

# Fabrication, Structures, and Properties of Acrylonitrile/Methyl Acrylate Copolymers and Copolymers Containing Microencapsulated Phase Change Materials

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**ABSTRACT:** The polyacrylonitrile-methyl acrylate (AN/MA mole ratio 100/0–70/30) copolymers and copolymers (AN/MA mole ratio 85/15) containing up to 40 wt % of microencapsulated *n*-octadecane (MicroPCMs) are synthesized in water. The MicroPCMs were incorporated at the step of polymerization. The effect of the MA mole ratio and MicroPCMs content on structures and properties of the copolymers were studied by using Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance (<sup>1</sup>H NMR), scanning electronic microscope (SEM), differential scanning calorimetry (DSC), thermogravimetry analysis (TG), gel permeation chromatography (GPC), and X-ray diffraction (XRD). The feeding ratio agreed well with the composition of

the AN/MA copolymers. The copolymers are synthesized in the presence of MicroPCMs. The melting point moves to lower temperature (206°C), while the decomposition temperature moves to higher temperature (309°C) with increasing of the MA mole ratio and microcapsules content. The number-average molecular weight of the copolymer is ~30,000. The crystallinity of the copolymer decreases with increasing of the MA mole ratio and microcapsules content. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 2776–2781, 2007

**Key words:** structure–property relations; thermal properties; melting point; supramolecular structures; differential scanning calorimetry (DSC)

## INTRODUCTION

Microencapsulated phase change materials (MicroPCMs) are tiny particles that cores are surrounded by coating or shell(s).<sup>1</sup> MicroPCMs have been used in the manufacture of thermoregulated fibers and fabrics<sup>2</sup>; however, there are still many tough problems in the evenly distribution of MicroPCMs in the polymer matrix.<sup>3</sup> The MicroPCMs are usually synthesized in water solution<sup>4</sup>; however, they aggregate in the process of drying. The aggregated microcapsules are destroyed in the melt extruding process or in the wet-spinning process,<sup>3,5</sup> or removed from the blend in the spinning process by the filter. If the MicroPCMs are added in the polymerization process using water as a solvent, the ratio of aggregated microcapsules will be decreased. The energy storage properties of the polymer will be strengthened.

The structures and properties of thermoregulated polyacrylonitrile–vinylidene chloride (PAN/VDC)

fibers have been studied.<sup>5</sup> The spinnability of the PAN/VDC – *N,N*-dimethyl formamide solution containing MicroPCMs decreases quickly with the increase of MicroPCMs content, since the ratio of aggregated microcapsules increases. The approach of melt-spinning PAN-based fiber containing MicroPCMs has never been reported. The key step for realizing melting process PAN-based polymer is to lower the melting point or enhance the decomposition temperature.<sup>6–8</sup> Methyl acrylate (MA) comonomers possess better flexibility, so the incorporation of MA will help to weaken the dipole–dipole interaction.<sup>7</sup> In this article, we incorporate microcapsules into AN/MA copolymer matrix at the step of polymerization. The fabrication, structures, and properties of AN/MA copolymer and the copolymer containing MicroPCMs are studied in detail.

## EXPERIMENTAL

### Materials

Acrylonitrile (AN) was purchased from Shanghai San Ai Si Reagent. Methyl acrylate (MA) was purchased from Shanghai Hua Qi (Shanghai, China). AN and MA were purified by removing inhibitor using atmospheric distillation, prior to use. Chain transfer agent-dodecyl mercaptan (RSH), was a product of Shanghai Qingpu syn-

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TABLE I  
Composition for Various AN/MA Copolymers

Sample no.	Molar ratio (feeding)	AN		MA		RSH		MicroPCMs (g)
		(g)	(mmol)	(g)	(mmol)	(mg)	(mmol)	
1	100/0	20.38	384	0	0	404.2	2.0	0
2	90/10	18.34	346	3.32	38	429.4	2.1	0
3	85/15	17.33	327	4.88	57	446.3	2.2	0
4	75/25	15.28	288	8.26	96	471.5	2.3	0
5	100/0	20.38	384	0	0	404.2	2.0	10
6	95/5	19.34	365	1.65	19	421.0	2.1	10
7	90/10	18.34	346	3.32	38	429.4	2.1	10
8	85/15	17.33	327	4.88	57	446.3	2.2	10
9	80/20	16.30	307	6.61	77	454.7	2.3	10
10	75/25	15.28	288	8.26	96	471.5	2.3	10
11	70/30	14.26	269	9.92	115	479.9	2.4	10

The mass of KSP is 4.20 g; the mass of SBS is 1.85 g/50 mL.

thetic reagent plant. Water-soluble redox initiator, potassium persulfate (KSP), was purchased from Medicament Company in China and sodium bisulfate (SBS) was a product of Hubei Province Medicament Company. Microencapsulated *n*-octadecane (MicroPCMs) was prepared in our laboratory.<sup>9</sup> The diameters of the microcapsules are in the range of 0.2–3  $\mu\text{m}$ . The thermal resistant temperature of the microcapsules is  $\sim 220^\circ\text{C}$ .

### Copolymerization

We adopted aqueous redox-initiated polymerization. An example of typical procedure for an 85/15 (the abbreviation 85/15 for the copolymers refers to the molar feed ratio of AN and MA) copolymer is given in detail as follows: The reactor was a 500 mL 3-necked flask fitted with a condenser, dynamoelectric stirrer, and dropping funnel. First, the flask was charged with 340 mL of deionized water and purged with dry nitrogen for 30 min while heating to the reaction temperature ( $40^\circ\text{C}$ ). The mixture of 327 mmol AN, 57 mmol MA, and 2.2 mmol RSH (2.0 wt % of total comonomers) was added followed by 4.20 g of SBS in 10 mL deionized water. After 5 min, 50 mL KSP saturation solution was added and the reaction was allowed to proceed for 3 h at  $40^\circ\text{C}$ .<sup>7</sup> The product was then directly filtered and washed with large amounts of deionized water. The white products were dried in a vacuum oven at  $70^\circ\text{C}$  till its weight was constant. The major reaction variables were comonomer ratio and the content of microcapsules (Tables I and II) but the total comonomer amount was kept constant at 384 mmol in all the experiments.

### Characterization of copolymers

FTIR spectra of various AN/MA copolymers and microcapsules were measured by using a BRUKER TENSOR37 spectrophotometer (wave-numbers  $400\text{--}4000\text{ cm}^{-1}$ ).

The surface morphology of the AN/MA copolymers and copolymers containing microcapsule was measured by using a Quanta 200 scanning electronic microscope (SEM). The sample powder was dissolved in *N,N*-dimethyl formamide (DMF) solution (5 wt %). One drop of the solution was placed on a glass wafer and air-dried overnight, and gold-coated.

$^1\text{H}$  NMR spectra were obtained by using a BRUKER AVANCE AV 300 MHz spectrometer. Dimethyl sulfoxide (DMSO) was used as a solvent.

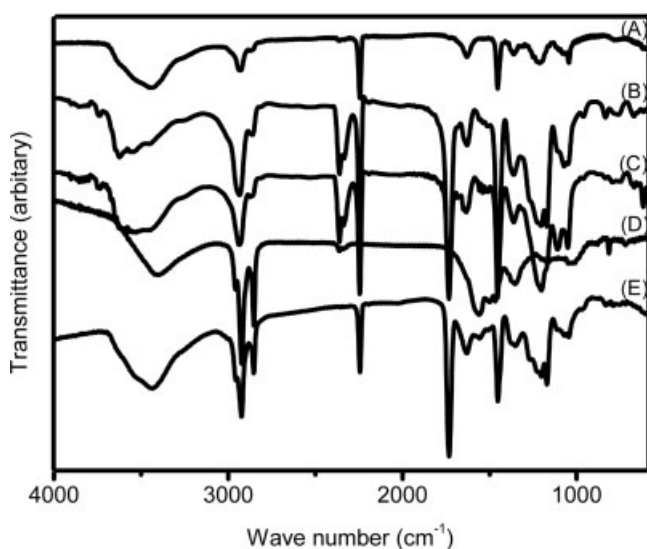
The melting point ( $T_m$ ) and decomposition temperature of the samples were evaluated using a differential scanning calorimeter (DSC, PERKIN ELMER DSC7). The heating rate was  $10^\circ\text{C}/\text{min}$  and the samples were heated from room temperature to  $350^\circ\text{C}$ , all under nitrogen ( $\text{N}_2$ ) atmosphere.

The thermal resistant temperatures of all the samples were obtained by using a thermogravimetry (TG, NETZSCH, STA409 PC/PG TG-DTA) at a heating rate of  $10^\circ\text{C}/\text{min}$  under a nitrogen ( $\text{N}_2$ ) atmosphere.

Molecular weight measurements from gel permeation chromatography (GPC) were conducted at  $40^\circ\text{C}$  with a Water  $M_{32}$  Separation Module, equipped with a Waters 410 differential refractometer detector and a

TABLE II  
Composition for 85/15 AN/MA Copolymers Containing Various Mass Ratios of MicroPCMs

Sample no.	Molar ratio (feeding)	Microcapsule (feeding)	
		(wt %)	(g)
12	85/15	5	1.11
13	85/15	10	2.23
14	85/15	15	3.34
15	85/15	20	4.46
16	85/15	25	5.57
17	85/15	30	6.68
18	85/15	35	7.77
19	85/15	40	8.92



**Figure 1** FTIR spectra of polymers: (A) Sample 1; (B) Sample 2; (C) Sample 3; (D) Microcapsule; (E) Sample 8.

Waters 510 chromatography pump coupled in parallel. DMF was used as a solvent.

Diffraction patterns of the AN/MA copolymers (85/15) containing microcapsules were obtained by using X-ray diffraction (XRD, D/max-2500, 40 kV, 100 mA, Cu K $\alpha$ 1) at room temperature. The scanning range was 3–50° (2 $\theta$ ).

## RESULTS AND DISCUSSION

FTIR spectra of microcapsule and polymers (Samples 1, 2, 3, and 8) are shown in Figure 1. The strong absorption peak at  $\sim 1734\text{ cm}^{-1}$  in the spectra of Samples 2 (90/10 AN/MA) and 3 (85/15 AN/MA) is associated with the carboxide group (C=O) stretching vibration. This specific peak is not observed in the spectrum of Sample 1 (PAN polymer) as expected. The absorp-

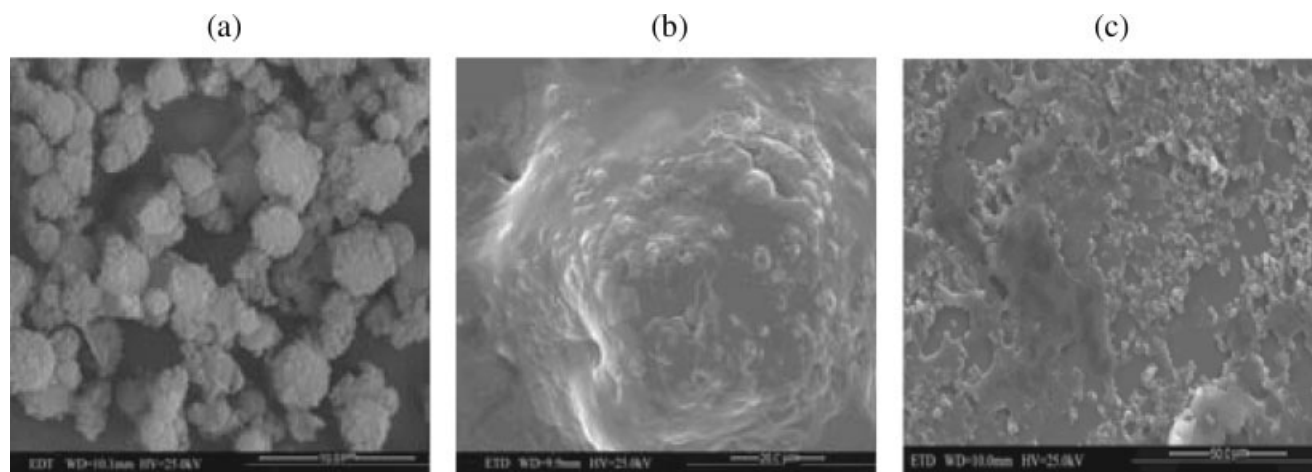
tion peaks at  $\sim 1204\text{ cm}^{-1}$  is associated with C—O group and C—N group stretching vibration. The characterized peak is smaller in the spectrum of Sample 1 than in that of Samples 2 and 3. These two characterized peaks in the spectra of the Samples 2 and 3 demonstrated the formation of AN/MA copolymer.

The strong absorption peak at  $\sim 2900\text{ cm}^{-1}$ , which is multiple peaks in the spectrum of microcapsule (D), is different from that in the spectra of Samples 1, 2, and 3 obviously. We can also see the multiple peaks in the spectrum of Sample 8 (85/15 AN/MA, 10 g microcapsule). So the microcapsules existed in the AN/MA copolymer.

The SEM micrographs of microcapsules and AN/MA copolymers containing microcapsules are shown in Figure 2. Micrographs (b) and (c) present the morphology of the various copolymers containing microcapsules. The microcapsules are distributed in the copolymer matrix uniformly. The dispersibility of the microcapsules is better than that in the polypropylene matrix.<sup>3</sup> The ratio of aggregated microcapsules in the AN/MA copolymers is relatively low.

The calculation results from  $^1\text{H}$  NMR spectra of Samples 3 and 4 are listed in Table III. The mole ratio of AN and MA in Sample 3 is 85.36 and 14.64 mol %, respectively. The mole ratio of AN and MA in Sample 4 is 75.68 and 24.32 mol %, respectively. The result shows that the copolymer compositions are agreed well with the feeding monomer ratios. This indicates that AN/MA copolymer is synthesized in water very well.<sup>10</sup>

The DSC curves of copolymers containing 10 g microcapsules are shown in Figure 3. A small endothermic peak at  $\sim 32\text{--}35^\circ\text{C}$ , which is caused by the melting of *n*-octadecane in the microcapsule, is observed on the DSC curve of copolymers containing MicroPCMs. The increase of the MA molar ratio pushes the exothermic temperature to the higher side



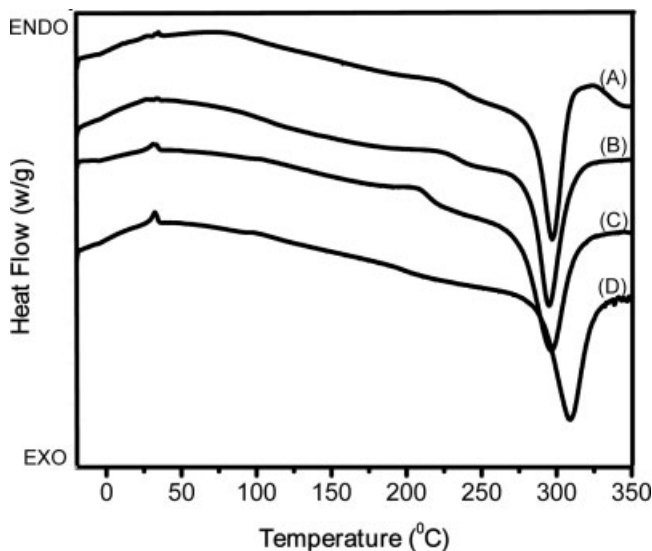
**Figure 2** Micrographs of microcapsules and AN/MA copolymers containing microcapsules: (a) Microcapsule; (b) Sample 6; (c) Sample 7.

**TABLE III**  
Composition of Samples 3 and 4 Calculated from  $^1\text{H}$  NMR

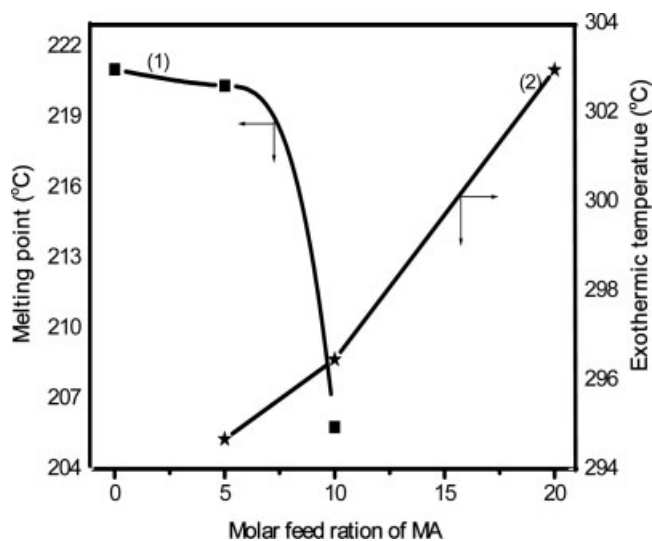
Sample no.	Feeding ratio (mol %)	Copolymer composition	
		AN (mol %)	MA (mol %)
3	85/15 AN/MA	85.36	14.64
4	75/25 AN/MA	75.68	24.32

and meanwhile depresses the melting point.<sup>6–8</sup> It is attributed to the cyclization more difficultly with increasing the MA molar ratio. This exothermic peak is primarily consistent with cyclization, the formation of ladder structure.<sup>11</sup> This result is expected as the incorporation of flexible MA monomers and microcapsules, which weakens the dipole–dipole interaction between  $-\text{CN}$  and  $-\text{CN}$ , increases the decomposition temperature. A small endothermic peak can be observed prior to the main exothermic, it is believed that the melting peak of PAN and its copolymers could be observed clearly only at very high heating rates (i.e.,  $60^\circ\text{C}/\text{min}$  or above) under a nitrogen atmosphere;<sup>6</sup> whereas, at slow heating rates, they degrade (undergo exothermic cyclization process) before melting.

The endothermic and exothermic peak data above  $200^\circ\text{C}$  of AN/MA copolymers containing MicroPCMs are plotted in Figure 4. The melting point decreases, while the decomposition temperature increases with the increase of molar ratio of MA. The peak temperature for cyclization of PAN homopolymer and 85/15 AN/MA copolymer have been reported to be about  $288$  and  $290^\circ\text{C}$ , respectively.<sup>12</sup> The melting temperature range of melt-spun high acrylonitrile copolymer fiber

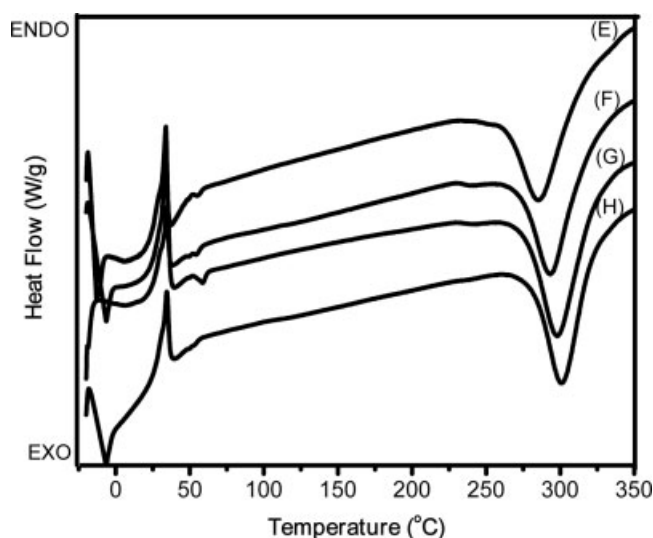


**Figure 3** DSC curves of copolymers containing 10 g microcapsules: (A) Sample 5; (B) Sample 6; (C) Sample 7; (D) Sample 8.

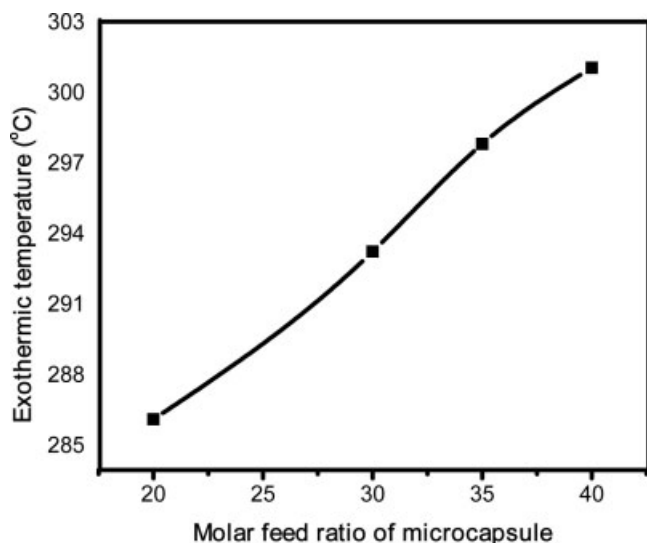


**Figure 4** Curves of relationship between (1) melting point ( $T_m$ ) and feeding molar ratio of MA and (2) decomposition temperature ( $T_d$ ) and feeding molar ratio of MA.

(Amlon<sup>®</sup>) was tested and that centered at  $\sim 225^\circ\text{C}$ .<sup>13</sup> In our research, it is noted that the exothermic temperature of 85/15 AN/MA copolymer containing 10 g microcapsules can rise up to  $\sim 309^\circ\text{C}$  and the melting point of 90/10 AN/MA copolymer containing 10 g microcapsules can be decreased to about  $206^\circ\text{C}$ , which is lower than the average melting point of Amlon<sup>®</sup> and the thermal resistant temperature of microcapsules ( $220^\circ\text{C}$ ).<sup>8</sup> This result is associated with the incorporation of MA units and the microcapsules, which disorder the symmetry of AN chain and increase the amorphous region of copolymer, therefore reducing the crystallinity and the melting point.

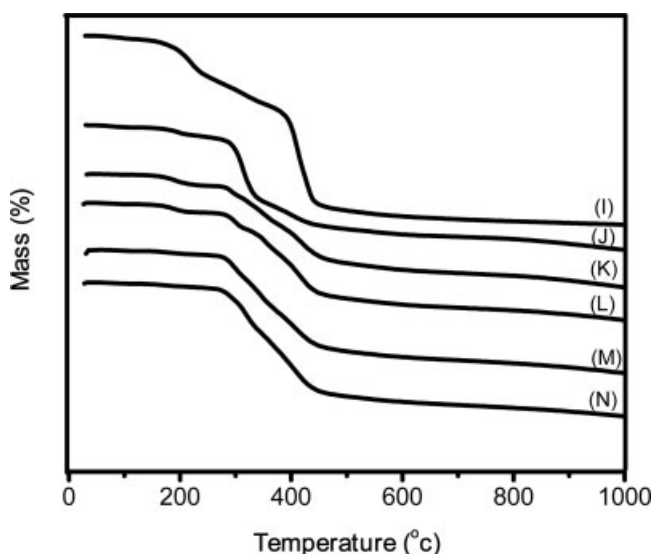


**Figure 5** DSC curves of 85/15 AN/MA copolymers containing microcapsules: (E) Sample 15; (F) Sample 17; (G) Sample 18; (H) Sample 19.



**Figure 6** The curve of relationship between microcapsules (mol %) and decomposition temperature ( $T_d$ ).

The DSC curves of 85/15 AN/MA copolymers containing various contents of microcapsules are shown in Figure 5. An endothermic peak at  $\sim 32\text{--}35^\circ\text{C}$ , which is also caused by the melting of *n*-octadecane in the microcapsule, is observed on all the DSC curves. The intensity of the peak is direct proportional to the content of MicroPCMs in the matrix. A systematic increase in the exothermic temperature of copolymers containing various contents of microcapsules is observed with increasing the content of microcapsules (Fig. 6). It is observed from the Figures 5 and 6 that the  $T_d$  increases from 286.7 to  $301.0^\circ\text{C}$  when the content of the microcapsules incorporated into the AN/MA system increases from 20 to 40 wt %. It seems



**Figure 7** TG diagrams of the microcapsules and copolymers containing microcapsules: (I) Microcapsules; (J) Sample 5; (K) Sample 6; (L) Sample 7; (M) Sample 9; (N) Sample 10.

**TABLE IV**  
Onset of Mass Loss in the TG Diagrams

Sample no.	Onset temperature ( $^\circ\text{C}$ )	DTG peak value ( $^\circ\text{C}$ )
5	169.5	195.4
6	165.2	191.2
7	166.1	188.7
9	165.5	187.8
10	152.6	170.5
Microcapsules	188.5	221.2

that the microcapsules act to increase the free volume among molecular chains and reduce the dipole-dipole interaction between the AN groups, leads to the cyclization more difficultly. Hence, the cyclization peak removes to the higher temperature.

TG diagrams of the microcapsules and copolymers containing microcapsules are shown in Figure 7. The thermal stability of the AN/MA copolymers decreases with increase of the mole ratio of MA (Table IV). The peak value and the onset temperature drop with the mole ratio of MA increasing, which disrupts the long-order of AN chain, leading to increase of the amorphous region of the copolymers. The results are consistent with that of Figures 3 and 5.

The previous research has approved that the copolymers of acrylonitrile-methyl acrylate are melt-processable when the methyl acrylate molar ratio is  $\sim 15\%$ .<sup>6-8,14</sup> The thermal behaviors of the copolymers containing MicroPCMs in our research are very similar to the results of previous research on acrylonitrile-methyl acrylate copolymers.<sup>6-8</sup> The thermal resistance of microencapsulated *n*-octadecane is  $\sim 220^\circ\text{C}$ .<sup>9</sup> In addition, the blend of MicroPCMs and polypropylene has already been melt-spun into fiber.<sup>3</sup> Therefore, the copolymers of acrylonitrile-methyl acrylate containing MicroPCMs are probably melt-processable. Such hypothesis needs further investigation.

Molecular weight distributions of 90/10 and 85/15 AN/MA copolymers are measured. The molecular weights of Sample 2 (90/10 AN/MA) and Sample 3 (85/15 AN/MA) are  $M_n = 32,419$ ,  $M_w = 74,846$  and  $M_n = 12,748$ ,  $M_w = 42,633$  respectively. The  $M_n$  of the copolymer is decreased obviously by increasing the

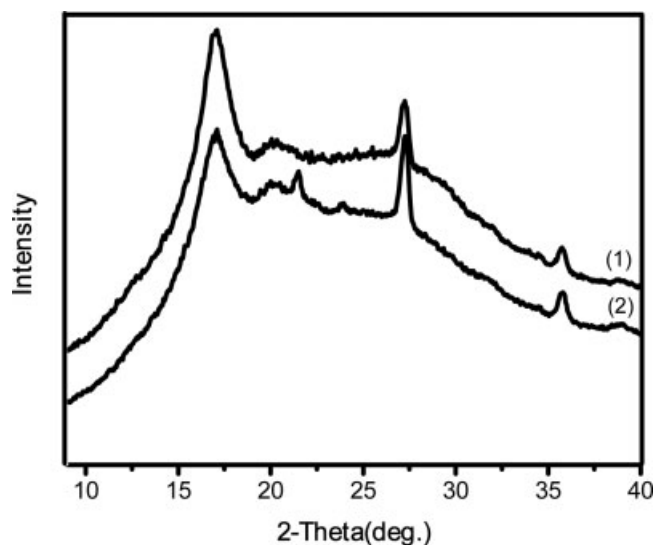
**TABLE V**  
The  $M_n$  of AN/MA Copolymers Obtained by Different Methods

Feed ratio	$M_{na}$ (GPC) <sup>a</sup>	$M_{nb}$ (GPC) <sup>b</sup>	$M_{nc}$ (GPC) <sup>c</sup>
85/15	12,748	18,700	14,300
90/10	32,419	20,200	20,600–32,200

<sup>a</sup>  $M_{na}$ : In our study, the  $M_n$  of AN/MA copolymer obtained by polymerization in water.

<sup>b</sup>  $M_{nb}$ : In the study of Godshall, the  $M_n$  of AN/MA copolymer obtained by solution polymerization.<sup>6</sup>

<sup>c</sup>  $M_{nc}$ : In the study of Bhanu, the  $M_n$  of AN/MA copolymer obtained by redox polymerization.<sup>13</sup>



**Figure 8** X-ray patterns of AN/MA copolymers containing microcapsules: (1) Sample 12; (2) Sample 16.

content of MA. The  $M_n$  of AN/MA copolymers obtained by different polymerization is shown in the Table V. It is observed that the number molecular weights of copolymers produced by polymerization in water are similar with that of copolymers in literature.<sup>6,8</sup>

X-ray patterns of Sample 12 (85/15 AN/MA containing 5 wt % microcapsules) and 16 (85/15 AN/MA containing 25 wt % microcapsules) are shown in Figure 8. The reflection peak of PAN is at  $17^\circ$  ( $2\theta$ ) and the reflection peaks of microcapsules are at  $27^\circ$  ( $2\theta$ ) and  $36^\circ$  ( $2\theta$ ). It is noted that the  $2\theta$  of all of the diffraction peaks is kept stable, which indicates that the crystalline form to be the same in the PAN homopolymer and AN/MA copolymers.

The XRD intensity of PAN is weakened, while the peak of microcapsules is strengthened as the content of microcapsules increases. The crystallinity of AN/MA copolymer drops from 43.1 to 40.4% when the content of microcapsules increases from 5 to 25 wt %. Hence, amorphous region of AN/MA copolymers increases due to the incorporation of microcapsules, leading to the slight decrease of crystallinity and melting point.

## CONCLUSIONS

The polyacrylonitrile–methyl acrylate (AN/MA mole ratio 100/0–70/30) copolymers and 85/15 AN/MA copolymers containing up to 40 wt % of MicroPCMs are synthesized in water. The composition agreed well with the feeding ratio of the AN/MA copolymers. The AN/MA copolymers are synthesized in the presence of MicroPCMs. The melting point of the copolymer moves to lower temperature ( $206^\circ\text{C}$ ), while the decomposition temperature of the copolymer moves to higher temperature ( $309^\circ\text{C}$ ) with the increase of the MA mole ratio and microcapsules content. The AN/MA copolymers containing MicroPCMs are probably melt-processable at a temperature in the range of  $206$ – $220^\circ\text{C}$ .

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