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Thermal Stability of Interpolymer Complexes Based on Poly(styrene-*co*-4-vinylpyridine) and Poly(styrene-*co*-itaconic Acid)

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Summary: Phase behaviour and specific interactions that occurred between poly (styrene-co-4-vinylpyridine) containing 20 mol % of 4-vinylpyridine (PS4VP20) and poly(styrene-co-itaconic acid) containing 17 mol % of itaconic acid (PSIA17) were investigated by differential scanning calorimetry (DSC) and Fourier Transform Infrared spectroscopy (FTIR).Due to favourable specific interactions among others, PSIA17/PS4VP20 system is miscible in the whole composition range, as evidenced by a single glass transition temperature (Tg), observed with each initial mixture, intermediate between those of the pure components. The Tg-composition dependence of this system fitted well the recent approach proposed by Brostow et al.(BCKV).Copolymerization of itaconic acid with styrene improved the thermal stability of PIA. The PSIA17/PS4VP20 blends showed a better thermal stability than their corresponding pure constituents. The degradation temperatures at maximum T_{dmax} of these complexes are higher than those of pure constituents. Due to specific interactions that occurred between the two constituents of the blends, the anhydride amount observed with PSIA17 decreased.FTIR spectroscopy analysis confirmed qualitatively the occurrence of inter-polymer interactions from the appearance of new bands, characteristic of associated pyridine at 1607 cm^{-1}, pyridinium ion at 1638 cm^{-1} and liberated carbonyl groups of PSIA17 at 1725 cm^{-1}. Quantitatively both fractions of liberated carbonyl and pyridinium species increased upon increasing PS4VP20 amount in the blend.

Keywords: interpolymer complexes; poly(styrene-*co*-itaconic acid); poly(styrene-*co*-4-vinylpyridine); thermal stability; thermogravimetry

Introduction

Novel materials with specific properties may be elaborated by mixing pairs of polymers. Unfortunately, most pairs of polymers are immiscible. It is well established now that depending on the strength and densities of interacting species incorporated within two dissimilar polymers, miscible polymer blends or interpolymer complexes are formed [1–6] as the number of effective specific interactions that occurred between the constituents of the polymer mixture increases. However due to several factors, not all the specific groups within the polymer chains get involved. It is therefore of importance to optimize the extent of intermolecular interactions to obtain effective interpolymer complexes.

We have previously incorporated within various polymers by copolymerization, proton donors such as acrylic acid or methacrylic acid and have mixed such copolymers with different basic copolymers to prepare interpolymer complexes.[7–10]

Itaconic acid, a monomer obtained from renewable resources at low cost, possesses two carboxylic acid groups. It might be of

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interest to substitute the above proton-donor monomers with this acid, expected to produce highly functionalized copolymers and to improve the possibility of developing specific interactions with proton-acceptors.

Although poly(itaconic acid) has a low thermal stability, Filipovic et al.[11] reported on the formation of interpolymer complexes based on of poly(itaconic acid) and poly(acrylamide) and their improved thermal stability.

We have in the first part of this contribution synthesized, characterized a poly(styrene-*co*-itaconic acid) containing 17 mol % of itaconic acid (PSIA17) and a poly(styrene-*co*-4-vinylpyridine) containing 20 mol % of 4-vinylpyridine (PS4VP20) and investigated the phase behaviour of these copolymers and the specific interactions that occurred between them within this system by thermogravimetry and differential scanning calorimetry (DSC).

Different glass transition temperature-composition behaviours were reported in the literature and several theoretical approaches have been used to describe such behaviours. The one recently proposed by Brostow et al. [12] will be applied to predict the composition dependence of the Tg of this binary system.

The expected interactions within PSIA17 copolymer and PSIA17/PS4VP20 blends will be analyzed in a second part of this contribution qualitatively and quantitatively by FTIR spectroscopy. The choice of these homoblends as a model will facilitate the quantitative FTIR analysis of the specific interactions that occurred between the two constituents of the blend.

Experimental Part

Materials

Poly (styrene-*co*-itaconic acid) (PSIA17) containing 17 mol% of itaconic acid and poly (styrene-*co*-4-vinylpyridine) (PS4VP20) containing 20 mol % of 4-vinylpyridine were synthesized by free radical solution polymerization at 60°C using azobisisobutyronitrile (AIBN) as the initiator, keeping the conversion relatively low. These copolymers obtained by precipitation in a large excess of adequate precipitants, were purified by repeated dissolution/precipitation cycles and dried under vacuum at 50°C for several days.

The styrene and 4-vinylpyridine contents in these copolymers were determined by ^{1}HNMR from the area ratio of appropriate peaks. ^{1}HNMR spectra were recorded on a Bruker 400 using deuterated THF and chloroform ($CDCl_3$) as solvents for PSIA and PS4VP, respectively, and tetramethylsilane as internal standard at room temperature.

Characterizations

Films of the different copolymers and their various blend system were prepared from THF solutions. These films, dried to constant weight in a vacuum oven at 50°C during several days to remove traces of solvent, were used in the thermal analyses.

FTIR spectra were recorded at 2cm^{-1} resolution and 60 scans on a Perkin-Elmer 1000 one spectrometer.

Thermogravimetric experiments were carried out with a Metler Toledo 851 analyzer at 10 °C/min under nitrogen atmosphere from 30 °C to 650 °C.

Glass transition temperatures (T_g) of PSIA17, PS4VP20 and of their binary PSIA17/PS4VP20 blends were determined by differential scanning calorimetry using a Metler Toledo 823 DSC, under nitrogen at 10°C/min. The samples were heated and cooled twice in the 40 – 180°C temperature range. The Tg values were determined at the midpoint of the second scan. Table 1 summarizes the characterization results obtained by the different techniques.

Table 1.
Characteristics of polymers.

Polymer	4VP or IA(mol %) in copolymer	Tg (°C)	T_{dmax} (°C)
PSIA17	17	90	409
PS4VP20	20	104	403

Results and Discussion

Thermogravimetric Analysis

The thermal degradation of poly (itaconic acid) (PIA) in nitrogen atmosphere, as reported by Filipovic et al.[11], is characterized by four peaks. The first peak in the 140 – 220°C temperature range, with T max of 185°C and the second peak in the 220 – 275°C region with Tmax of 230°C, were attributed to release of water adsorbed to the hydrophilic polymer and to anhydride ring formation, respectively. The decarboxylation and carbonization processes, characterized by two other peaks occurred between 270°C and 450°C.

Thermal degradation processes in various copolymers of styrene with maleic acid or fumaric acid, reported by M.S. Zeliazkow[13,14] confirmed the effect of stereo regularity on the degradation of these copolymers. The first stage of degradation of poly(styrene-co-maleic acid) containing 49.mol % of maleic acid, as described by this author showed two minor steps with minima around 145°C and 187°C, assigned to adsorbed water and anhydride formation, respectively. The hydrophobic character of styrene moiety, incorporated within poly(itaconic acid) backbone by copolymerization will reduce the amount of adsorbed water by this later and therefore improve the thermal stability of the PSAI copolymer compared to PIA.

The weight loss of PSAI17 is much lower than that of PIA in this temperature range**.** Figure 1 illustrates thermogravimetric (TG) and derivative thermogravimetric (DTG) curves of the PSIA17, PS4VP20 copolymers and their blends of different ratios as cast from THF.

Two stages of degradation are depicted with the as-cast PSIA17 copolymer. Similar trend of degradation than that of P(S-co-MA) occurred with this copolymer containing a relatively lower itaconic acid mol %, in its first stage of degradation.

This PSIA17 copolymer showed, in the 100 – 270°C temperature range a shoulder at 154°C attributed to a release of small amount of adsorbed water in the polymer by the hydrophilic groups of the PSIA17 and a peak at 204°C due to the formation of traces of anhydrides.

The second step of degradation that occurred between 338°C and 460°C with a T_{max} of 409°C, corresponds to the degradation of the main chain. Compared to PIA[11] or P(S-co-MA),[14,15] PSIA17 displayed a thermal stability in the 270 – 330°C region as evidenced by the absence of DTG peak at 315°C, observed with poly(itaconic acid) or at 225°C and

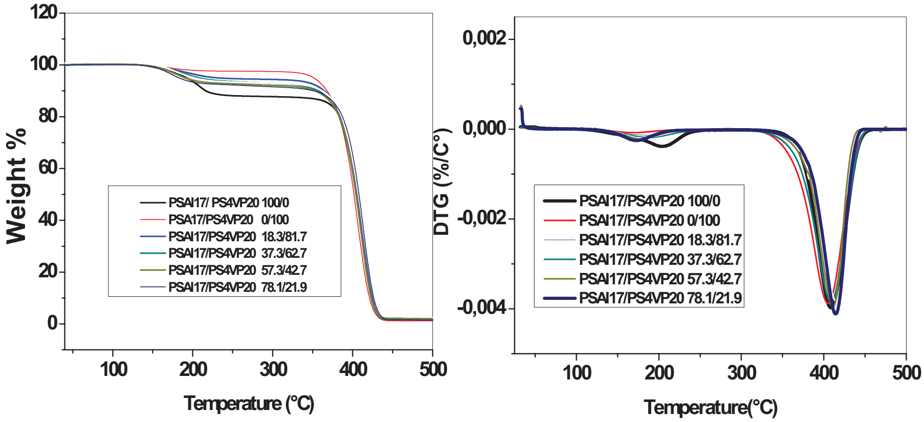


Figure 1.
Thermogravimetric TGA (a) and derivative thermogravimetric DTGA curves (b) of PSIA17/PS4VP20 of different ratios.

Table 2.
Thermogravimetric data of PSIA17, PS4VP20 and their different blends.

System	T10% °C	T50% °C	Td max °C	Td total °C	Char at Td total (%)
PSIA17/PS4VP20 0/100	370	400	403	449	2.33
PSIA17/PS4VP20 18.3/81.7	370	406	412	450	3.00
PSIA17/PS4VP20 37.3/62.7	365	405	411	449	4.08
PSIA17/PS4VP20 57.3/42.7	363	405	411	449	3.40
PSIA17/PS4VP20 78.1/21.9	367	408	412	449	2.33
PSIA17/PS4VP20 100/0	237	405	409	450	3.35

322°C for p(S-co-MA) and attributed to decarboxylation. Any decarboxylation of PSIA17 may occur at higher temperature and will be overlapped with the main chain degradation.

The main degradation of PS4VP20 occurred through a single step between 303°C and 456°C with a T_{dmax}. at 403°C. A small amount of water is released between 115°C and 235°C with a $T_{d\ max}$ appearing at 168°C.

Two stages of degradation are observed with the as-cast blends of this system. As it is shown in Figure 1, a single peak of degradation, shifting to higher temperature as PS4VP20 content increases in the blend, is observed in the first stage of their degradation, confirming the presence of specific interactions that occurred between the itaconic acid and the pyridine groups. The amount of adsorbed water in the blend decreased. The anhydride formation also decreased and is delayed to higher temperature as the fraction of PS4VP20 increases in the blend.

As it is shown, the blends of different ratios showed a better thermal stability than their corresponding pure constituents. The d(TG) curves showed that the second step of degradation of the blends shifted to higher temperatures compared to those of the pure components. These results also confirm that, due to specific interactions that occurred between the two constituents of the blends, the anhydride amount observed with PSIA17 decreased. These results are expected to be evidenced by FTIR spectroscopy. Table 2 gathers the thermogravimetric data of PSIA17, PS4VP20 and their different blends.

Differential Scanning Calorimetry Analysis

Poly(itaconic acid) (PIA) is a polymer of low thermal stability. Its glass transition temperature cannot be determined.[11] The incorporation of styrene moieties within PIA by copolymerization increased its thermal stability. Figure 2 shows the second scan DSC thermograms of PSIA17, PS4VP20 and

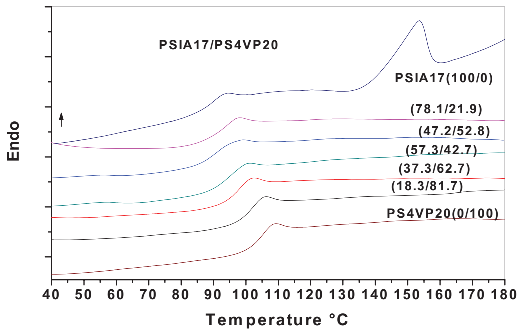


Figure 2.
DSC thermograms of PSIA17, PS4VP20 and their blends of different ratios.

their blends of different ratios in the 40 – 180°C temperature range. PSIA17 displays two peaks in this temperature range. The first one, at 90°C, is attributed to Tg of PSIA17 and the second peak in the 130 – 160°C temperature range, corresponds to the formation of itaconic anhydride in agreement with the endothermic peak observed with PIA.[11] The disappearance of this peak, observed upon PS4VP20 addition in the blend may indicate the presence of preferential itaconic acid-pyridine interactions over the formation of anhydrides.

Due to these favourable specific interactions among others, PSIA17/PS4VP20 system is miscible in the whole composition range, as evidenced by a single Tg observed with each blend, intermediate between those of the pure components as shown in Figure 3.

A quantification of the interactions that occurred within these blends was attempted using Brostow et al. (BCKV) approach[13] expressed by the following equation:

$$T_{g,blend} = w_1 T_{g,1} + (1 - w_1) T_{g,2} + w_1(1 - w_1)[a_0 + a_1(2w_1 - 1) + a_2(2w_1 - 1)^2] \quad (1)$$

where $T_{g,i}$ and w_i are the glass transition temperature and the weight fraction of the pure component i, respectively. a_i are adjustable parameters, determined from the experimental Tg-composition curves shown in Figure 3. a_0 measures the extent of the strength of specific interactions.The low negative $a_1 = -0.83$ value observed with this system indicates that the maximum of interactions occurred at a volume fraction of PSAI17 close to 0.5 while $a_2 = 22.08$ reflects a moderate complexity of the system.

FTIR Spectroscopy

The specific interactions that occurred between the carboxylic groups of PSIA17 and the pyridine nitrogen atom of PS4VP20 within the blends were evidenced by FTIR spectroscopy. The room temperature spectrum of PSIA17 shows in the 3600 -2400 cm^{-1} region a broad band centred around 3200 cm^{-1} and a satellite band at 2630 cm^{-1} due to carboxylic groups. In the carbonyl 1900-1650 cm^{-1} region, this copolymer displayed two bands attributed to free and to self-associated carboxylic acid groups at 1742 cm^{-1} and 1707 cm^{-1}, respectively. Two other small peaks, also observed at 1782 cm^{-1} and 1865 cm^{-1}, are attributed to small amount of five member cyclic anhydrides due to drying under vacuum. The PS4VP20 copolymer absorbs strongly in the pyridine ring 1650-1550 cm^{-1} region. The characteristic peak of free pyridine, expected at 1597 cm^{-1}, is overlapped with styrene ring in this region.

Changes are observed in these regions when PSIA17 is added to PS4VP20. The broad bands in 3600-2400 cm^{-1} of the PSIA17 are affected by the progressive addition of the basic P4VP20 copolymer.

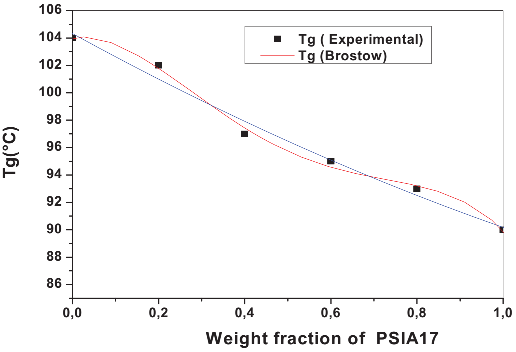


Figure 3.
Tg of PSIA17/PS4VP20 versus weight fraction of PSIA17.

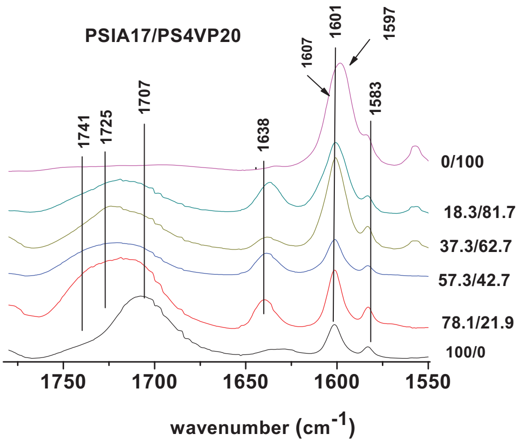
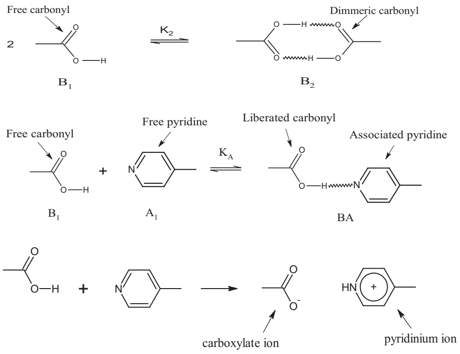


Figure 4.
FTIR spectra of PSIA17, PS4VP20 and their blends in the 1800-1550 cm^{-1} region.

The intensity of the band at 3200 cm^{-1} decreases, while a broadening and an important shift to lower wave numbers up to 2520 cm^{-1} are observed with the satellite band initially centred at 2630 cm^{-1}. This is due to the dissociation of some of the dimers and their replacement by interactions between the constituents of different nature within the blends. The inter-polymer interactions that occurred between the two copolymers within the blend system were also investigated in both the carbonyl 1900-1650 cm^{-1} and pyridine 1650-1500 cm^{-1} region where significant changes were observed. In the carbonyl region, in which PS4VP20 does not absorb, three bands at 1742 cm^{-1}, 1725 cm^{-1} and 1707 cm^{-1} corresponding to free, associated and cyclic carboxylic dimer groups are shown upon addition of PSIA17. The small anhydride contribution observed with PSIA17 at 1782 cm^{-1} decreased with an increase of PS4VP20 in the blend.

Three contributions at 1597 cm^{-1}, 1607 cm^{-1} and 1638 cm^{-1}, attributed to free pyridine ring, hydrogen bonded pyridine "associated" and pyridinium ion, respectively are shown in the 1650-1550 cm^{-1}region. In agreement with DSC results, the miscibility of PSIA17/PS4VP20 blends is qualitatively evidenced by the appearance of new bands characteristic of the associated pyridine at 1607 cm^{-1}, the pyridinium ion at 1638 cm^{-1} and the liberated carbonyl groups of PSIA17 at 1725 cm^{-1} as illustrated in schemes below: FTIR spectra of PSIA17, PS4VP20 and their blends in the 1800-1550 cm^{-1} region are shown in Figure 4;



A quantitative analysis of these interactions was carried out in these regions using adequate curve fitting procedures.

The fraction of free carbonyl is calculated from the equation below:

$$F_{free}^{carbonyl} = \frac{A_{free}^{carbonyl}}{A_{free}^{carbonyl} + A_{liberated}^{carbonyl} + \frac{\varepsilon_{free}}{\varepsilon_{dim}} A_{dimeric}^{carbonyl}} \tag{2}$$

where A is the band area of the corresponding species and $\varepsilon_{free}/\varepsilon_{dim}$ is the absorptivity ratio of 1.1.[15]

Table 3.
summarizes the various parameters. The Tg-composition dependence fitted well this recently theoretical proposed Brostow et al. (BCKV) approach.

System	Brostow et al. (BCKV)
PSIA17/PS4VP20	$a_0 = 5.078$ $a_1 = -0.83$ $a_2 = 22.08$

The fraction of the free pyridine is calculated assuming an absorptivity ratio of 1[16] from:

$$F_{free}^{pyridine} = \frac{A_{free}^{pyridine}}{A_{free}^{pyridine} + A_{associated}^{pyridine} + A_{pyridinium}} \tag{3}$$

Table 4.
Curve fitting data from infrared spectra of PSIA17/PS4VP20 blends in the 1800-1650 cm^{-1} region.

PSIA17/S4VP20	Free carbonyl			Dimeric carbonyl			Liberated carbonyl		
	$\nu(cm^{-1})$	$W1/2(cm^{-1})$	F(%)	$\nu(cm^{-1})$	$W1/2(cm^{-1})$	F(%)	$\nu(cm^{-1})$	$W1/2(cm^{-1})$	F(%)
100/0	1744	18	0.08	1705	32	0.92	–	–	0
78.1/21.9	1745	18	0.11	1707	33	0.51	1729	29	0.38
57.3/42.7	1744	20	0.13	1707	33	0.43	1728	30	0.44
37.3/62.7	1744	20	0.12	1707	35	0.41	1726	30	0.47
18.3/81.7	1745	19	0.10	1707	35	0.50	1726	29	0.40

Table 5.
Curve fitting data from infrared spectra of PSIA17/PS4VP20 blends in the 1650-1570 cm^{-1} region.

PSIA17/PS4VP20		0/100		18.3/81.7		37.3/62.7		57.3/42.7		78.1/21.9	
Styrene	$\nu(cm^{-1})$	1601	1583	1601	1583	1601	1583	1601	1583	1601	1582
	$W_{1/2}$ (cm^{-1})	7.4	06	10	6	8	6	9	6	8	6
Free Pyridine	$\nu(cm^{-1})$	1597		1596		1596		1596		1597	
	$W_{1/2}(cm^{1})$	10		11.5		11		9.00		9.50	
	Fraction	0.86		0.32		0.20		0.10		0.27	
Associated pyridine	$\nu(cm^{-1})$	1604		1607		1605		1604		1605	
	$W_{1/2}(cm^{-1})$	7.42		11.4		12		12		08	
	Fraction	0.14		0.24		0.18		0.2		0.1	
Pyridiniumion	$\nu(cm^{-1})$	—		1637		1638		1639		1639	
	$W_{1/2}(cm^{-1})$	—		16		15		18		17	
	Fraction	—		0.44		0.62		0.70		0.63	

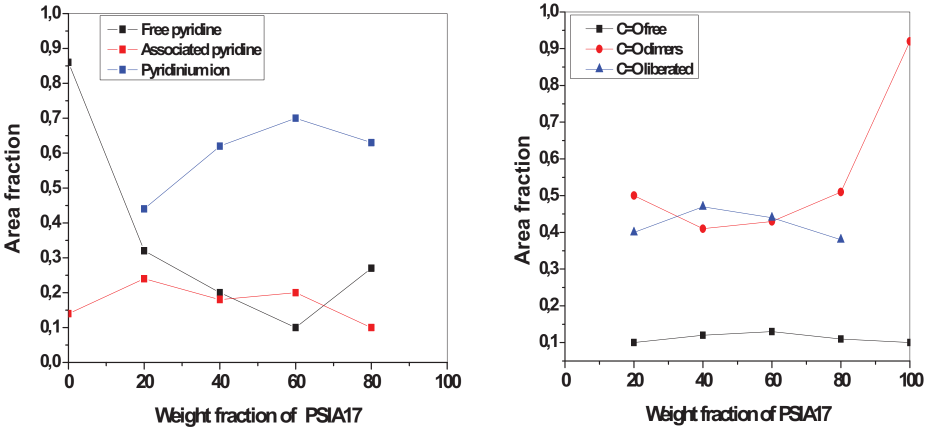


Figure 5.
Variations of the area fractions of the different species for PSIA17/PS4VP system with PSIA17 content.

The obtained results are summarized in Tables 4, 5. Figure 5 shows the variations of the area fractions of the different species with PSIA17 content.

Conclusion

Interpolymer complexes based on poly (styrene-co-4-vinylpyridine) and poly (styrene-co-itaconic acid) were elaborated due to the effective specific itaconic-pyridine interactions that occurred between their pure components and were evidenced by FTIR.

A single Tg, intermediate between those of the pure components, was observed with each initial mixture. The Tg-composition dependence of this PSIA17/PS4VP20 system fitted well the recent approach proposed by Brostow et al.(BCKV).

The copolymerization of itaconic acid with styrene improved the thermal stability of PIA. Moreover PSAI17/PS4VP20 system showed a better thermal stability than its corresponding pure constituents. The degradation temperatures at maximum T_{dmax} of these complexes are higher than those of pure constituents. As a result of the specific interactions that occurred within these mixtures, the anhydride amount observed with PSIA17 decreased.

FTIR spectroscopy analysis confirmed the occurrence of interpolymer interactions from the appearance of new characteristic bands and from the increase of both fractions of liberated carbonyl and pyridinium species upon increasing PS4VP20 amount in the mixture.

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[1] M. Jiang, M. Li, M. Xiang, H. Zhou, *Adv Polym Sci.* **1999**, *146*, 121.
[2] V. V. Khuthoryanskiy, *Int. J. Pharm.* **2007**, *33*, 15.
[3] Y. He, B. Zhu, Y. Inoue, *Prog. Polym. Sci.* **2004**, *29*, 1021.
[4] L. Zhu, L. Li, X. Yang, R. Yu, S. Zheng, *J. Macromolecular Sci. Part B: Physics*, **2012**, *2*, 368.
[5] S. W. Kuo, C. H. Hsu, *Polymer International* **2010**, 59,7, 998.
[6] M. T. Garay, C. Alava, M. Rodriguez, *Polymer* **2000**, *41*, 5799.
[7] K. Elmiloudi, S. Djadoun, *J. Poly. Sci. : Part B: Poly. Phys.*, **2009**, *47*, 923.
[8] S. Djadoun, F. E. Karasz, F. Metref, *Macromol.Symp.* **1994**, *78*, 155.
[9] N. Abdellaoui-Arous, A. S. Hadj Hamou, S. Djadoun, *Thermochimica Acta* **2012**, *547*, 22.
[10] K. Elmiloudi, S. Djadoun, N. Sbirrazzuoli, S. Geribaldi, *Thermochimica Acta* **2009**, 483[1,2] 49.
[11] M. Krusic Kalagasidis, E. Dzunuzovic, S. Trifunovic, J. J.Filipovic, Eur Polym J., **2004**, **40,** 793.
[12] W. Brostow, R. Chiu, I. M. Kalogeras, A. Vassilikou-Dova, *Mater. Lett.* **2008**, *62*, 3152.
[13] M. S. Zeliazkow, Polym deg. *Stab.* **2006**, *91*, 1233.
[14] M. S. Zeliazkow, *Polym deg. Stab.* **2001**, 74 [3] 579.
[15] C. S. Cleveland, S. P. Fearnly, Y. Hu, M. E. Wagman, P. C. Painter, M. M. Coleman, *J Macromol Sci Phys* **2000**, *B39*, 197–223.
[16] L. Jose, L. C. Cesteros, I. Katime, *J. Appl Spectrosc.* **1996**, *50*, 893.