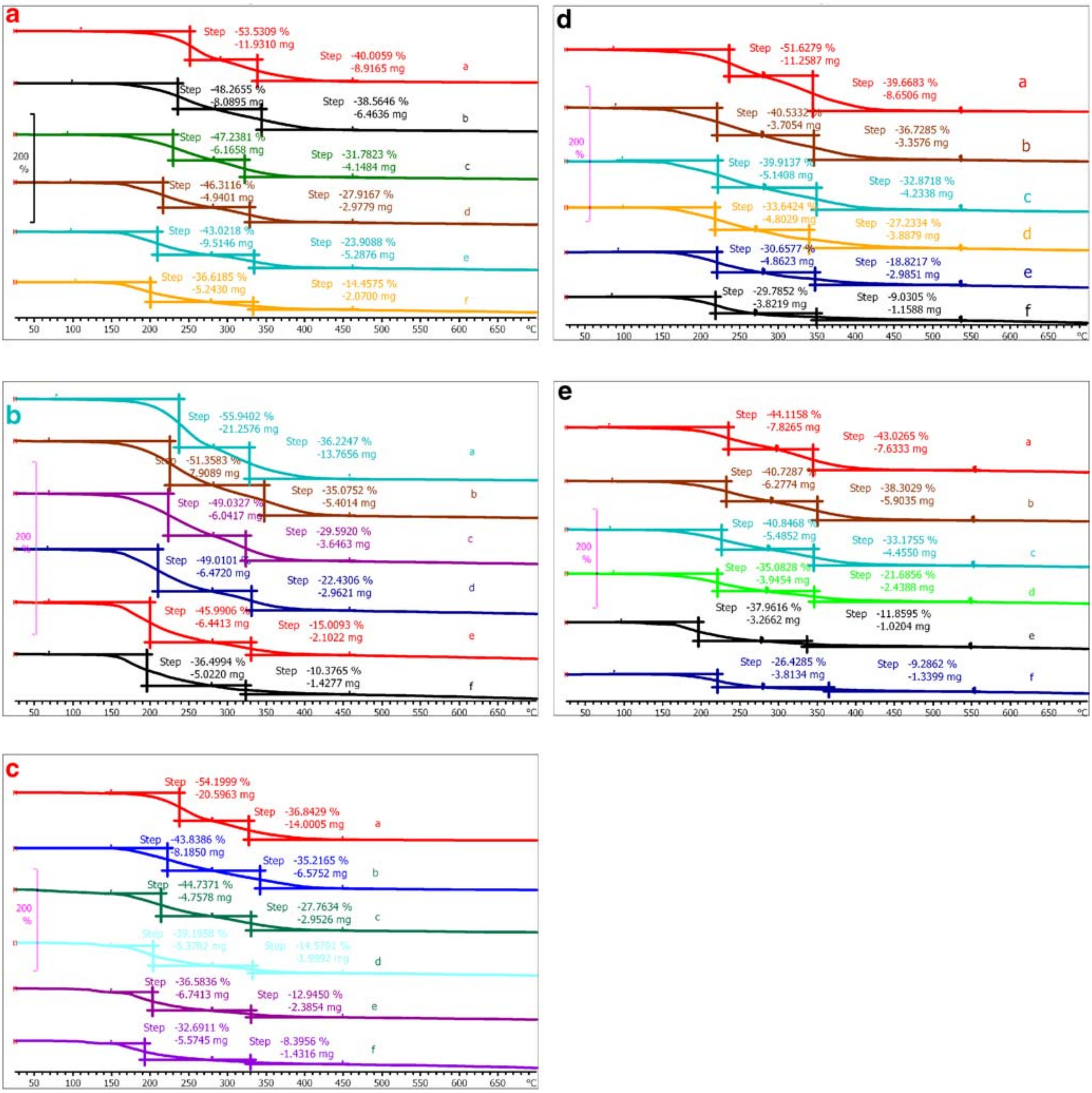

Fig. 2 TGA curves of Ag-PAMAM composites with different mass ratio of Ag nanoparticles to **a** G1; **b** G2; **c** G3; **d** G4 and **e** G5 PAMAM

nanocomposites, the mass ratio of Ag nanoparticles to PAMAMs is: (a) 0:10; (b) 0.2:10; (c) 0.4:10; (d) 0.6:10; (e) 0.8:10; (f) 1.0:10.) were collected.

Results and discussion

The morphology of Ag/PAMAMs nanocomposites was observed by transmission electron microscope, and it is shown in Fig. 1.

It shows that the Ag nanoparticles in different generations of PAMAM are near-spherical and quite uniform in size with a diameter of 15 nm. So it can be concluded that PAMAMs can be considered as a good template to prepare silver nanoparticles.

Figure 2 shows the TGA curve of the Ag/PAMAMs nanocomposites with the different mass ratio of Ag nanoparticles to different generations of PAMAM in argon atmosphere. The weight-losing ratios for all samples accelerate between 130 and 450 °C. All of the curves of PAMAMs and Ag/PAMAMs nanocomposites can be marked by two stages for the total weight-losing curves; the point of intersection is about 280 °C in each curve. According to the data in Table 1, the total weight-losing ratio of pure PAMAMs is much higher than that of Ag/PAMAMs nanocomposites. As the loading of Ag nano-

Table 1 The weight-losing ratio of Ag-PAMAMs composites with different mass ratio of Ag nanoparticles to PAMAMs at different stages

The numbers of generations	Serial number	The mass ratio	The total weight-losing ratio (%)	The weight-losing ratio (%)		The ratio (%) of the losing PANAM to the total PANAM weight		The ratio of the losing PANAM at two temperature stages
				130–280	280–450	130–280	280–450	
G1	a	00:10	93.53	53.53	40.00	53.53	40.00	1.34
	b	0.2:10	86.83	48.27	38.56	49.26	39.35	1.25
	c	0.4:10	79.02	47.24	31.78	49.21	33.10	1.49
	d	0.6:10	74.23	46.31	27.92	49.27	29.70	1.66
	e	0.8:10	66.93	43.02	23.91	46.76	25.99	1.80
	f	1.0:10	51.08	36.62	14.46	40.69	16.07	2.53
G2	a	00:10	92.16	55.94	36.22	55.94	36.22	1.54
	b	0.2:10	86.44	51.36	35.08	52.41	35.80	1.46
	c	0.4:10	78.62	49.03	29.59	51.07	30.82	1.66
	d	0.6:10	71.44	49.01	22.43	52.14	23.86	2.19
	e	0.8:10	60.99	45.99	15.00	49.99	16.30	3.07
	f	1.0:10	46.88	36.50	10.38	40.56	11.53	3.52
G3	a	00:10	91.04	54.20	36.84	54.20	36.84	1.47
	b	0.2:10	79.06	43.84	35.22	44.73	35.94	1.24
	c	0.4:10	72.50	44.74	27.76	46.60	28.92	1.61
	d	0.6:10	53.77	39.20	14.57	41.70	15.50	2.69
	e	0.8:10	49.53	36.58	12.95	39.76	14.08	2.82
	f	1.0:10	41.09	32.69	8.40	36.32	9.33	3.89
G4	a	00:10	91.30	51.63	39.67	51.63	39.67	1.30
	b	0.2:10	77.26	40.53	36.73	41.36	37.48	1.10
	c	0.4:10	72.79	39.92	32.87	41.58	34.24	1.21
	d	0.6:10	60.87	33.64	27.23	35.79	28.97	1.24
	e	0.8:10	49.48	30.66	18.82	33.33	20.46	1.63
	f	1.0:10	38.82	29.79	9.03	33.10	10.03	3.30
G5	a	00:10	87.14	44.11	43.03	44.11	43.03	1.03
	b	0.2:10	79.03	40.73	38.30	41.56	39.08	1.06
	c	0.4:10	74.03	40.85	33.18	42.55	34.56	1.23
	d	0.6:10	56.77	35.08	21.69	37.32	23.07	1.62
	e	0.8:10	49.82	37.96	11.86	41.26	12.89	3.20
	f	1.0:10	35.72	26.43	9.29	29.37	10.32	2.84

particles increases, the total weight-losing ratio of pure PAMAMs decreases rapidly; it proves that the Ag nanoparticles could efficiently improve the thermal stability of PAMAMs. And the loading of Ag nanoparticles mainly enhances the thermal stability of PAMAMs in high temperature region (280~450 °C). Moreover, the ratios of the losing PAMAMs at the low temperature region of 130~280 °C to the high temperature region of 280~450 °C increase as the loading of Ag nanoparticles increases.

To obtain a more precise analysis on thermal stability, the samples were investigated by differential derivative thermal gravimetry. The weight-losing rate (dm/dT, which is defined as the change of mass with temperature, the unit is mg $°C^{-1}$) with temperature for all samples is compared in Fig. 3. The dm/dT curve for PAMAMs is significantly deeper and sharper than that of Ag/PAMAMs nanocomposites. The weight-losing ratio at each temperature inflexion is given in Table 1 and Fig. 2. The weight-losing rates for

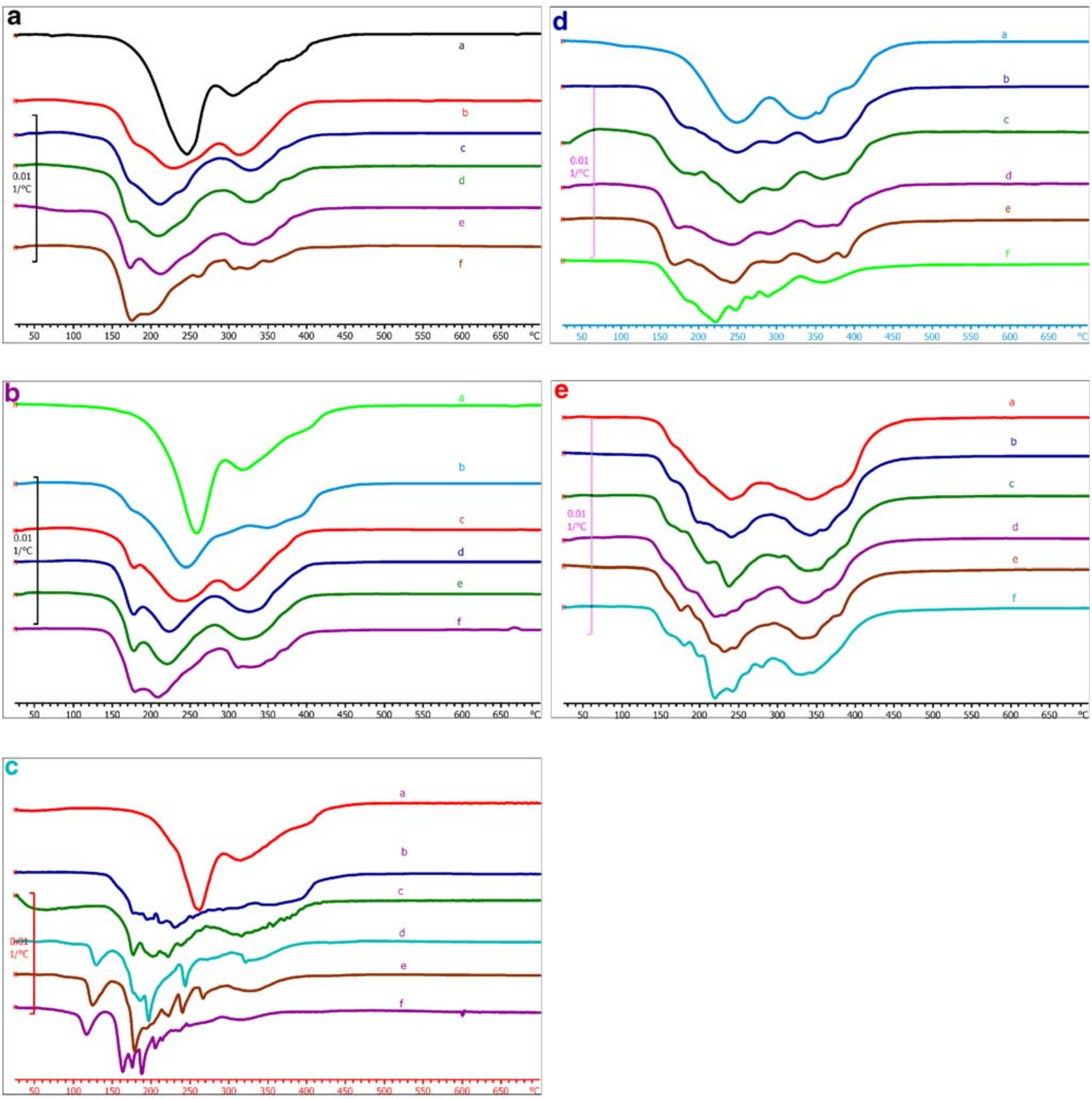

Fig. 3 DTG curves of Ag/PAMAM composites with different mass ratio of Ag nanoparticles to **a** G1; **b** G2; **c** G3; **d** G4 and **e** G5 PAMAM

all samples accelerate at about 200 °C until they reach their inflexion, accompanied by a dramatic weight drop. The weight-losing rate of PAMAMs is higher than that of Ag/PAMAMs nanocomposites, and the weight-losing rate is decreased when the silver percent was increased, indicating that the silver nanoparticles may enhance the thermal stability of the polymer. The weight loss of the samples seems to stop further at the high temperature region of 450~700 °C.

All of the DTG curves of PAMAMs have two large peaks between 200 and 320 °C, while the DTG curves of Ag/PAMAMs nanocomposites have more than two peaks; it may indicate the formation of some different intermediate Ag+/PAMAM type [19] of composites in the thermolysis process. As the loading of Ag nanoparticles increase, in all curves a main inflexion about 175 °C occur, which corresponds to the initial stage of thermolysis of PAMAMs, it shows that the appearance of Ag nanoparticles can accelerate the initial thermolysis of PAMAMs. At the same time, the two large peaks of PAMAMs shift to the lower temperature, which proves that the weight-losing ratio at the lower temperature stage will increase in the total weight-losing ratio when the loading of Ag nanoparticles increases.

Conclusions

In this work, Ag/PAMAMs nanocomposites with different mass ratio of Ag nanoparticles to different generations of PAMAM were synthesized successfully. It is found that the amount of Ag nanoparticles could efficiently affect the thermal stabilities of PAMAMs. As the mass ratio of Ag nanoparticles increased, the weight-losing ratio decreased, and the proportion of weight-losing ratio of the lower temperature stage to the higher temperature increased, which has shown that the loading of Ag nanoparticles could well improve the thermal stabilities of PAMAMs in the higher temperature region (280~450 °C). Moreover, the multistage decomposition profile of DTG is observed. It can be concluded that the Ag/PAMAMs nanocomposites with higher silver loading might contain some intermediate Ag/PAMAMs type of composite.

Acknowledgment This program is financially supported by Natural Science Foundation of Hebei Province (E200800440).

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