

Miscibility and Thermooxidative Degradation of Poly(vinyl chloride)/Biodegradable Aliphatic–Aromatic Copolyester Blends

Branka Andričić, Tonka Kovačić, Ivka Klarić

Department of Organic Chemical Technology, Faculty of Chemical Technology, University of Split, Teslina 10/V, 21000 Split, Croatia

Received 20 December 2004; accepted 7 July 2005

DOI 10.1002/app.23605

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The miscibility of poly(vinyl chloride) (PVC) and a biodegradable aliphatic–aromatic copolyester (AAC) was investigated by differential scanning calorimetry. The thermooxidative degradation of the blends was investigated thermogravimetrically. The blends were prepared by dissolution in 1,2-dichloroethane and precipitation with methanol. The investigated blends were completely miscible with the glass-transition temperatures best predicted by the Fox equation. Fourier transform infrared analysis showed that the interactions responsible for miscibility were the hydro-

gen bonds between the blend components. The thermooxidative stability of the PVC/AAC blends was improved compared to that of pure PVC. Furthermore, when AAC was added, the dehydrochlorination rate of PVC decreased, and the maximum rate shifted to a higher temperature. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 2158–2163, 2006

Key words: FT-IR; miscibility; polyesters; poly(vinyl chloride) (PVC); thermogravimetric analysis

INTRODUCTION

Although blends of nonbiodegradable polymers (most synthetic polymers) and biodegradable ones (synthetic or natural) cannot be considered biodegradable, many investigations have been performed in this field. The main reason is the decreasing amount of nonbiodegradable components in polymeric waste because of the biodegradability of single components. After biodegradable component removal, the other components are more prone to photodegradation and thermooxidative degradation. Among them, attention has been paid to the investigation of low-density polyethylene/starch blends,^{1,2} blends of biodegradable aliphatic polyesters with poly(vinyl acetate),³ poly(ethylene oxide),⁴ polyepichlorohydrin,⁵ linear low-density polyethylene,⁶ polystyrene (PS),⁷ and polycarbonate (PC).⁸ Aliphatic polyesters alone, such as poly(ϵ -caprolactone) and poly(3-hydroxybutyrate), are rather expensive and do not provide optimal material properties. To overcome these difficulties, a group of aliphatic–aromatic copolyesters (AACs) were synthesized and exist on the market under different trade names (e.g., Ecoflex from BASF, Eastar grades from Eastman). It has been proven that the copolyesters of aliphatic diols and a defined mixture of aliphatic dicarboxylic acid with 35–55 mol % terephthalic

acid exhibit acceptable thermal and mechanical properties and biodegradability.⁹

From this point of view, we studied blends of poly(vinyl chloride) (PVC) and biodegradable AAC. It was of interest to us to study whether AAC could be substituted for any common modifier of PVC. Some blend compositions may be attractive for plastic packaging. Because of the characteristic chemical interactions between PVC and aliphatic polyesters, such as poly(ϵ -caprolactone),^{10,11} good compatibility or even miscibility would be expected. The miscibility of blends is ascertained by the measurement of their glass-transition temperatures (T_g 's). The use of T_g in the determination of polymer/polymer miscibility is based on the premise that a single T_g indicates that the domain size is below d_d , where $2 \leq d_d \leq 15$ nm.¹²

Specific interactions between the blend components were detected with Fourier transform infrared (FTIR) spectroscopy. The advantage of FTIR that is not available to differential scanning calorimetry (DSC) is that it is possible to identify the interactions responsible for miscibility.^{13–15}

Further, the thermooxidative degradation of the PVC/AAC blends in the temperature range 50–650°C was investigated.

EXPERIMENTAL

Sample preparation

The PVC studied was the commercially available On-grovil S-5258 (Borsod Chemical, Hungary) with K_{value}

Correspondence to: B. Andričić (branka@ktf-split.hr).

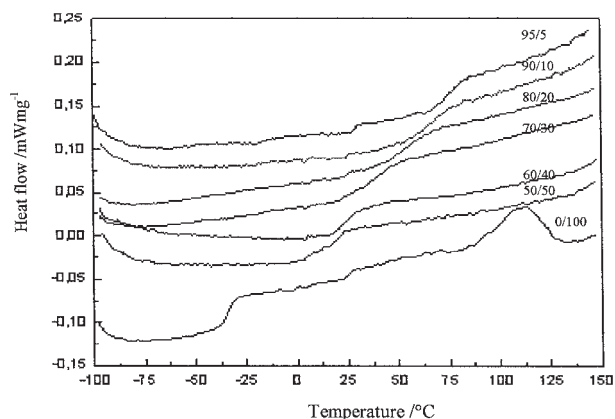
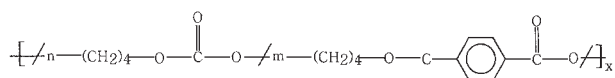


Figure 1 DSC heating curves of the PVC/AAC blends.

$= 58 \pm 1$ and a chlorine content of 56%. AAC (Eastman Chemical Co., Kingsport, TN) was a copolymer of 1,4-butandiole and adipic and terephthalic acid with a number-average molecular weight of 20,030 g/mol (as determined by the end-group analysis method).¹⁶ The repeating unit of a random copolymer may be represented as follows:



The defined PVC/AAC mass ratios were 100/0, 95/5, 90/10, 80/20, 70/30, 60/40, 50/50, and 0/100. The polymer blends were prepared by the solution blending method with 1,2-dichloroethane as a cosolvent. Each polymer was dissolved separately in the solvent and then mixed in the previously mentioned ratios. After 1 h of stirring with a magnetic stirrer, coprecipitation with methanol was performed. The precipitate

was washed several times with methanol, dried for 24 h at room temperature, and then dried in a vacuum oven at 40°C until a constant mass was reached. For the DSC and thermogravimetry (TG) measurements, dry samples were pressed in hydraulic press (500 N/mm²) at room temperature.

DSC measurements

The thermal characteristics, that is, T_g and melting temperature (T_m), of the coprecipitated blends were determined with a Netzch DS 200 instrument (Selb, Germany). The samples were heated to 150°C, cooled to -100°C, and then reheated to 150°C with heating/cooling rates of 10°C/min.

IR spectroscopy

IR spectroscopic measurements were performed on a PerkinElmer Spectrum One FTIR spectrophotometer (Norwalk, CT). The samples were ground with KBr and pressed into disc form, and 10 scans were collected with a spectral resolution of 4 cm⁻¹.

TG measurements

The thermooxidative degradation of the samples was performed on a TGS-2 thermobalance (PerkinElmer) in the temperature range 50–650°C at a heating rate of 10°C/min in synthetic air with 29% O₂ (Messer, Gumpoldskirchen, Austria). The following characteristics of TG curves were measured: the initial temperature of thermooxidative degradation (T_{onset}) as a measure of thermooxidative stability, the temperature at the maximal rate of the first degradation step (T_{max}),

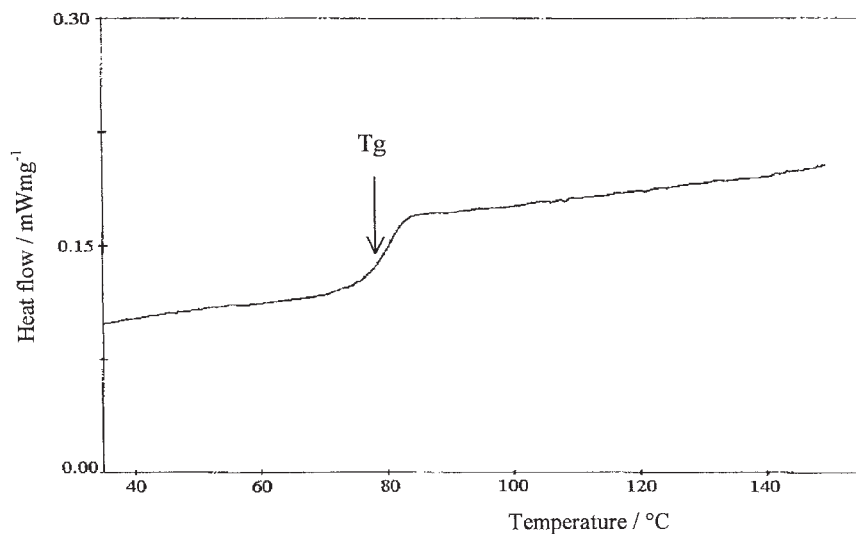


Figure 2 DSC heating curve of PVC (100/0 blend).

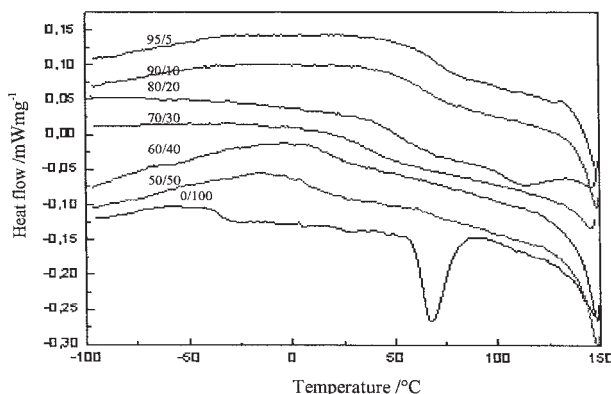


Figure 3 DSC cooling curves of the PVC/AAC blends.

and the mass loss for the corresponding degradation step (Δm_i).

RESULTS AND DISCUSSION

Miscibility of the PVC/AAC blends

The DSC second heating curves of the 95/5...0/100 PVC/AAC blends and the 100/0 blend (PVC) are presented in Figures 1 and 2. The cooling curves of the 95/5...0/100 PVC/AAC blends are shown in Figure 3. The characteristic phase-transition temperatures and the change in the specific heat at the glass-transition temperature (ΔC_p) of the starting components (PVC and AAC) are summarized in Table I. It was evident that the pure AAC (the 0/100 blend) was a semicrystalline polymer with a relatively low T_m . All of the PVC/AAC blends showed one T_g and no T_m (Fig. 1). AAC alone crystallized on cooling, but there were no crystallization processes in the PVC/AAC blends (Fig. 3); this suggested that, in the PVC/AAC blends, AAC was completely amorphous.

If the criterion of a unique T_g is accepted as the indicator of miscibility, it was obvious that the investigated PVC/AAC blends were completely miscible.

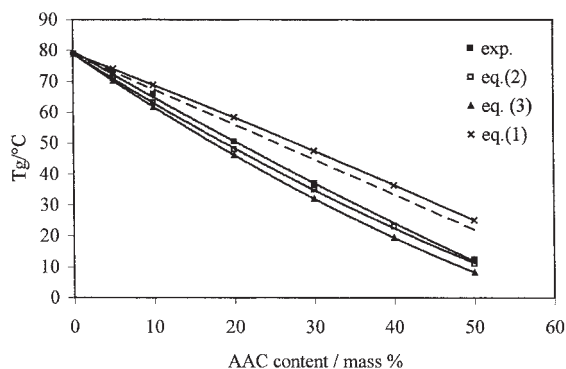


Figure 4 Plot of experimental and theoretically predicted T_g values versus AAC content in the PVC/AAC blends.

TABLE I
Phase Transition Characteristics of PVC (100/0) and AAC (0/100)

	T_g (°C)	ΔC_p (J g ⁻¹ °C ⁻¹)	T_m (°C)	T_c (°C)
PVC	79	0.308	—	—
AAC	-35	0.228	95	75

T_c = crystallization temperature.

The change in T_g values in the PVC/AAC blends decreased monotonically with increasing AAC content (Fig. 4). Because of this fact, we considered that AAC may have acted as the plasticizer for PVC. The prediction of T_g related to the composition of the PVC/AAC blends was made according to several equations.^{10,12}

With the assumption that ΔC_{pi} does not depend on temperature, Couchman and Karasz¹⁷ derived the following expression:

$$\ln T_g = \frac{w_1 \Delta C_{p1} \ln T_{g1} + w_2 \Delta C_{p2} \ln T_{g2}}{w_1 \Delta C_{p1} + w_2 \Delta C_{p2}} \quad (1)$$

where T_g is the glass-transition temperature of the blend and w_i is the mass fraction, ΔC_{pi} the difference in the specific heat at the glass-transition temperature, and T_{gi} is the glass-transition temperature of component i , respectively.

With the assumption that $\Delta C_{p1} \cong \Delta C_{p2}$, the Fox¹⁰ equation was made:

$$1/T_g = w_1/T_{g1} + w_2/T_{g2} \quad (2)$$

However, if the ratio $\Delta C_{p1}/\Delta C_{p2} = k$ is introduced, Utracki¹² proposed

$$\ln T_g = \frac{w_1 \ln T_{g1} + w_2 \ln T_{g2}}{w_1 + kw_2} \quad (3)$$

The experimental results of T_g , with the same concave pattern followed, were in best agreement with those predicted by the Fox¹⁰ equation. It was obvious that T_g deviations from the rule of mixtures were negative, which is the main characteristic of miscible blends, with miscibility achieved due to specific interactions. The interaction between the hydrogen of the asymmetric carbon atom in PVC and the oxygen of the ester group in AAC was the most probable specific interaction, although within some polyester/chlorinated polymer groups, dipolar interactions between C=O and C—Cl may have been responsible for miscibility.

FTIR analysis

FTIR spectra of the PVC/AAC blends are presented in Figure 5. The pure PVC (100/0 blend) spectrum char-

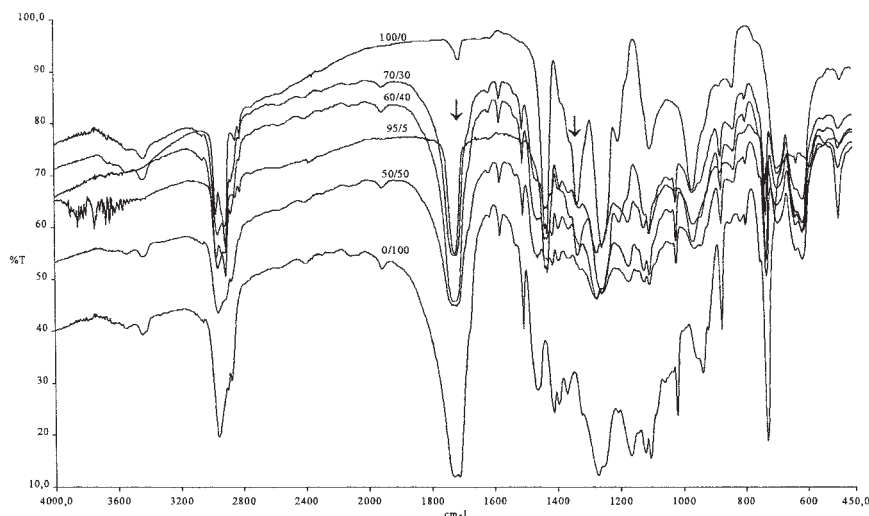


Figure 5 FTIR spectra of the PVC/AAC blends.

acteristic peaks were as follows: —C—Cl stretching at 692 cm^{-1} , —CH_2 bending at 1430 cm^{-1} , and —C—H bending at 1254 and 1332 cm^{-1} (C—H in —CHCl). In AAC (0/100 blend), the spectrum peak at 730 cm^{-1} was due to —CH_2 rocking vibrations, the peaks at $1100\text{--}1300\text{ cm}^{-1}$ represented C—O stretching in aliphatic and aromatic components of the polyester, and a strong band due to C=O stretching in both the aliphatic and aromatic polyester components appeared at $1715\text{--}1730\text{ cm}^{-1}$. The peak detected in PVC at 1332 cm^{-1} shifted to 1330 cm^{-1} in the 80/20 blend, to 1325 cm^{-1} in the 70/30 blend, and finally to 1322 cm^{-1} in the 60/40 and 50/50 blends. At the same time, a strong doublet of C=O vibrations detected in AAC became more sharp, and in the 95/5 blend, a single peak at 1725 cm^{-1} appeared. The peak position changes are listed in Table II. We believe that these peak shifts indicated the existence of interactions of the carbonyl oxygen in AAC with the α -hydrogen in PVC and resulted in miscibility of the polymer pair.

Thermooxidative degradation of the PVC/AAC blends

TG curves of the thermooxidative degradation of the PVC/AAC blends are presented in Figure 6, and the

TABLE II
Position Changes of —C=O Group Peak with Composition in PVC/AAC Blends

PVC/AAC	Position of —C=O group peak (cm^{-1})
0/100	1716, 1731
50/50	1719, 1733
60/40	1717, 1730
70/30	1717, 1729
80/20	1721, 1725
90/10	1725
95/5	1725

corresponding differential thermogravimetric (DTG) curves are presented in Figure 7. The thermal degradation of the 100/0 blend (PVC) in air started at about 240°C and proceeded through three main degradation steps. It was known, until now, that the first step (ca. $240\text{--}410^\circ\text{C}$) corresponds to the dehydrochlorination (DHC) of PVC; in the second step (ca. $410\text{--}500^\circ\text{C}$), polyene oxidation takes place, and the third step (ca. $500\text{--}650^\circ\text{C}$) is complete oxidation without residue.^{18,19} During the first step, some benzene is also formed,¹⁸ and that is why Δm in the first step was higher than the total chlorine content (Table III). The thermooxidative degradation of the 0/100 blend took place in two steps. The highest Δm (ca. 90%) occurred between 320 and 440°C , and the rest of the sample degraded completely up to 650°C . In the PVC/AAC blends, the degradation steps occurred consecutively: (1) PVC DHC, (2) AAC degradation, (3) polyene oxidation, and (4) total degradation of both components (Fig. 7). The characteristic temperatures T_{onset} and T_{max} are plotted in Figure 8. It was evident that the addition of 5% AAC had no influence on T_{onset} and T_{max} . After that, changes in both characteristics were close to linearity, but AAC had much more influence on T_{max} than on T_{onset} . In the blends containing more than 10% AAC, the rate of DHC decreased (Fig. 7). It seemed that the two polymers in the blends exhibited synergism of the investigated properties and might be successfully used for some applications.

CONCLUSIONS

According to the DSC measurements, the PVC/AAC blends were completely miscible. A decrease in T_g in the blends was well predicted by the Fox¹⁰ equation. AAC might have been the polymeric plasticizer for PVC. The mechanism responsible for the miscibility was hydrogen bonding between C=O in AAC and the α -hydrogen in PVC, as found by FTIR.

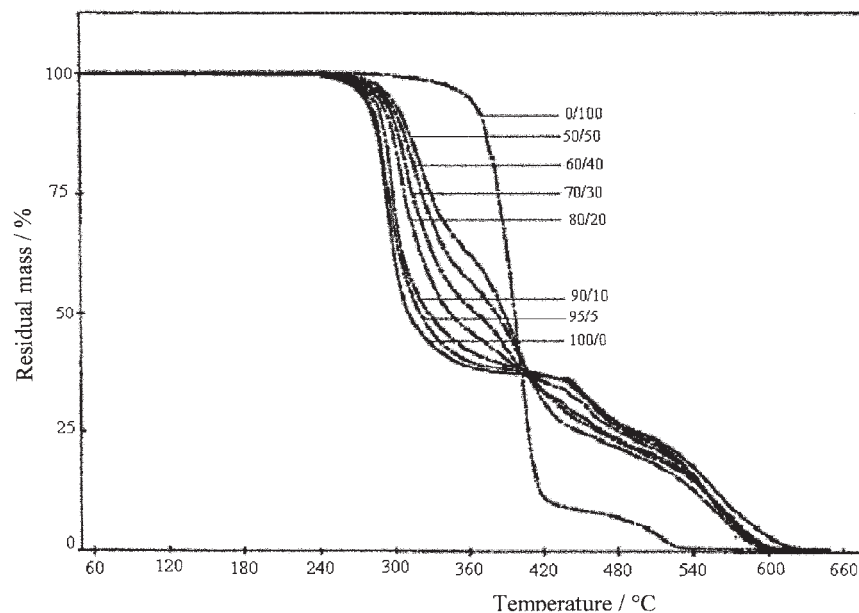


Figure 6 TG curves of the PVC/AAC blends.

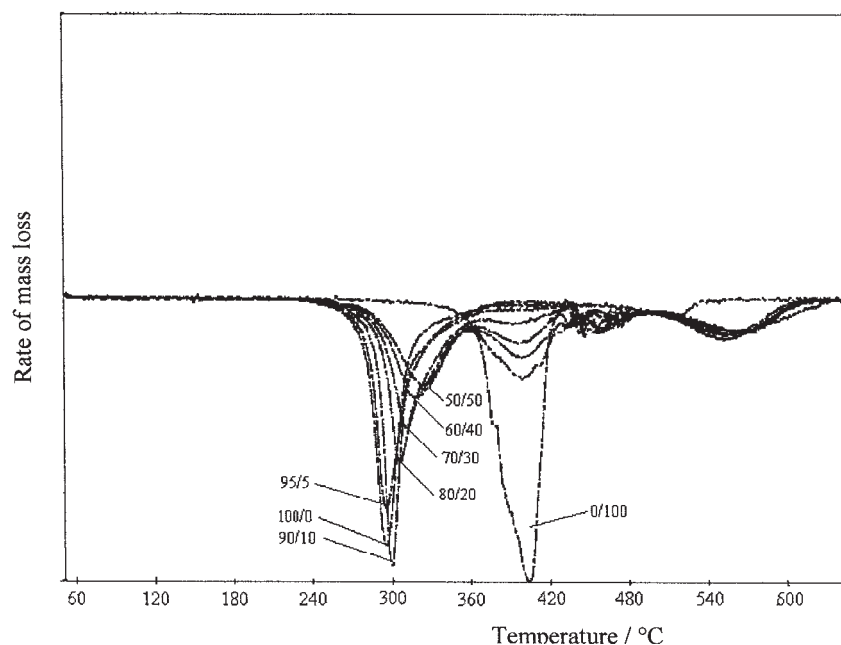


Figure 7 DTG curves of the PVC/AAC blends.

TABLE III
Mass Losses in the Corresponding Degradation Steps in
the Thermooxidative Degradation of the PVC/AAC
Blends

PVC/AAC	Δm_1 (%)	Δm_2 (%)	Δm_3 (%)
100/0	63	12	25
95/5	62	13	25
90/10	61	14	25
80/20	61	15	24
70/30	57	20	23
60/40	43	34	23
50/50	37	41	22
0/100	91	9	—

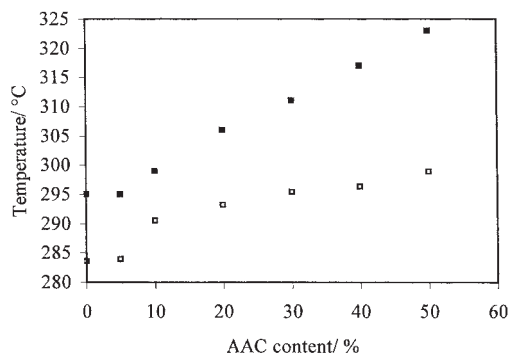


Figure 8 Plot of (□) T_{onset} and (■) T_{max} versus AAC content in the PVC/AAC blends.

Compared to pure PVC, the miscible blends of PVC/AAC had improved thermooxidative stability. At the same time, the DHC rate of PVC reached its maximum at higher temperatures.

References

1. Bikiaris, D.; Prinos, J.; Panayiotou, C. *Polym Degrad Stab* 1997, 58, 215.
2. Davis, G.; Bulson, H.; Harisson, D.; Billet, E. *Macromol Symp* 2003, 197, 265.
3. Shin, T. K.; Kim, J.; Choi, H. J.; Jhon, M. S. *J Appl Polym Sci* 2000, 77, 1348.
4. Park, S. H.; Lim, S. T.; Shin, T. K.; Choi, H. J.; Jhon, M. S. *Polymer* 2001, 42, 5737.
5. Kim, J.; Lim, S. T.; Choi, H. J.; Jhon, M. S. *Macromol Chem Phys* 2001, 202, 2634.
6. Kim, J.; Kim, J. H.; Shin, T. K.; Choi, H. J.; Jhon, M. S. *Eur Polym J* 2001, 37, 2131.
7. Chun, Y. S.; Kyung, Y. J.; Jung, H. C.; Kim, W. N. *Polymer* 2000, 41, 8729.
8. Hirotsu, T.; Ketelaars, A. A. J.; Nakayama, K. *Polym Degrad Stab* 2000, 68, 311.
9. Witt, U.; Müller, R. J.; Deckwer, W. D. *J Environ Polym Degrad* 1997, 5, 81.
10. Aubin, M.; Prud'homme, R. E. *Macromolecules* 1988, 21, 2945.
11. Clark, M. B.; Burkhardt, C. A.; Gardella, J. A. *Macromolecules* 1991, 24, 799.
12. Utracki, L. A. *Polymer Alloys and Blends: Thermodynamics and Rheology*; Hanser: Munich, 1990.
13. Kim, C. H.; Park, J. K.; Hwang, T. S. *Polym Eng Sci* 1996, 36, 535.
14. Kuo, S. W.; Huang, C. F.; Chang, F. C. *J Polym Sci* 2001, 39, 1348.
15. Sharma, L.; Kimura, T. *Polym Adv Technol* 2003, 14, 392.
16. Magud, A.; Rota, M. *Polimeri* 1983, 4, 241.
17. Couchman, P. R.; Karasz, F. E. *Macromolecules* 1978, 11, 117.
18. Knüman, R.; Bockhorn, H. *Combust Sci Tech* 1994, 101, 285.
19. Klarić, I.; Roje, U.; Bravar, M. *J Appl Polym Sci* 1996, 61, 1123.