

## Flame retardant synergism of rubber and $Mg(OH)_2$ in EVA composites

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### Abstract

A synergistic effect on flame retardancy was found when acrylonitrile butadiene ultra-fine fully vulcanized powdered rubber (NB-UFPR) was incorporated into ethylene vinyl acetate/nano-magnesium hydroxide (EVA/nano-MH) composite by a new process. The fire performance of EVA and EVA composites was compared in this communication by cone calorimeter test (CCT). The CCT data indicated that the addition of NB-UFPR in EVA/nano-MH system not only reduced the heat release rate, but also prolonged the ignition time of the composite, which is contrary to the effect of NB-UFPR when it was added alone in EVA polymer. Thermogravimetric analysis revealed that nano-MH accelerated the loss of acetic acid, but NB-UFPR assisted to reduce nano-MH's accelerating effect. FTIR spectra showed a new absorption at  $3374\text{ cm}^{-1}$  in the blends of EVA/NB-UFPR and EVA/NB-UFPR/nano-MH.

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### 1. Introduction

The application of ethylene vinyl acetate copolymer (EVA) has been limited by its inherent flammability, especially in cable industry. Inclusion of additives is an effective route to inhibit ignition and lower heat release rate during combustion. There has been a trend recently, driven primarily by environmental and safety considerations, towards the use of halogen free retardant systems, including intumescent formulations and hydrated fillers. Magnesium hydroxide (MH) has been considered to be an environmentally benign flame retardant in wire and cable industry. However, as a hydrophilic inorganic filler, it is difficult to disperse evenly in the hydrophobic polymer matrix. In addition, low effectiveness makes it necessary to incorporate at a very high content in polymers to gain a

satisfying low flammability. Both poor dispersion and high loadings deteriorate the material's mechanical properties, especially toughness [1]. Ternary composites containing both filler and elastomer had been investigated by some scientists as an effective means of enhancing the toughness of filled thermoplastics [2–6]. However, the studies were focused mainly on the improvement of mechanical properties, seldom on the effect to flammability. Up to now, no unsaturated elastomer has been found capable of improving the flame retardance of plastics. In this letter, we will report a special unsaturated elastomer, acrylonitrile butadiene ultra-fine fully vulcanized powdered rubber (NB-UFPR) that improves the flame retardancy of EVA/nano-MH composites when a new manufacturing process is used. The NB-UFPR can be prepared by spray-drying method [7,8]. Acrylonitrile butadiene rubber latex should be mixed with a certain amount of irradiation sensitizer before being irradiated with  $\gamma$ -ray. By spray-drying method, NB-UFPR with basically the same particle size of micelles in NB latex can be obtained. NB-UFPR is easily dispersed

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uniformly in related polymer matrix and can be used as a toughening agent for plastics because of their special structure [7–16]. In order to make nano-MH also to disperse well in EVA matrix, another reported process [17] developed by our group was used in this work. Nano-MH slurry was premixed with irradiated rubber latex before co-spray-drying procedure to get a composite flame retardant (CFR) of NB-UFPR and nano-MH. The so-obtained CFR was then melt-blended with EVA to get ternary composites with better flame retardancy than EVA/nano-MH binary composites.

## 2. Experimental section

### 2.1. Materials and formulations

EVA (Levamelt 500) with 50% vinyl acetate and melt flow index of 2.7 g/10 min was provided by Lanxess. Unmodified nano-MH of hexagonal platelets with average length of 90 nm and thickness of 20 nm was supplied by Yixing Reagent Chemical Factory. Acrylonitrile butadiene latex (Chemigum Latex 248) with solid content of 55 wt% and average micelle size of about 200 nm was provided by Eliokem.

### 2.2. Sample preparation

All the samples were prepared by using a Haake Rheomix Banbury mixer with the same procedures. EVA was added into the mixer with rotational speed of 20 rpm at 160 °C. Nano-MH filler (or CFR or NB-UFPR) was added after EVA polymer was melted and the mixing was carried out at 50 rpm for 10 min. The obtained composites were finally compression molded at 160 °C for 10 min under 10 MPa into sheets of suitable thickness. Samples for testing were cut from the compressed sheets according to the standards mentioned in the following part.

### 2.3. Measurement and characterization

#### 2.3.1. Fire performance

The cone calorimeter (Fire Test Technology) was used to test the materials' fire performance according to ISO5660 under an external heat flux of 35 kW/m<sup>2</sup>. The dimension of the samples was 100 × 100 × 4 mm<sup>3</sup>. Heat release rate (HRR), ignition time (IT), mass loss rate (MLR), effective heat combustion (EHC), and other quantifiable parameters including the yield of carbon dioxide and carbon monoxide were recorded simultaneously.

#### 2.3.2. Thermal stability

Thermal degradation behavior of the samples was studied by thermogravimetric analyzer (TGA, Perkin–Elmer, USA) at a heating rate of 10 °C/min under nitrogen.

#### 2.3.3. FTIR measurement

Fourier Transform Infrared spectroscopy (FTIR, Nicolet Magna-IR760, Thermo Electron, US) was used to identify new chemical bonds.

Table 1  
Formulation of EVA composites

Sample	EVA	Nano-MH	NB-UFPR	CFR <sup>a</sup>	Nano-MH content, %
EVA0	100	—	—	—	0
EVA1	75	25	—	—	25
EVA2	60	—	40	—	0
EVA3	45	—	—	55	25

<sup>a</sup> CFR is the mixture of NB-UFPR and nano-MH by weight ratio of 6/5.

#### 2.3.4. Morphology observation

Morphology of the composites was observed by transmission electron microscope (TEM, Philips Tecnai 20, Netherlands) on ultra-thin slices of about 70 nm which were microtomed at –50 °C.

## 3. Result and discussion

### 3.1. Fire performance

The formulations of the composites are listed in Table 1. Fire performance of EVA and EVA composites was tested by cone calorimeter. Fig. 1 shows the HRRs of the samples during combustion. It can be found from Fig. 1 that HRR curve of EVA2 is higher than that of EVA0 and the ignition of EVA2 also happened earlier, which indicates that NB-UFPR itself contributes to increase the flammability of materials. Comparing the HRR curve of EVA0 with that of EVA1, incorporation of 25% flame retardant nano-MH into EVA makes a decrease of HRR and a 35-s delay of ignition. To our surprise, a further reduction of HRR (curve EVA3) was obtained when the same amount of nano-MH premixed with NB-UFPR was used. NB-UFPR did not act as a component which accelerates the burning of EVA, but as a synergistic retardant of nano-MH to reduce the burning rate of EVA. Table 2 lists some data from CCT including peak HRR, ignition time (IT), effective heat combustion (EHC), mass loss rate (MLR), and mean yield of carbon dioxide and carbon monoxide. It can be found that EVA3 shows the longest delay in ignition and the lowest HRR, EHC and MLR, which indicate that the incorporation of

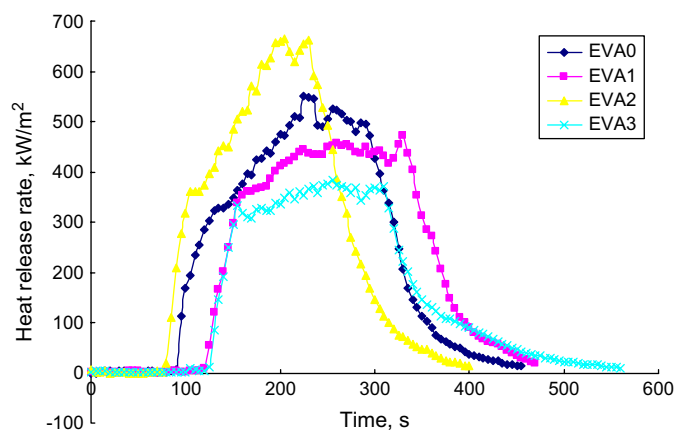


Fig. 1. Heat release rate (HRR) curves for EVA0 (virgin EVA), EVA1 (EVA/nano-MH), EVA2 (EVA/NB-UFPR) and EVA3 (EVA/CFR) under a heat flux of 35 kW/m<sup>2</sup>.

Table 2  
Cone calorimetric data for EVA and its composites under a heat flux of 35 kW/m<sup>2</sup>

Sample Code	Description	IT, s	Peak HRR, kW/m <sup>2</sup>	Mean EHC, MJ/kg	Mean MLR, g/s	Mean CO yield, kg/kg	Mean CO <sub>2</sub> yield, kg/kg
EVA0	Virgin EVA	81	551	26.0	0.10	0.03	2.0
EVA1	EVA/nano-MH	109	470	26.1	0.10	0.02	1.9
EVA2	EVA/NB-UFPR	70	663	25.0	0.11	0.04	1.93
EVA3	EVA/CFR	115	384	24.7	0.08	0.03	1.85

NB-UFPR into the nano-MH flame retardant system can help to improve the flame retardancy of EVA. It is important to find out the reason that the NB-UFPR, which increased the flammability of EVA when it was added alone in EVA, could improve the flame retardancy of EVA/nano-MH composites.

### 3.2. Decomposition of EVA and its composites

TG curves for EVA and its composites are shown in Fig. 2 and the relevant data are summarized in Table 3. EVA undergoes two degradation steps as shown in Fig. 2. The first decomposition step is due to the loss of acetic acid and the second involves random chain scission of the remaining material, forming unsaturated vapour species, such as butene and ethylene [18,19].

From Fig. 2 and Table 3, it can be found that EVA1 shows lower decomposition rate in the second step but higher in the first step than EVA0. The incorporation of nano-MH lowers the decomposition rate of the second step but accelerates the loss of acetic acid. It is obvious that the –OH groups on the fillers can assist  $\beta$ -hydrogen leaving. That is to say that the loss of acetic acid can be catalyzed by nano-MH. Polymer/clay nanocomposites have been studied widely [19–21] and Costache reported similar catalyzing function of –OH groups on the edges of montmorillonite layers.

By comparison of the curves of EVA0 and EVA2, it can be found that adding NB-UFPR into EVA resin slightly accelerates EVA's first step thermal degradation. However, the onset

temperature ( $T_{\text{onset}}$ ) and the maximum loss rate temperature ( $T_{\text{max}}$ ) of the first degradation step of EVA2 were slightly increased (2 °C).

To our surprise, ternary composite EVA3, which contains both NB-UFPR and nano-MH, shows an obvious decrease of decomposition rate than EVA1 in its first degradation step. In addition,  $T_{\text{onset}}$  and  $T_{\text{max}}$  of the first degradation step of EVA3 were also increased over 12 °C compared to the other three samples. It is obvious that the inclusion of NB-UFPR particles in EVA3 resulted in a delay of VA's  $\beta$ -elimination reaction. This should be the main reason that the EVA/CFR composite has better flame retardancy than EVA/nano-MH has at the same nano-MH loading. The dilution of VA groups in EVA3 caused by NB-UFPR may deteriorate the effect of nano-MH on accelerating loss of acetic acid. But we still need to find out if other reasons can also explain the phenomenon that the inclusion of NB-UFPR can inhibit the loss of acetic acid in EVA.

### 3.3. FTIR analysis

FTIR spectra were studied in an attempt to explain why NB-UFPR could inhibit the loss of acetic acid. Fig. 3 shows the FTIR spectra of EVA0, NB-UFPR, EVA2 (EVA/NB-UFPR), CFR (NB-UFPR/nano-MH) and EVA3 (EVA/CFR). As can be seen, a new absorption peak at 3374 cm<sup>-1</sup>, which generally should be the absorption peak of N/H hydrogen bond [22], appears in EVA/NB-UFPR blend (EVA2) and EVA/CFR blend (EVA3). If the new absorption peak at 3374 cm<sup>-1</sup> indicated the hydrogen bonds between –CN on NB-UFPR and  $\beta$ -hydrogen on EVA polymer chain, it could be easier for us to understand the reason that the loss rate of acetic acid was reduced after the inclusion of NB-UFPR because the existence of hydrogen bonds could make the  $\beta$ -hydrogen on EVA more stable. Unfortunately the hydrogen bonds between –CN on

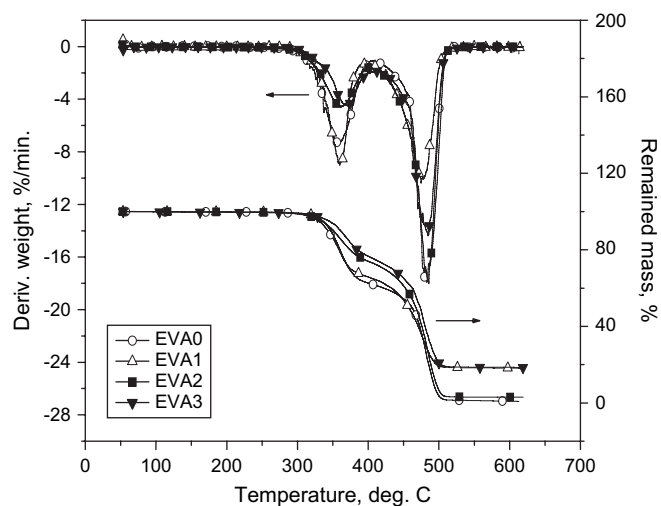


Fig. 2. TGA curves of EVA0 (virgin EVA), EVA1 (EVA/nano-MH), EVA2 (EVA/NB-UFPR) and EVA3 (EVA/CFR) under nitrogen.

Table 3  
TGA data for EVA0 (virgin EVA), EVA1 (EVA/nano-MH), EVA2 (EVA/NB-UFPR) and EVA3 (EVA/CFR) under nitrogen

Sample	Step 1		Step 2		Residue, wt%
	$T_{\text{onset}}$ , °C	$T_{\text{max}}$ , °C (rate, %/min)	$T_{\text{onset}}$ , °C	$T_{\text{max}}$ , °C	
EVA0	327	358 (7.4)	464	483	2
EVA1	330	359 (11.7)	442	476	18
EVA2	329	360 (7.7)	443	485	3
EVA3	342	372 (10.0)	457	485	19

<sup>a</sup> This value was obtained by dividing the peak value of the first degradation step of the derivative curve in Fig. 2 by the content of EVA in each composite.

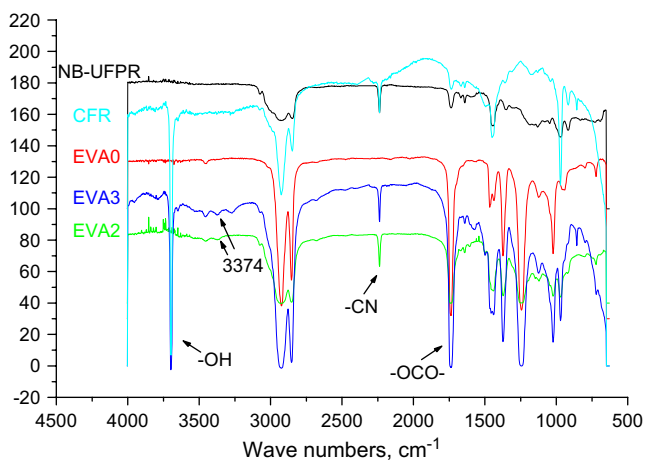


Fig. 3. FTIR spectra of EVA0 (virgin EVA), NB-UFPR, EVA2 (EVA/NB-UFPR), CFR (NB-UFPR/nano-MH) and EVA3 (EVA/CFR).

NB-UFPR and  $\beta$ -hydrogen on EVA have not been reported before; therefore, further research is needed for understanding what contributes to absorption peak  $3374\text{ cm}^{-1}$  and its relationship with the  $\beta$ -elimination of acetic acid.

### 3.4. Dispersion of nano-MH

Nano-MH in EVA3 has been found dispersed better in EVA matrix than in EVA1 as shown in Fig. 4. Some MH particles were found to aggregate tightly in EVA1, but no compact agglomeration was found in EVA3. Nano-MH particles with thickness of about 20 nm can be observed in EVA3, while the thinnest platelets observed in EVA1 have the thickness of 40–50 nm. Obviously, the incorporation of NB-UFPR ensures to get more uniform nano-MH dispersion. The uniform dispersion of nano-MH should be another important reason that EVA3 (EVA/CFR blend) had better thermal stability and better flame retardancy than EVA1 (EVA/nano-MH blend).

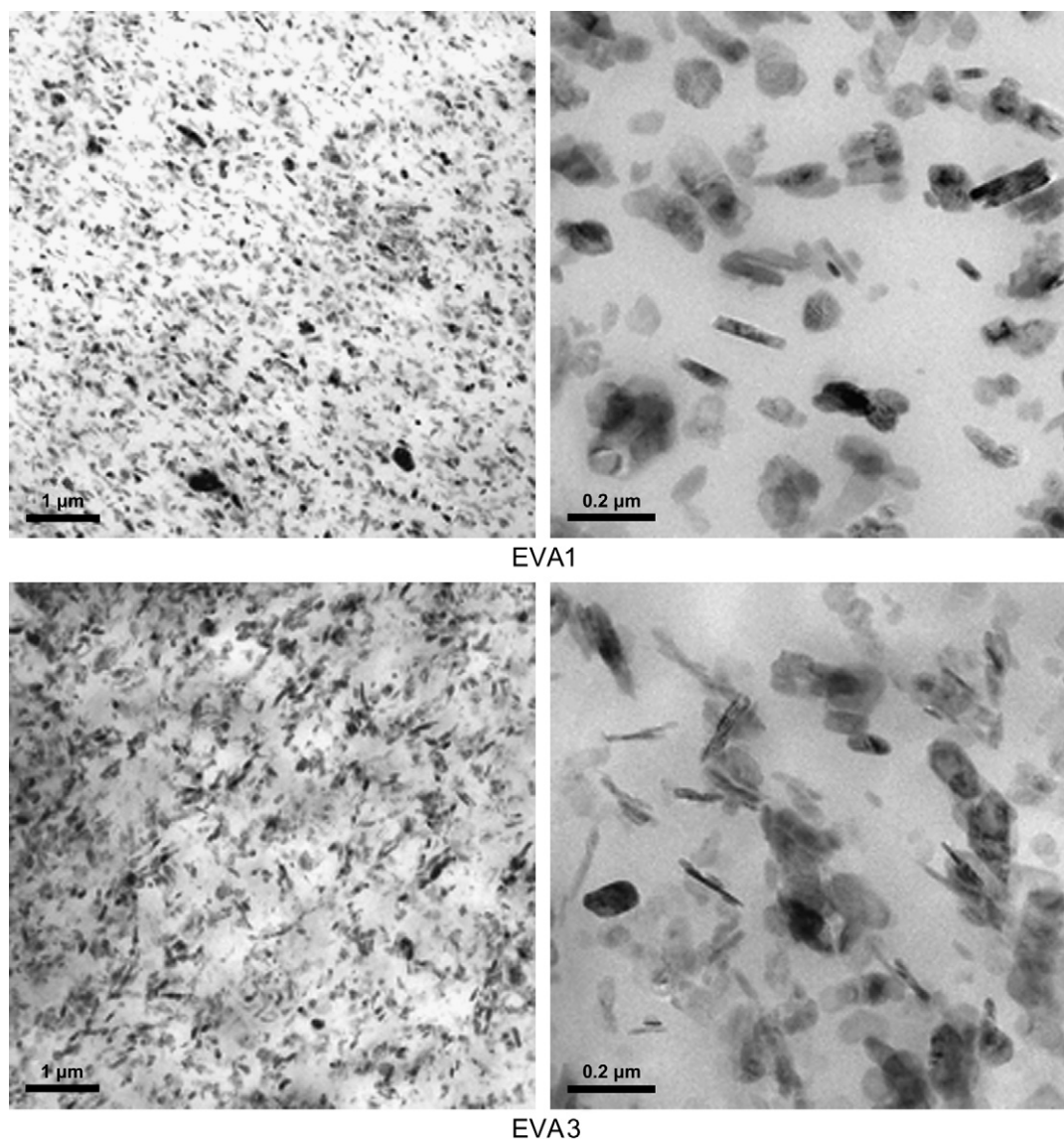


Fig. 4. TEM images of EVA1 (EVA/nano-MH) and EVA3 (EVA/CFR).



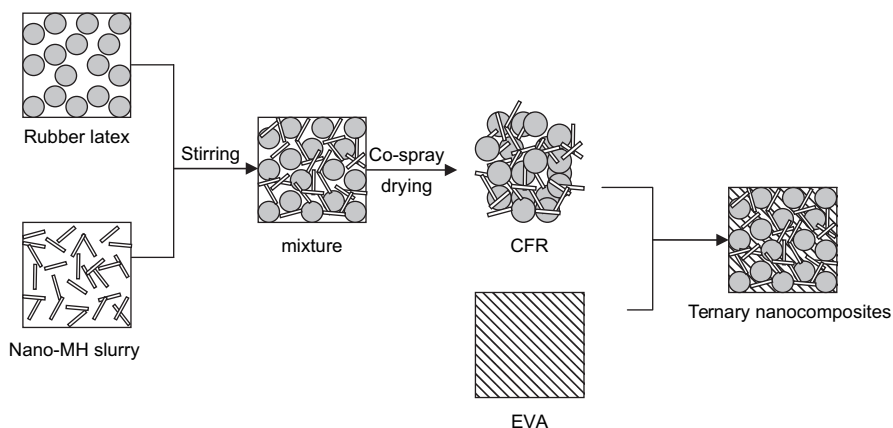


Fig. 5. Schematic illustration for the preparation of EVA/CFR nanocomposites.

In order to understand why nano-MH can be dispersed so well in EVA3, we need to go back to the preparation process of EVA3 (Fig. 5). Nano-MH slurry was firstly prepared by an emulsifier. After mixing with irradiated NBR latex, nano-MH platelets were partitioned by crosslinked UFPR particles in the mixture. The partitioned structure of CFR was maintained after co-spray drying. During the process of melt blending, the separated nano-MH platelets were hard to aggregate due to the partitioning effect. As a result, nano-MH platelets were dispersed well in ternary EVA/CFR composite.

#### 4. Conclusion

It has been found that NB-UFPR can have a synergistic effect on flame retardancy with nano-MH in EVA, which is opposite to the effect of NB-UFPR when it is blended alone with EVA. The synergistic effect comes from the facts that NB-UFPR can deteriorate the effect of nano-MH on accelerating the loss of acetic acid from EVA and can help nano-MH to disperse well in EVA matrix. Some strong interaction existed on the interface between NB-UFPR and EVA and less EVA in EVA/CFR ternary composite makes the  $\beta$ -elimination of acetate groups more difficult. Excellent dispersion of nano-MH in EVA matrix is another important reason for the flame retardant synergism.

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#### References

- [1] Hornsby PR. *Int Mater Rev* 2001;46:199–210.
- [2] Hornsby PR, Watson CL. *Polym Degrad Stab* 1996;30:73–87.
- [3] Wang J, Tung JF, Ahmad Fuad MY, Hornsby PR. *J Appl Polym Sci* 1996; 60:1425–37.
- [4] Pukanszky B, Fudos F, Kolarik J, Lednický F. *Polym Compos* 1990;11: 98–104.
- [5] Jancar J, Dibenedetto AT. *J Mater Sci* 1995;30:1601–8.
- [6] Wang Z, Shen X, Fan W, Hu Y, Qu B, Gui Z. *Polym Int* 2002;51:653–7.
- [7] Liu Y, Zhang X, Wei G, Gao J, Huang F, Zhang M, et al. *Chin J Polym Sci* 2002;20:93–8.
- [8] Qiao J, Wei G, Zhang X, Zhang S, Gao J, Zhang W, et al. *US Patent* 6,423,760; 2002.
- [9] Zhang X, Liu Y, Gao J, Huang F, Song Z, Wei G, et al. *Polymer* 2004;45: 6959–65.
- [10] Zhang M, Liu Y, Zhang X, Gao J, Huang F, Song Z, et al. *Polymer* 2002; 43:5133–8.
- [11] Liu Y, Zhang X, Gao J, Huang F, Tan B, Wei G, et al. *Polymer* 2004;45: 275–86.
- [12] Huang F, Liu Y, Zhang X, Wei G, Gao J, Song Z, et al. *Macromol Rapid Commun* 2002;23:786–90.
- [13] Huang F, Liu Y, Zhang X, Gao J, Song Z, Tan B, et al. *Sci China Ser B Chem* 2004;34:432–40.
- [14] Peng J, Qiao J, Zhang S, Wei G. *Macromol Mater Eng* 2002;287: 867–70.
- [15] Peng J, Zhang X, Qiao J, Wei G. *J Appl Polym Sci* 2002;86:3040–6.
- [16] Zhang X, Wei G, Liu Y, Gao J, Zhu Y, Song Z, et al. *Macromol Symp* 2003;193:261–76.
- [17] Dong W, Liu Y, Zhang X, Gao J, Huang F, Song Z, et al. *Macromolecules* 2005;38:4551–3.
- [18] Zanetti M, Kashiwagi T, Falqui L, Camino G. *Chem Mater* 2002;14: 881–7.
- [19] Costache MC, Jiang DD, Wilkie CA. *Polymer* 2005;46:6947–58.
- [20] Zanetti M, Costa L. *Polymer* 2004;45:4367–73.
- [21] Gregoriou VG, Kandilioti G, Bollas ST. *Polymer* 2005;46:11340–50.
- [22] Bellamy LJ, editor. *The infra-red spectra of complex molecules*. London: Chapman and Hall Ltd.; 1975. p. 277–93.