Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Effect of Styrene-Butadiene-Styrene Block Copolymer on the Kinetic of Thermooxidative Degradation of High-Impact Polystyrene

T. Holjevac-Grguric[a]; V. Rek[a]; Z. Jelcic[b]
[a] Faculty of Chemical Engineering and Technology, Zagreb, Croatia [b] INA Polymers d.o.o. Zitnjak b.b., Zagreb, Croatia

To cite this Article Holjevac-Grguric, T. , Rek, V. and Jelcic, Z.(1998) 'Effect of Styrene-Butadiene-Styrene Block Copolymer on the Kinetic of Thermooxidative Degradation of High-Impact Polystyrene', Journal of Macromolecular Science, Part A, 35: 7, 1375 — 1384

To link to this Article: DOI: 10.1080/10601329808002126

URL: http://dx.doi.org/10.1080/10601329808002126

J.M.S.—PURE APPL. CHEM., A35(7&8), pp. 1375–1384 (1998)

EFFECT OF STYRENE-BUTADIENE-STYRENE BLOCK COPOLYMER ON THE KINETIC OF THERMOOXIDATIVE DEGRADATION OF HIGH-IMPACT POLYSTYRENE

T. Holjevac-Grguric, V. Rek
Faculty of Chemical Engineering and Technology
Marulicev trg 19
Zagreb, Croatia

Z. Jelcic
INA Polymers d.o.o.
Zitnjak b.b.
Zagreb, Croatia

ABSTRACT

The stability of polyolefins and their blends is very important for their practical use under high temperatures. The effect of styrene-butadiene-styrene block copolymers on the intensity of the thermo-oxidative degradation of HIPS can be followed through kinetic parameters. In styrene-butadiene copolymers soft, polybutadiene phase (PB), and hard, polystyrene phase (PS) have a different sensibility on thermal degradation. The thermooxidative stability of high impact polystyrene (PS-HI) and blends of PS-HI and styrene-butadiene-styrene copolymer, (SBS) were investigated. The investigation were done by isothermal DSC analysis. The kinetic parameters of the thermooxidative degradative process: the reaction rate constants, the reaction orders, and the activation energies have been determined. The total area under the exothermic curve was used to calculate the isothermal heat of degradation. On the basis of the heat of the thermooxidative degradation the conversion (α) and the rate of the thermooxidative degradation ($d\alpha/dt$) have been obtained. The experimental data have been tested with kinetic model for autocatalytic reactions: $d\alpha/dt\ (k\alpha^m\ (1\text{-}(\ \alpha)^n$. The activation energy has been determined by Arrhenius equation. On the basis of the calcu-

www.dekker.com

lated kinetic parameters the order of thermooxidative stability of the investigated system has been obtained. The experimental data have a good agreement with the autocatalytic model.

INTRODUCTION

The stability of polymer materials under high temperatures is very important for their practical use and processing, thus the investigations of their thermooxidative stability are very important. The styrene-butadiene copolymers (PS-PB), under high temperatures are susceptible on thermooxidative degradation. The first step of the thermooxidative degradation PS-PB copolymers and their blends is degradation of polybutadiene (1, 2).

Some of the radicals formed in the degradation of polybutadiene can act as initiators of the oxidation of the polystyrene (2). The kinetic of thermooxidative degradation can be followed by differential scanning calorimetry and IR spectroscopy. In this paper, the thermooxidative stability of high-impact polystyrene (PS-HI), styrene-butadiene-styrene block copolymer (SBS) and PS-HI/SBS blends was investigated. Structure changes occurred by thermooxidative degradation were followed by IR spectroscopy.

EXPERIMENTAL

Materials and Specimens Preparation

The investigations were done with high impact polystyrene, (PS-HI), 457, OKI, Croatia, Zagreb, with the content of polybutadiene, PB, 8% weight, styrene-butadiene-styrene block copolymer, (SBS), a commercial grade, Kraton 1101, Shell. Co., Germany, with the content of polystyrene, (PS), 29% weight and PS-HI/SBS blends. The compositions of starting copolymers and blend compositions of the PS-HI/SBS systems are given in Table 1.

Blends of PS-HI/SBS were prepared by using twin extruder Haake Record 90 (laboratories system) with the intensive mixing profile, Haake TW 100 with following temperatures in zone 150/200/200/150 and the frequency of rotation 60 min^{-1}. The specimens for investigations were obtained by compression molded at 230°C; mold temperature 40°C and rate 100 mm/s.

Measurements

The thermooxidative degradation was studied by differential scanning calorimetry, on a differential scanning calorimeter, DSC 2910, TA Instruments;

TABLE 1. Paramters of Kinetic Model

SAMPLE	PS-HI / SBS % wght	$k\ 10^3$ (s^{-1})					m					n					Ea (kJ/mol)
		150 °C	155 °C	160 °C	165 °C	170 °C	150 °C	155 °C	160 °C	165 °C	170 °C	150 °C	155 °C	160 °C	165 °C	170 °C	
1	100	/	0.79	1.37	1.47	1.49	/	0.41	0.53	0.39	0.29	/	0.84	1.10	1.34	1.13	62.62
2	90 /10	/	0.94	1.55	1.48	6.00	/	0.31	0.44	0.32	0.60	/	1.30	1.29	1.18	1.90	135.14
3	45 / 55	/	1.90	2.45	3.84	3.84	/	0.29	0.25	0.29	0.29	/	1.32	1.43	1.40	1.26	81.01
4	100	1.93	2.94	4.89	7.17	/	0.43	0.33	0.37	0.42	/	1.46	1.28	1.43	1.40	/	140.03

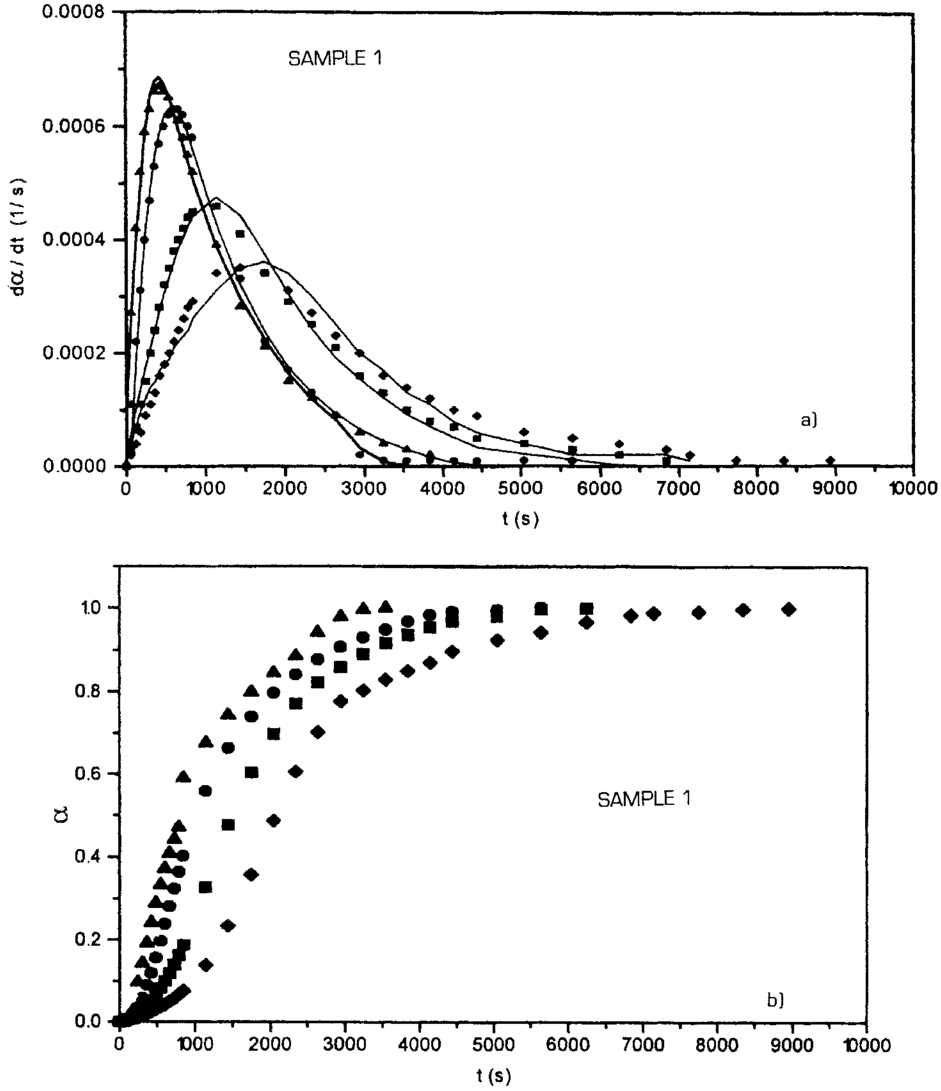

Figure 1. Reaction rate (dα/dt) (a) and conversion (α) (b) as a function of time for PS-HI, sample 1 and PS-HI/SBS 90/10, sample 2; solid lines are results of computer modeling.

◆ 155°C ■ 160°C ● 165°C ▲170°C

sample size was 13 mg, heating rate 5°C/min in oxygen atmosphere. The isothermal thermooxidation was performed at temperatures 150, 155, 160, 165 and 170°C, in a open aluminum pan with oxygen flow 40 ml. IR spectra, before and after thermooxidative degradation was performed on a Fourier Transform Infrared Spectroscopy (FTIR), Nicolet 5 DX-FTIR.

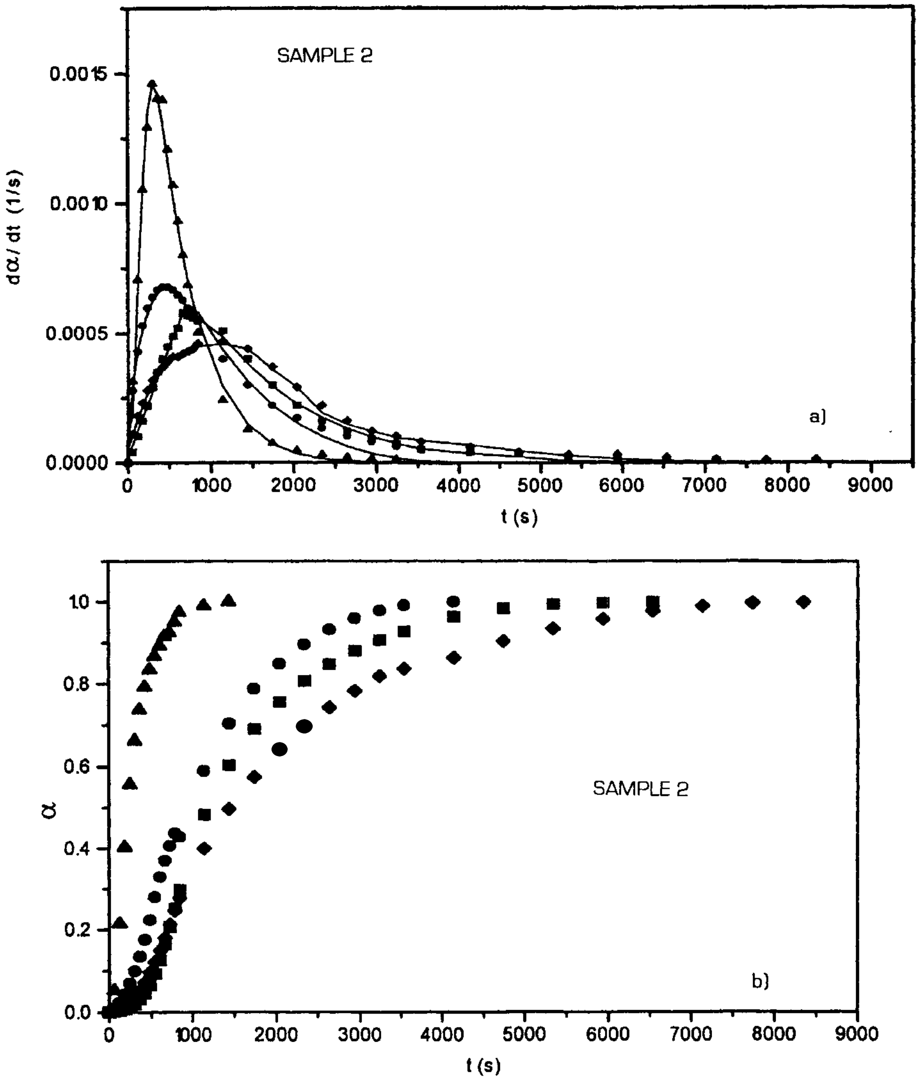

Figure 1. Continued

RESULTS AND DISCUSSION

The isothermal thermooxidation of the investigated samples at temperatures 150, 155, 160, 165 and 170°C results with a curve exotherm, because the oxidative degradation is an exothermic process. Supposing that the amount of heat evolved in oxidation is proportional to conversion of thermooxidative degradation, the conversion (α) and reaction rate ($d\alpha/dt$) were determined using the following relationship (3);

$$\frac{d\alpha}{dt} = \frac{1}{\Delta H_T}\,\frac{dH}{dt} \tag{1}$$

$$\alpha = \frac{\Delta H_P}{\Delta H_T} \tag{2}$$

ΔH_T total heat of thermooxidative degradation
ΔH_P partial heat of thermooxidative degradation

Reaction rate profiles obtained from isothermal experiments were fitting to a kinetic model for autocatalytic reactions (4, 5, 6):

$$\frac{d\alpha}{dt} = k\,\alpha^{m}\,(1-\alpha)^{n} \tag{3}$$

k is reaction rate described by Arrhenius relation:

$$k(T) = Z\,e^{-Ea/RT} \tag{4}$$

m and n are reaction orders.

The reaction rate dα/dt, as a function of time, t, for PS-HI, SBS, PS-HI/SBS 90/10 i PS-HI/SBS 45/55 blends is shown on Figures 1 and 2.

Figure 3 shows the reaction rate as a function of time on temperature 160°C for samples with different content of soft, PB, phase.

For all investigated systems, with increment of thermooxidation temperature, the conversion (α) and the reaction rate (dα/dt) increase. The rate maximums are shifted to lower time. Samples with higher content of soft, PB, phase, have higher conversion in the same time range, at all examined temperatures. As the content of polybutadiene increases in investigated copolymers and blends, the rate of thermooxidative degradation is higher, and rate profile maximum is moved to lower times (Figures 1-3). The thermooxidation rate profile dα/dt/t, for all samples, obtained by a computer modeling on the base of the autocatalytic kinetic model (relation 3), are shown as solid line at Figures 1-3. The good agreement of the experimental results and the results obtained by modeling is evident (Figures 1-3). The parameters of kinetic model k, m and n determined by nonlinear regression analyze, are shown in Table 1. Activation energy, Ea, was determined from Arrhenius relationship. The obtained values of Ea are shown in Table 1.

IR spectras of samples, obtained before and after thermooxidative degradation, confirm that the polybutadiene component, soft phase, is responsible for

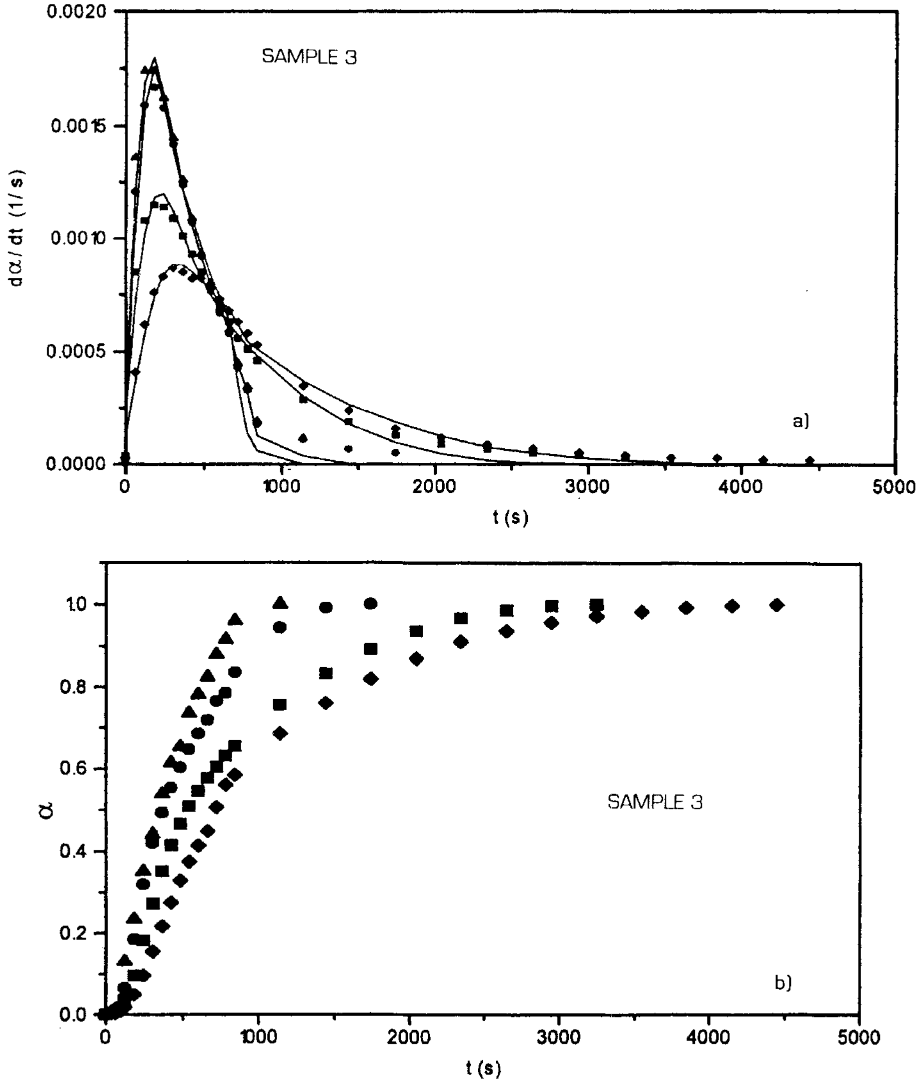

Figure 2. Reaction rate (dα/dt) (a) and conversion (α) (b) as a function of time for PS-HI/SBS 45/55, sample 3 and SBS, sample 4; solid lines are results of computer modeling.

◆ 155°C ■ 160°C • 165°C ▲170°C

(continued)

thermooxidation. After exposure copolymers PS-HI, SBS and PS-HI/SBS blends to temperature and oxygen in DSC apparatus, the intensities of the band due to the diene sequences (at 960 cm^{-1}) is decreased, while the intensity of the band due to hydroxyl group (at 3440 cm^{-1}) and carbonyl group (at 1730 cm^{-1}) are increased (5).

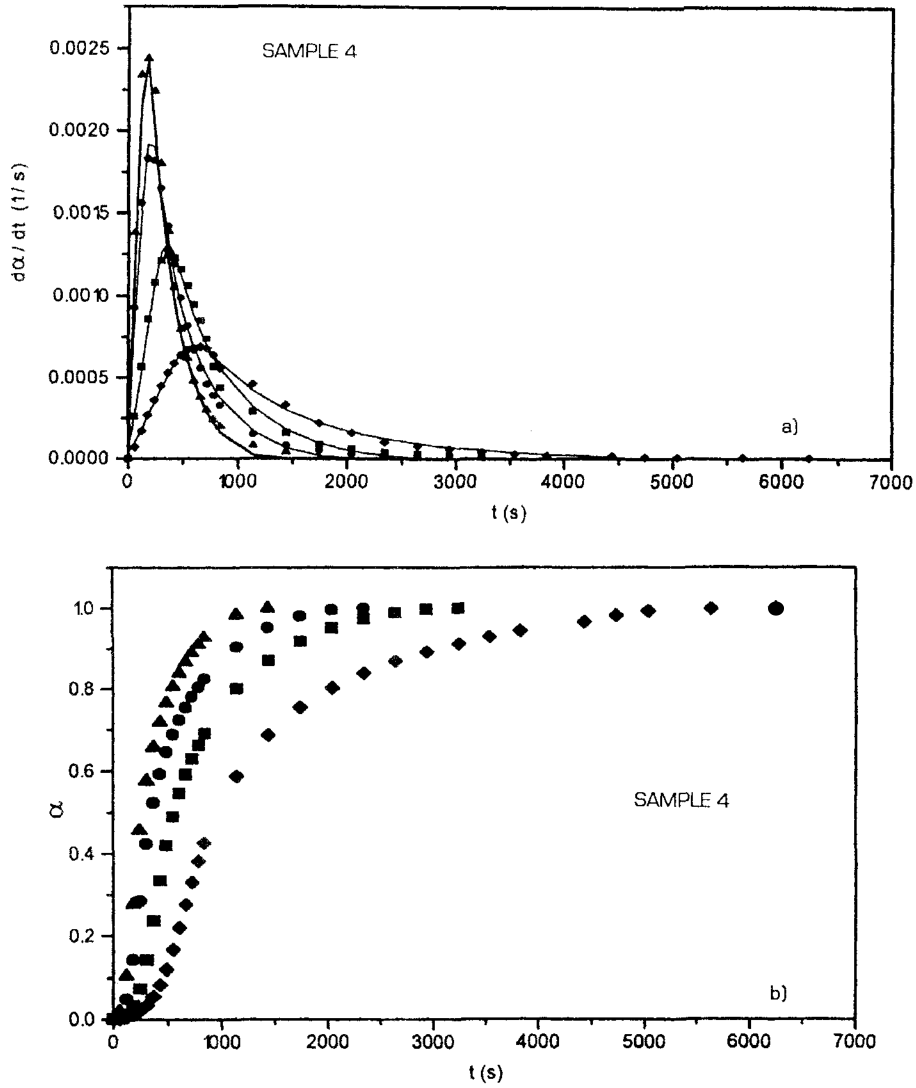

Figure 2. Continued

CONCLUSION

The isothermal differential scanning calorimetry can be successfully used for investigation of the kinetic of thermooxidative degradation of PS-HI, SBS and PS-HI/SBS blends. Testing the experimental data show the good agreement with the autocatalytic kinetic model. The parameters of thermooxidative degradation k, m, n and Ea were determined. The profiles of thermooxidative degradation show

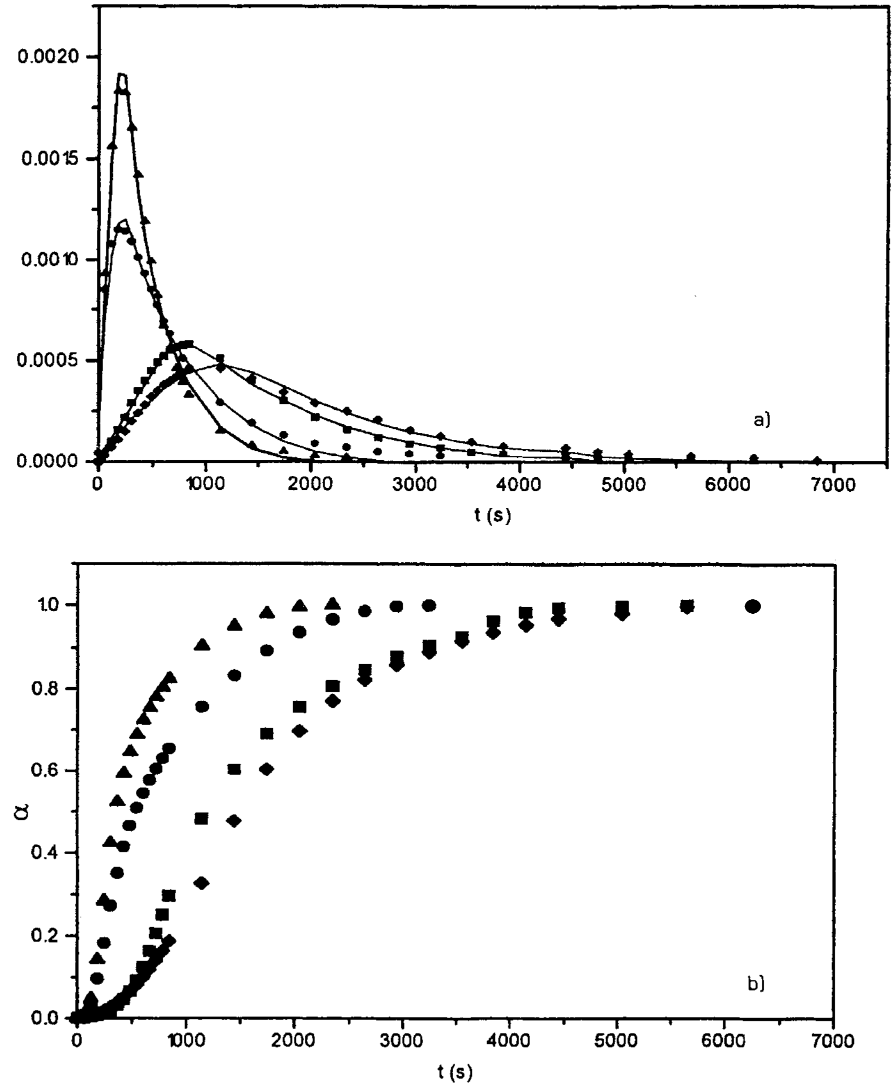

Figure 3. Reaction rate (dα/dt) (a) and conversion (α) (b) as a function of time for PS-HI, sample 1 and PS-HI/SBS 90/10 (sample 2), PS-HI/SBS 45/55 (sample 3) and SBS (sample 4) at temperature 160°C; ◆ sample 1 ■ sample 2 ● sample 2 ▲ sample 4.

that the addition of SBS into PS-HI changes the rate of thermooxidative degradation of PS-HI/SBS blends. It is due to the higher content of soft, polybutadiene phase in sample. With increment of the content of soft, polybutadiene phase in sample, the rate of thermooxidative degradation increases as well as conversion. The stability order obtained is as follow:

$(PS\text{-}HI)_1 > (PS\text{-}HI/SBS)_2 > (PS\text{-}HI/SBS)_3 > (SBS)_4$

The results of IR spectra confirm the same stability order of the investigated copolymers and their blends.

REFERENCES

[1] L. Reich and S.S. Stivala, *Elements of Polymer Degradation*, McGraw-Hill Comp., New Jersey, 1971.

[2] Y. Israeli, J. Lacoste, J. Lemaire, and S. Sivaram, *J. Polym. Sci.; Polym. Chem., 32,* 3, 465, (1994).

[3] Du Pont Thermal Analysis Technical Literature.

[4] P. J. Heines, *Thermal Methods of Analysis,* Blackie Academic and Professional, Glasgow, 1995.

[5] C. Adam, J. Lacoste, and J. Lemaire, *Polym. Deg. Stab., 26,* 269, (1989).