

# Influence of Backbone Rigidity on the Curing and the Dielectric Relaxations of Unsaturated Polyesters

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**ABSTRACT:** Unsaturated polyesters with maleic acid and different molar ratio of phthalic anhydride to adipic acid were produced, mixed with styrene, and cured. The degree of double bonds conversion, determined by differential scanning calorimetry ( $\alpha_{\text{DSC}}$ ), indicating the initial curing, increases significantly with the molar ratio of phthalic anhydride. On the other hand, the degree of double bonds conversion of maleate ( $\alpha_{\text{UP,FTIR}}$ ) and styrene ( $\alpha_{\text{St,FTIR}}$ ) units determined by Fourier transform infrared spectroscopy after prolonged curing are considerably higher than  $\alpha_{\text{DSC}}$  and increase slightly with the molar ratio of phthalic anhydride. Polyester containing phthalic anhydride without adipic acid (M5P5) has the lowest tetrahydrofuran uptake and diffusion parameter  $D/\alpha^2$  due to its more rigid segments, in opposite to polyester con-

taining adipic acid (M5A5) having the highest values. According to dielectric spectroscopy measurements, two different relaxations were determined, one beginning above 130°C (with peak above 180°C) attributed to  $\alpha$ -relaxation (dielectric glass transition) and a second one at lower temperatures, attributed to  $\beta$ -relaxation. The peak of  $\beta$ -relaxation is at around 130, 75–80, and 30°C for the rigid, intermediate rigidity/flexibility, and flexible polyesters, respectively. The  $\alpha$ -relaxation is determined at low frequencies and the  $\beta$ -relaxation at intermediate or high frequencies. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 1984–1993, 2011

**Key words:** unsaturated polyesters; FTIR; DSC; dielectric spectroscopy; relaxations; swelling

## INTRODUCTION

Unsaturated polyester (UP) resins cured with styrene have been used commercially since the 1940s, as matrix with glass-fiber reinforcements for reinforced composite materials. The availability of a wide variety of raw materials encouraged the development of a wide range of resins specifically tailored for many unique products.<sup>1–3</sup> Thus, the UPs are used in coatings, marine craft, land transportation, building, and construction as well as for large fabricated products (such as chemical and petroleum storage tanks). They are very popular, because of their low-manufacturing cost, easy processing, low densities etc.<sup>1,4</sup>

The curing of the UPs follows a free radical copolymerization between the unsaturated units contained in the polyester chains and a vinylic comonomer such as styrene, leading to network formation.<sup>1</sup> Curing is a highly exothermic reaction and can be easily monitored by differential scanning calorimetry (DSC) and subsequently the heat of reaction, the

kinetics, and the mechanism of curing process can be determined.<sup>5–8</sup> The final crosslinked structure of the UPs depends on the amount of vinylic comonomer, the extent of unsaturation in the resins, the number and type of unsaturated units in the backbone, the extent of the maleate to fumarate isomerization, the steric hindrances, and the electric effect of the acid and glycol units, as well as the type and concentration of initiator and accelerator. The glass transition temperature of the network shifts to higher temperature with increasing double bonds concentration.<sup>9</sup> The type of the polyester monomer units influences the crosslinked density of the thermoset, so that a high number of methylene groups in the macromolecular backbone leads to low-final crosslinked density. More details of research results concerning the synthesis, curing, structure, and properties of UPs are reported in.<sup>1,10</sup>

When a crosslinked polymer is immersed in a proper solvent, absorption takes place leading to the swelling of the polymer. As a result, the three-dimensional network gets extended until equilibrium swelling is achieved, at which the rate of solvent absorption is equal to the rate of desorption.<sup>11</sup> The three-dimensional crosslinked network of UP resists to the attack and the penetration of the most corrosive chemical and nonpolar solvents, although

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solvents such as lower ketones, chlorinated aliphatics, and aromatics penetrate to cured polyesters.<sup>1</sup>

Cured polyesters are insulators and have relatively low-dipolar characteristics.<sup>1</sup> A strong industrial interest in dielectric and electrical properties of polymers reflects the growing use of these materials in printed board circuitry, microwave assemblies for radar, etc. Fundamental investigations of the dielectric properties of the polymers offer much information about different molecular motions and relaxation processes.<sup>12</sup> A unique characteristic of the dielectric spectroscopy (DS) is the wide frequency range (from  $10^{-5}$  Hz up to  $10^{11}$  Hz) of the alternate electrical field applied to polymers.<sup>12,13</sup> The  $\alpha$ -relaxation observed at the highest temperature is associated with the "dielectric glass transition" and at lower temperatures  $\beta$ -relaxation or even  $\gamma$ -relaxation can be detected. The  $\alpha$ -relaxation is associated to the beginning of segmental mobility within the polymer backbone, whereas the  $\beta$ - and  $\gamma$ -relaxations are associated to fluctuations of short side chains.<sup>4,12</sup> Chemical structure and polarity are the basic factors controlling dielectric response in polymers. Large changes in dielectric response occur at transitions such as the  $\alpha$ -relaxation or the  $\beta$ - and  $\gamma$ -relaxations that involve more local molecular motion and are seen as dielectric loss maxima.<sup>13,14</sup> DS is a proper method to study the relaxation of UP resins.<sup>15-18</sup>

The aim of this work is to study the influence of backbone rigidity on the curing and the dielectric relaxations of UPs based on maleic acid (which is an unsaturated acid). The rigidity of the polyesters can be alternated during their synthesis by varying the ratio of phthalic anhydride (i.e., an aromatic anhydride, which imparts rigidity on the backbone) to adipic acid (i.e., a linear aliphatic acid, which enhances the flexibility of the backbone). To have the same degree of unsaturation, the percentage of maleic acid used and the amount of mixed styrene will be the same in all polyesters. The initial curing of polyesters will be studied with DSC, whereas their prolonged curing and their structure will be studied with Fourier transform infrared (FTIR) spectroscopy. The flexibility/rigidity of the segments between the crosslinks will be estimated from the swelling of the cured polyesters in an appropriate organic solvent, that is, tetrahydrofuran (THF). The relaxations of the cured UPs will be determined with DS and correlated to their structure.

## EXPERIMENTAL

UPs were synthesized using maleic acid (p.a., Merck) as the unsaturated acid, phthalic anhydride (p.a., Merck), adipic acid (p.a., Merck) and ethylene glycol (p.a., Merck) under different molar ratios, by

the azeotropic distillation method, in a 2-L vapor reflux reactor. The experimental polyesterification procedure has been previously described in detail.<sup>7,10</sup> Because glycols are generally volatile and they are removed from the reactor together with water, the necessary amount of glycol was in a molar excess of 10% over the stoichiometry (i.e., the molar ratio of ethylene glycol to the sum of moles of acids and anhydride was 1.10 : 1). After the polyesterification, the polyesters were mixed and diluted with styrene (p.a., Merck) in a proportion of 30 : 100 w/w (styrene/synthesized polyester), at temperature of 70°C for  $\sim$  45 min. The polyester-styrene mixtures were cured in an appropriate casting form at room temperature for about 48 h (referred hereafter as cured polyesters). The curing system consisted of methyl ethyl ketone peroxide (MEKP, Technical grade, NEOTEX) as initiator and cobalt naphthenate (CoNp, Technical grade, Fluka) as accelerator. The amount of CoNp and of MEKP was 1 and 3 mL per 100 g of polyester-styrene mixture, respectively.

The curing of the polyester-styrene mixture was studied using DSC. After carefully mixing 10–20 g of polyester-styrene mixture with the appropriate amount of accelerator in an aluminum pan, the initiator was quickly added, homogeneously mixed, and a sample of  $\sim$  30 mg was transferred into an aluminum crucible, weighted, and then inserted into the sample holder of the DSC apparatus. The measurements were carried out in a Netzsch differential scanning calorimeter DSC 200 by cooling at 0°C with liquid nitrogen and then heating up to 180°C, with a heating rate of 10°C/min, under nitrogen flow.

The dielectric relaxations of cured polyesters were studied using DS with an Impedance Analyzer (Hewlett Packard, type: 4192ALF) in the frequency range from  $10^3$  Hz up to  $10^7$  Hz. The measurement cell containing the cured polyester specimen was connected with the Impedance Analyzer and inserted in an oven. The cured polyesters were measured under isothermal conditions at 17 different temperatures (from 20 to 180°C, by 10°C increase and 5-min residence time at each temperature). The total duration of this first thermal treatment was about 2.5 h. Afterward, the cured polyesters derived from the first thermal treatment were measured again using the previously described procedure, and cured polyesters from this second thermal treatment were derived.

The cured polyesters (as previously described), first and second thermally treated were characterized by FTIR with a PerkinElmer FTIR system spectrum GX, using a proper disc of polyester with KBr. To estimate the network density of the cured polyesters, first and second thermally treated, their swelling ability in an appropriate organic solvent (THF) at room temperature was determined. For this

**TABLE I**  
**Synthesis of Unsaturated Polyesters Including Mixing with Styrene, Their Curing, and Thermal Treatment**  
**During Dielectric Spectroscopy**

Synthesis of unsaturated polyesters					Mixing	Curing and thermal treatment		
Code	Raw materials (composition % molar ratio)				Styrene (30 % w/w)	Curing room temperature, $t_{\text{total}} = 2$ days	Thermal treatment of cured polyesters during Dielectric Spectroscopy (DS) heating program from 20 up to 180°C, $t_{\text{total}} = 2.5$ h	
	Diacids and anhydride			Glycol			First thermal treatment	Second thermal treatment
Polyester-styrene mixture	Maleic acid (M)	Adipic acid (A)	Phthalic anhydride (P)	Ethylene glycol Et(OH) <sub>2</sub>		Cured polyesters	Code*	
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
M5A5	50	50	–	110	X	M5A5-0	M5A5-I	M5A5-II
M5A3P2	50	30	20	110	X	M5A3P2-0	M5A3P2-I	M5A3P2-II
M5A2P3	50	20	30	110	X	M5A2P3-0	M5A2P3-I	M5A2P3-II
M5P5	50	–	50	110	X	M5P5-0	M5P5-I	M5P5-II

\* The cured polyesters are distinguished with the last character of their code: -0 (column 7), -I (column 8), and -II (column 9).

purpose, the polyesters were cast in the form of cylindrical discs. THF was chosen, because it is a good solvent for both polystyrene and linear (i.e., non-cured) UPs.<sup>19,20</sup> The solvent uptake was determined by weighting the discs at certain time intervals.

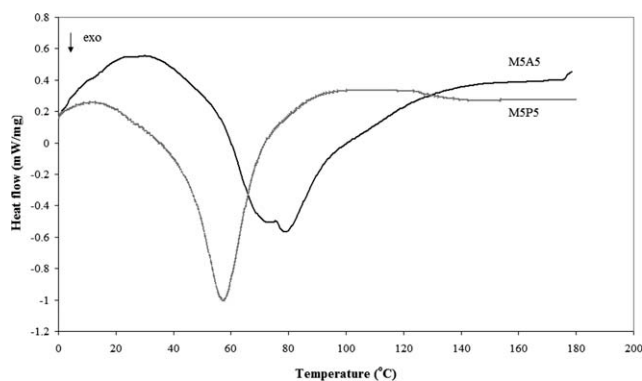
## RESULTS AND DISCUSSION

Table I presents two main columns, that is, one for the synthesis of UPs including their mixing with styrene and a second for their curing and their thermal treatment during the DS measurements. Four different UPs were synthesized with the same feed molar ratio of maleic acid and different molar ratio of phthalic anhydride to adipic acid and then they were mixed with styrene. All polyester-styrene mixtures were cured giving the corresponding cured polyesters. Cured polyesters thermally treated during the DS measurement are also presented.

Figure 1 shows the DSC thermograms of the polyesters M5A5 and M5P5. All polyesters exhibit a sharp exothermic peak attributed to the highly exothermic curing reactions (copolymerization of maleate double bonds of the backbone with styrene). During the curing of UP, a free radical chain-growth polymerization between the double bonds of the polyester backbone and the styrene takes place. The curing process can be divided into five stages, that is, induction, microgel formation, transition, macrogelation, and postgelation.<sup>21</sup> In the induction stage, the initiator decomposes and reacts with styrene to form styryl radicals. In the microgel formation stage, radicals react with maleate double bonds of UP to

form primary copolymers (microgels).<sup>21</sup> The free styrene monomer is restrained within the gel; the double bond of styrene polymerizes in homopolymer blocks until it reacts with the double bond of maleate unit.<sup>22</sup> In the transition stage, intermolecular reaction occurs among microgels to form larger clusters. Dispersed UP-rich domains with size around 2  $\mu\text{m}$  were formed. When the reaction progresses, more domains are formed and are connected with each other to form a cocontinuous structure.<sup>21,22</sup> At the gel point, a crosslinking network is formed through either the intermolecular reaction among microgels, microgel clusters, or dispersed UP-rich domains (macrogelation).<sup>21</sup>

Table II shows the results of DSC containing the onset temperature ( $T_{\text{onset}}$ ), the peak temperature ( $T_p$ ), the final temperature of the exotherm ( $T_f$ ), the heat released ( $-\Delta H$ ) due to the exothermal curing reaction, and the degree of double bonds conversion of the UP-styrene mixture ( $\alpha_{\text{DSC}}$ ) during the DSC. The curing of the UPs is a free radical copolymerization between the unsaturated units contained in the polyester chains and the double bond of styrene, leading to the formation of a network structure. During the curing reaction, an amount of heat is released that is proportional to the amount of the double bonds (of the maleate unit and the styrene) that are reacting. According to the literature, the exotherm during the polymerization of the double bonds of styrene and maleate units is  $\Delta H_S = -73 \times 10^3 \text{ J mol}^{-1}$  and  $\Delta H_{\text{UP}} = -59 \times 10^3 \text{ J mol}^{-1}$ , respectively.<sup>23</sup> The degree of double bonds conversion of



**Figure 1** DSC thermograms of the polyesters M5A5 and M5P5 (for their codes, see Table I).

the UP–styrene mixture during the DSC ( $\alpha_{\text{DSC}}$ ) can be estimated taking into consideration the exotherm experimentally determined by DSC in respect to the total theoretically expected exotherm (by reacting all double bonds of both styrene and maleate units). The values of  $\alpha_{\text{DSC}}$  were determined according to eqs. (1) and (2), based on the procedure described in detail in the literature.<sup>7</sup>

$$a_{\text{DSC}} = \frac{\Delta H}{\Delta H_{\text{total}}} \quad (1)$$

where  $\Delta H$  is the exotherm calculated from the DSC peak in Joule per gram and  $\Delta H_{\text{total}}$  the exotherm of the UP–styrene mixture in Joule per gram. The value of  $\Delta H_{\text{total}}$  can be estimated from Eq. (2):<sup>7</sup>

$$\Delta H_{\text{total}} = \frac{S \cdot \Delta H_S \cdot \alpha_S + \text{UP} \cdot \Delta H_{\text{UP}} \cdot \alpha_{\text{UP}}}{S \cdot M_S + \text{UP} \cdot M_{\text{UP}}} \quad (2)$$

where  $S$  is the mole of styrene (S) double bonds, UP the mole of maleate (UP) double bonds,  $\alpha_S$ ,  $\alpha_{\text{UP}}$  the

degree of double bonds conversion of styrene and maleate, respectively, which are equal to one by reacting all double bonds,  $M_S$  the molecular weight of styrene unit (g/mol), and  $M_{\text{UP,C=C}}$  the molecular weight of polyester unit, which contains 1 mol of C=C bonds (g/mol).<sup>7</sup>

The temperature  $T_{\text{onset}}$  has values between 43 and 54°C, whereas  $T_p$  is between 57 and 79°C,  $T_f$  is between 70 and 101°C, and  $-\Delta H$  has values between 99 and 179 J/g. By replacing the adipic acid (M5A5) with the phthalic anhydride (M5P5), the characteristic DSC temperatures ( $T_{\text{onset}}$ ,  $T_p$ , and  $T_f$ ) decrease, whereas the  $-\Delta H$  and the  $\alpha_{\text{DSC}}$  (%) values increase. Furthermore, in polyesters containing both phthalic anhydride and adipic acid, that is, polyesters M5A3P2 and M5A2P3, by increasing the amount of phthalic anhydride in respect with the amount of adipic acid, the DSC characteristic temperatures decrease, whereas the  $-\Delta H$  and the  $\alpha_{\text{DSC}}$  (%) values increase. The different behavior of polyester with phthalic units compared to that with adipic units will be interpreted below.

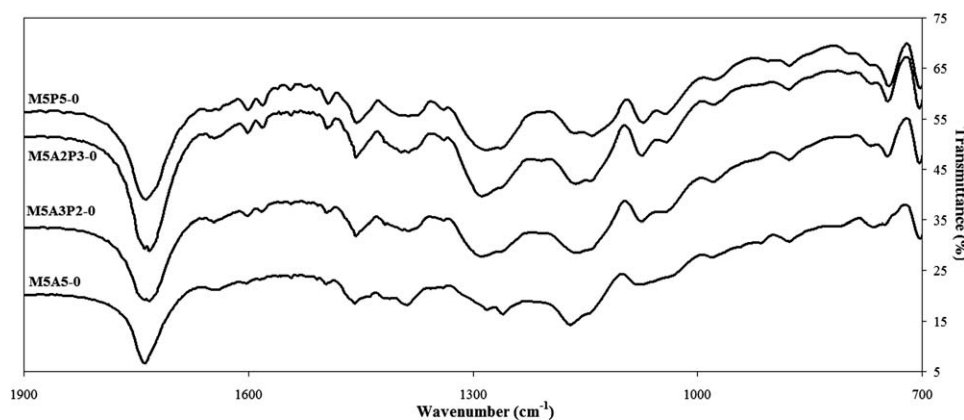
Figure 2 shows the FTIR spectra (in the region of 1900–700  $\text{cm}^{-1}$ ) of the cured polyesters (Table I, column 7). According to the literature,<sup>7,10,24</sup> the polyesters exhibit the absorption bands of the corresponding stretching vibrations of –OH from glycol (at 3400–3200  $\text{cm}^{-1}$ , not shown in Fig. 2), of –CH<sub>2</sub>– (at 2980–2950  $\text{cm}^{-1}$ , not shown in Fig. 2) and of >C=O from ester groups (at 1750–1735  $\text{cm}^{-1}$ ). They also exhibit the absorption bands of the C=C stretching vibrations in the aromatic ring (originating from the styrene and/or the phthalic units) at 1600, 1580, and 1500  $\text{cm}^{-1}$ . Around 1465  $\text{cm}^{-1}$  appears the peak due to –CH<sub>2</sub>– bending vibrations, whereas at 1390  $\text{cm}^{-1}$  appears the peak of the glycolic –OH in-plane-bending vibrations. Two bands arising from C–O stretching vibrations of carboxyl groups appear at 1275 and 1250  $\text{cm}^{-1}$ , whereas the corresponding vibrations of

**TABLE II**  
Characteristic Data of DSC Scans of Unsaturated Polyester–Styrene Mixtures Including the Degree of Double Bonds Conversion (for Their Codes, See Table I)

Code Polyester–styrene mixture	Heating of polyester–styrene mixture during DSC heating program from 0 up to 180°C, $t_{\text{total}} = 18$ min					Code Cured polyesters, thermally treated by DSC
	$T_{\text{onset}}$ (°C)	$T_p$ (°C)	$T_f$ (°C)	$-\Delta H$ (J/g)	Degree of double bonds conversion ( $\alpha_{\text{DSC}}$ )	
(1)	(2)	(3)	(4)	(5)	(6)	(7)
M5A5	54.0	78.7	101.0	98.8	0.32	M5A5-DSC
M5A3P2	52.6	70.8	97.0	126.1	0.41	M5A3P2-DSC
M5A2P3	43.5	70.3	90.0	162.5	0.53	M5A2P3-DSC
M5P5	45.2	57.3	69.9	179.0	0.58	M5P5-DSC

$T_{\text{onset}}$ , onset temperature of the exotherm;  $T_p$ , peak temperature of the exotherm;  $T_f$ , final temperature of the exotherm;  $-\Delta H$ , exotherm during the curing reaction;  $\alpha_{\text{max,UP}}$ , degree of double bonds conversion of the unsaturated polyester–styrene mixture.





**Figure 2** FTIR spectra of the cured polyesters (for their codes, see Table I).

ester groups appear at  $1165\text{ cm}^{-1}$ . Additionally, the peak at  $1070\text{ cm}^{-1}$  is attributed to the glycolic C—O stretching vibrations, whereas the absorption bands at  $875$ ,  $750$ ,  $698$ , and  $668\text{ cm}^{-1}$  are due to the aromatic ring (originating from the styrene and/or the phthalic units). Finally, at  $982$  and  $912\text{ cm}^{-1}$  appear the peaks attributed to the unreacted residual double bonds of the maleate units and the styrene, respectively. The FTIR spectra of the thermally treated polyesters (Table I, columns 8 and 9) show the same absorption bands as the corresponding cured polyesters, that is, the thermal treatment does not affect the characteristic absorption bands.

The unreacted double bonds can be quantitatively estimated from the FTIR spectra. Specifically, the degree of double bonds conversion for the polyester ( $\alpha_{\text{UP,FTIR}}$ ) and the styrene ( $\alpha_{\text{St,FTIR}}$ ) can be determined from the peak magnitude<sup>7,10,25</sup> or the peak area<sup>26</sup> of their characteristic peaks, that is, the peak at  $982\text{ cm}^{-1}$  for the double bonds of the UP and the peak at  $912\text{ cm}^{-1}$  for the double bonds of the styrene. The  $>\text{C}=\text{O}$  peak at  $1750\text{--}1735\text{ cm}^{-1}$  was chosen as internal standard to correct the differences between the thickness of KBr–polyester discs. Thus

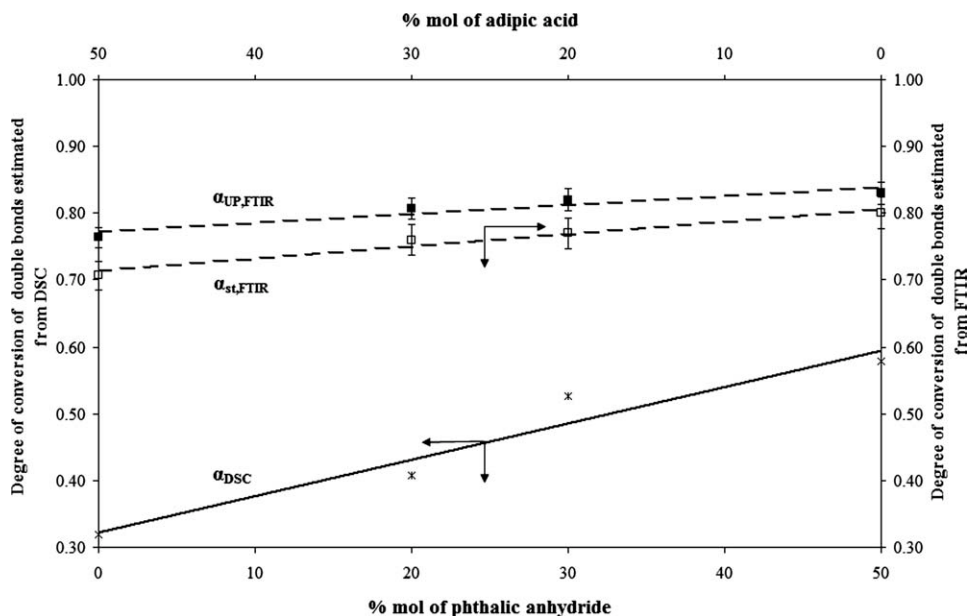
$$\alpha_{\text{UP,FTIR}} = 1 - \frac{A_t(982)}{A_i(982)} \quad (3)$$

and

$$\alpha_{\text{St,FTIR}} = 1 - \frac{A_t(912)}{A_i(912)} \quad (4)$$

where  $A_i$  and  $A_t$  are the normalized absorbance (i.e., divided by the peak magnitude or area at  $1750\text{--}1735\text{ cm}^{-1}$ ) before the reaction starts and after a certain treatment, respectively. The method was applied using the peak magnitude.<sup>7,10</sup> The value of  $A_i$  was calculated from the FTIR spectra of the UP–styrene mixture. The degree of double bonds conversion for polyester ( $\alpha_{\text{UP,FTIR}}$ ) and styrene ( $\alpha_{\text{St,FTIR}}$ ) for cured,

first and second thermally treated polyesters, were also calculated. Figure 3 presents the degree of conversion of double bonds of polyester–styrene mixture (Table I, column 1, symbolized as  $\alpha_{\text{DSC}}$ , concerning the sum of double bonds of styrene and maleate units) estimated from DSC and the degree of conversion of double bonds of cured polyesters, first and second thermally treated polyesters (Table I, columns 7–9, symbolized as  $\alpha_{\text{UP,FTIR}}$ ,  $\alpha_{\text{St,FTIR}}$  for maleate and styrene units, respectively), as mean values, estimated from FTIR, versus the percentage of phthalic anhydride. The mean value of each group of polyesters (e.g., M5A5-0, M5A5-I, and M5A5-II) was used due to their low deviation (less than 5%). The values of  $\alpha_{\text{DSC}}$  increase significantly with increasing the molar percentage of phthalic anhydride. A slight increase occurs for  $\alpha_{\text{UP,FTIR}}$  and  $\alpha_{\text{St,FTIR}}$  in respect to the molar percentage of phthalic anhydride. The degrees of double bonds conversion determined by FTIR are considerably higher than those determined by DSC due to the more prolonged curing of the polyesters examined by the FTIR. The curing of the polyester–styrene mixture during DSC takes place by heating them up to  $180^\circ\text{C}$  for a total heating time of only 18 min. Contrarily, the polyesters, which were characterized by FTIR, have been previously cured for 48 h at room temperature. Furthermore, the first thermally treated polyesters are more intensely treated, that is, by heating them up to  $180^\circ\text{C}$ , for a total heating time of 2.5 h and additional 2.5 h (total heating time of 5 h) for the second thermally treated polyesters. Therefore, the degree of conversion of double bonds at the beginning of the curing of UPs is represented by the curve (line) determined by DSC and at prolonged curing by that of FTIR. These results will be interpreted in below, taking also into consideration the flexibility/rigidity of the segments between the



**Figure 3** Degree of conversion of double bonds estimated from DSC ( $\alpha_{\text{DSC}}$ ) and degree of conversion of double bonds ( $\alpha_{\text{UP,FTIR}}$ ,  $\alpha_{\text{St,FTIR}}$  for maleate and styrene units, respectively) estimated from FTIR, versus the percentage of phthalic anhydride.

crosslinks. The latter can be estimated from the swelling of the cured polyesters in THF.

The swelling of cured, first and second thermally treated polyesters, was followed from the solvent uptake versus time. The equilibrium time (corresponding to the time that the maximum uptake of THF was achieved) was in the range of 22–74 h. Based on the diffusion theory, the diffusion-controlled uptake of THF into the polyester mass can be approached by the Fick equation:<sup>27</sup>

$$\frac{(Q_t - Q_0)}{(Q_\infty - Q_0)} = \left(\frac{6}{\pi^{0.5}}\right) \cdot \left(\frac{D \cdot t}{\alpha^2}\right)^{0.5} \quad (5)$$

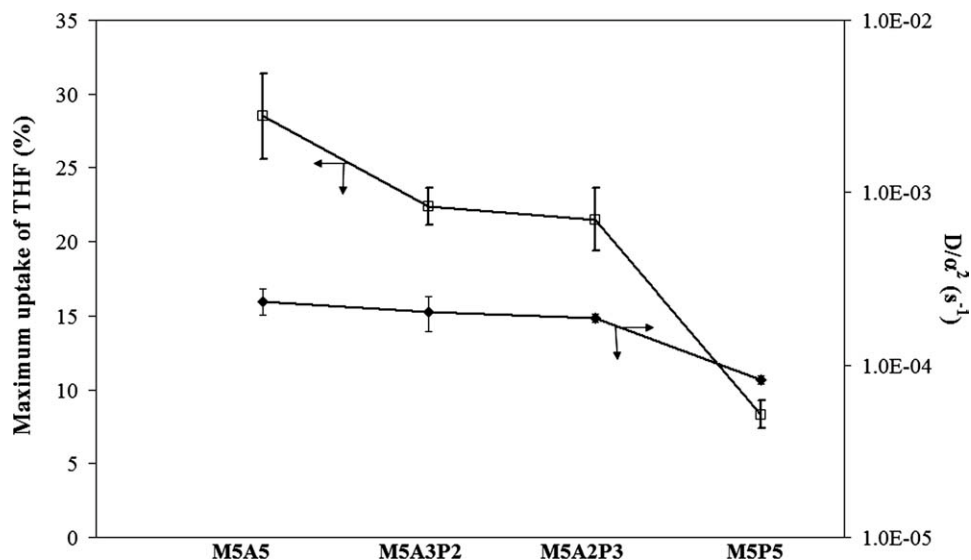
where  $Q_t$ ,  $Q_0$ , and  $Q_\infty$  are the solvent uptake at time:  $t$ , 0 and at equilibrium, respectively (in grams),  $D$  the diffusion coefficient, and  $\alpha$  the effective path. By plotting  $(Q_t - Q_0)/(Q_\infty - Q_0)$  versus  $t^{0.5}$ ,  $D/\alpha^2$  can be determined from the slope of the initial linear part of the curve.

Figure 4 presents the mean values of maximum THF uptake and  $D/\alpha^2$  of the cured polyesters, first and second thermally treated polyesters (Table I, columns 7–9). The mean values of each group of polyesters (e.g., M5A5-0, M5A5-I, and M5A5-II) were used due to their low deviation (less than 3%). Polyester M5P5 containing phthalic anhydride without adipic acid has the lowest THF uptake and  $D/\alpha^2$  due to its more rigid segments. On the other hand, polyester M5A5 containing adipic acid without phthalic anhydride has the highest THF uptake and  $D/\alpha^2$  due to its less rigid segments. In polyesters

containing both phthalic anhydride and adipic acid, the values of the maximum uptake of THF and of  $D/\alpha^2$  are very close. Given that the maximum uptake of THF is a thermodynamic parameter, whereas the ratio  $D/\alpha^2$  is a kinetic one, from both the thermodynamic and the kinetic point of view, the polyesters containing phthalic units have higher network density than the polyesters containing adipic units.

From the swelling results of the cured polyesters, the flexibility/rigidity of the segments between the crosslinks can be estimated and its contribution for the interpretation of the results concerning the double bond conversion determined by FTIR and DSC can be evaluated. For the interpretation of the swelling results of polyesters M5A5 and M5P5 (Fig. 4), three approaches are considered.

1. Reactivity of double bonds. For the synthesis of the two polyesters, the same molar ratio of maleic acid was used, and both polyesters were mixed with the same proportion of styrene. Thus, the polyesters have the same reactivity due to the same amount of double bonds.
2. Rigidity of macromolecule segments. Polyester M5A5 contains four (4) methylene groups per structural unit in the backbone (from the adipic acid) and, consequently, is more flexible than M5P5, which contains an aromatic ring (from the phthalic anhydride), respectively, and therefore it is expected that styrene could diffuse easier in the former. However, the most

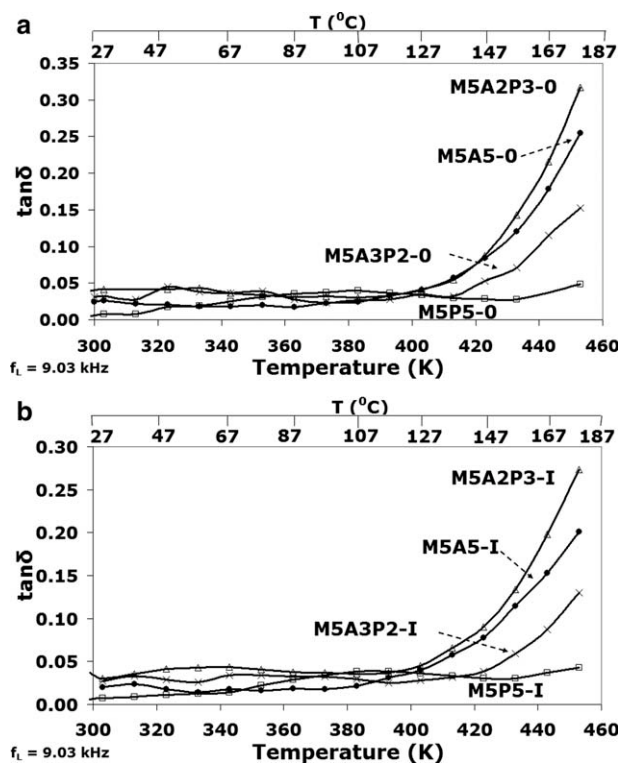


**Figure 4** Maximum uptake of tetrahydrofuran (THF) (%) and  $D/\alpha^2$  (estimated from the Fick equation) for the cured polyesters (for the codes, see Table I).

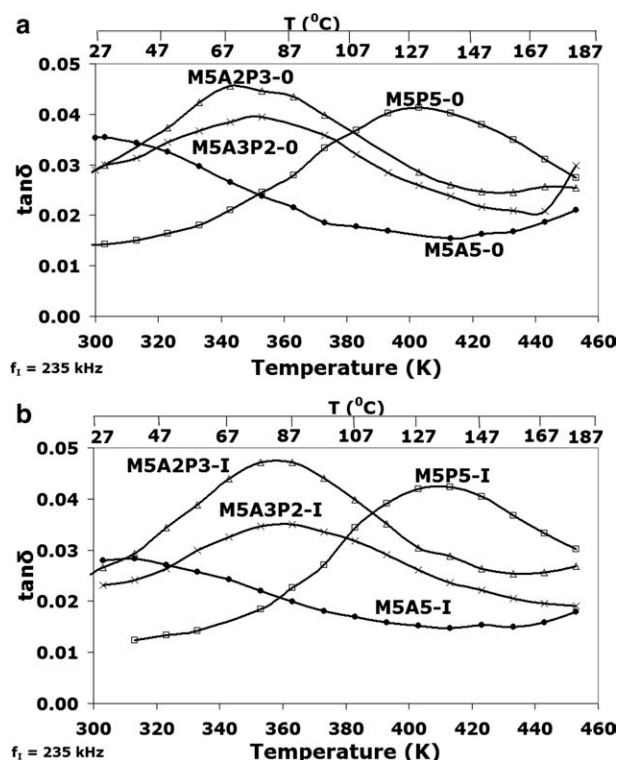
rigid polyester M5P5 has the highest double bond conversion by DSC concerning the sum of double bonds of styrene and maleate units. On the other hand, there is a slight increase of double bond conversion by FTIR ( $\alpha_{UP,FTIR}$  and  $\alpha_{St,FTIR}$ ) with increasing percentage of phthalic anhydride for the cured polyesters, first and second thermally treated, which have been treated under more intense conditions. The latter remark means that M5P5 has a slightly higher degree of double bonds conversion than M5A5. Thus, the conversion of double bonds is highly influenced from the rigidity of the macromolecular segments only in the less intense curing conditions (during DSC), that is, at the initial stage of curing and then by more intense conditions (during curing and thermal treatments), that is, at the extended curing progress, is only slightly influenced.

- Packing volume. It is known from the literature<sup>28</sup> that aryl polymers (i.e., polymers with aromatic rings in their backbone and other bulky groups) have much higher values of packing volume ( $370 \text{ cm}^3/\text{mol}$  of structural unit) compared to polyethylene and polystyrene ( $7.2$  and  $33 \text{ cm}^3/\text{mol}$  of structural unit, respectively). Therefore, polyester M5P5 has higher packing volume than M5A5 due to the rigid groups of phthalic anhydride, which are bulkier than the aliphatic methylene chain of adipic acid. The bulky phthalic unit is responsible for the increased intermolecular distances; thus, the styrene molecules can easily diffuse between the polyester M5P5 macromolecules, opposite to

polyester M5A5. By higher curing duration, the styrene molecules have more time available to diffuse between the macromolecules of polyester M5A5. However, the degree of double bond conversion of polyester M5P5 remains higher than that of M5A5. This indicates higher network



**Figure 5**  $\tan \delta$  versus temperature of the cured polyesters (for their codes, see Table I) at 9.03 kHz: (a) during the first thermal treatment by DS; (b) during the second thermal treatment by DS.



**Figure 6**  $\tan \delta$  versus temperature of the cured polyesters (for their codes, see Table I) at 235 kHz: (a) during the first thermal treatment by DS; (b) during the second thermal treatment by DS.

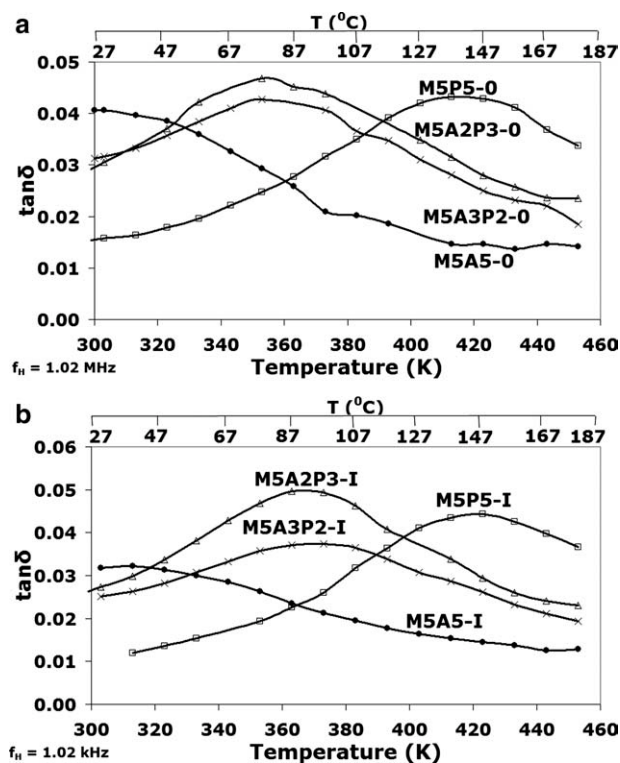
density of M5P5, which is in accordance with the swelling results. Furthermore, the macromolecular segments of M5P5 are more rigid than those of M5A5, leading to lower THF uptake and  $D/\alpha^2$  value.

The results of the initial cured and thermally treated polyesters by DS are presented in Figures 5–7, as loss tangent ( $\tan \delta$ ) versus temperature, to determine the relaxations of the networks. Three characteristic frequencies were chosen, that is, a low ( $f_L = 9.03$  kHz), an intermediate ( $f_I = 235$  kHz), and a high frequency ( $f_H = 1.02$  MHz). It is noticed that the curves in these figures have been plotted based on the experimental data points and not by mathematical simulation.

Figure 5(a,b) shows the beginning of a relaxation peak at high temperatures (above 130°C), as the beginning of an abrupt change. The measurements were carried up to 180°C to avoid the thermal degradation of the polyesters. At lower temperatures (below 130°C), no distinct peaks are observed. However, by increasing the dielectric frequency from 9.03 to 235 kHz, distinct peaks are observed [Fig. 6(a,b)]. The question is arisen whether these relaxations concerns  $\alpha$ - or  $\beta$ -relaxation, which will be answered as follows.

According to literature,<sup>29</sup> by plotting loss tangent against temperature, a given relaxation moves to higher temperature by increasing the frequency. If the relaxation in Figure 6(a) was the same as that of Figure 5(a), then the peak of the former [i.e., Fig. 6(a)], due to the higher frequency, should have been shifted at higher temperatures, that is, above 180°C, which does not occur. Furthermore, the scale of the  $\tan \delta$  axis of Figure 6(a) is almost 10 times lower than that of Figure 5(a). Consequently, there are two different relaxations, one beginning above 130°C (with peak above 180°C), determined from Figure 5(a,b), and a second one at lower temperatures, determined from Figures 6(a,b) and 7(a,b). The  $\alpha$ -relaxation observed at the highest temperature is associated with the “dielectric glass transition.”<sup>2,3,16–18</sup> Therefore, the second peak at lower temperatures corresponds to the  $\beta$ -relaxation that involves more local molecular motion.<sup>14</sup>

According to Figure 6(a), the  $\beta$ -relaxation of the rigid polyester M5P5 is at around 130°C and that of the flexible polyester M5A5 is at around 30°C. For both polyesters M5A3P2 and M5A2P3, with intermediate rigidity/flexibility, the  $\beta$ -relaxation is at around 75–80°C. By increasing the frequency from 235 kHz to 1.02 MHz, the peaks of the  $\beta$ -relaxation are slightly shifted to higher temperatures. The dielectric relaxation temperatures of the polyesters at



**Figure 7**  $\tan \delta$  versus temperature of the cured polyesters (for their codes, see Table I) at 1.02 MHz: (a) during the first thermal treatment by DS; (b) during the second thermal treatment by DS.

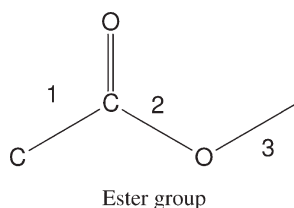


TABLE III  
Dielectric Relaxation Temperature

Code	Dielectric relaxation temperature (°C)		
	Onset temperature, $f_L = 9.03$ kHz	Peak temperature, $f_I = 235$ kHz	Peak temperature, $f_H = 1.02$ MHz
	Cured polyesters [Figs. 5(a), 6(a), and 7(a)]		
M5A5-0	130	30	30
M5A3P2-0	140	78	83
M5A2P3-0	130	75	80
M5P5-0	>170	133	143
	Cured polyesters, first thermal treatment [Figs. 5(b), 6(b), and 7(b)]		
M5A5-I	130	35	40
M5A3P2-I	150	87	95
M5A2P3-I	130	85	93
M5P5-I	>170	137	148

the three characteristic frequencies are summarized in Table III.

Polyester M5A5 has flexible molecular segments between crosslinks due to the methylene groups of the adipic acid, and, therefore, it is expected to exhibit relaxations. Concerning polyester M5P5, aromatic units (as that of phthalic unit) as part of the main chain exert a profound influence on virtually all important properties of the resulting polymer. The chain-stiffening aromatic ring in the polyester backbone is separated from each other by three consecutive single bonds of the ester group.<sup>30</sup>



The two tetrahedral angles associated with these bonds permit some degree of chain flexibility, which limits mechanical and thermal properties of the resulting polymers.<sup>30</sup> Even though polyester M5P5 has rigidity, the movement of the molecular segments between crosslinks is permitted through the polyester groups, leading to the appearance of relaxations. These relaxations of polyester M5P5 appear at higher temperatures than those of the flexible polyester M5A5.

## CONCLUSIONS

The degree of double bonds conversion, determined by DSC ( $\alpha_{DSC}$ ), indicating the initial curing, increases significantly with the molar ratio of phthalic anhydride. On the other hand, the degree of double bonds conversion of maleate ( $\alpha_{UP,FTIR}$ ) and styrene ( $\alpha_{St,FTIR}$ ) units determined by FTIR after prolonged

curing are considerably higher than  $\alpha_{DSC}$  and increase slightly with the molar ratio of phthalic anhydride. Polyester containing phthalic anhydride without adipic acid (M5P5) has the lowest THF uptake (thermodynamic parameter) and  $D/\alpha^2$  (kinetic parameter concerning the diffusion) due to its more rigid segments, whereas polyester containing adipic acid (M5A5) has the highest THF uptake and  $D/\alpha^2$  due to its less rigid segments, that is, it is more flexible. The higher degree of double bond conversion of polyester M5P5 than that of M5A5 is due to its higher packing volume, permitting easier diffusion of styrene molecules, and, therefore, this cured polyester has higher network density.

Based on DS measurements for all cured polyesters, two different relaxations were determined, one beginning above 130°C (with peak above 180°C) and a second one at lower temperatures. The  $\alpha$ -relaxation observed at the highest temperature is associated with the "dielectric glass transition," and the second peak at lower temperatures corresponds to the  $\beta$ -relaxation that involves more local molecular motion. For the  $\beta$ -relaxation of the rigid polyester M5P5, the corresponding peak is at around 130°C and that of the flexible polyester M5A5 is at around 30°C. For both polyesters M5A3P2 and M5A2P3, with intermediate rigidity/flexibility, the corresponding peak of the  $\beta$ -relaxation is at around 75–80°C. The  $\alpha$ -relaxation is determined at low frequencies and the  $\beta$ -relaxation at intermediate or high frequencies.

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