

# Chemical structure/mechanical properties of para-aminostyrene (PAS)-terminated telechelic polyimides

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We have synthesized a difunctional model compound PAS-HFDE-PAS, obtained by condensation between a dianhydride (6-HFDA), hexafluoroisopropylidene-2,2'-bis(phthalic acid anhydride) and two mole equivalents of para-aminostyrene (PAS) amines. It was then characterized using spectroscopic and thermal methods, including a kinetic study of monomer reactivity in the temperature range of 100–300°C. The results enabled us to study and characterize two series of PAS-functionalized polyimides synthesized in the laboratory: phenylenediamine (PAS *a* polyimide) and cardo diamine (PAS polyimide) based. Thermomechanical data obtained with these polyimides showed the presence of two phase transitions,  $\alpha$  and  $\beta$ , associated with vitreous transition and with oscillation of phenylenebenzimidazole structures around the  $C(CF_3)_2$  flexible linkage of HFDA. A study of chemical structure (determined by  $^1H$  and  $^{19}F$  n.m.r.)/properties correlation study was carried out by determining the effect of molar mass and the type of diamine on the thermomechanical properties of telechelic polyimides before cross-linking.  
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## INTRODUCTION

In a continuation on our work on cross-linkable polyimides<sup>1,2</sup>, we have studied prepolymers of variable mass, functionalized with para-aminostyrene (PAS) at chain ends. Although a number of prepolymers bearing acetylene, cyanate, maleimide, propargylic or nadimide chain ends have been studied<sup>3</sup>, relatively little work has been devoted to the *para*-aminostyrene function, whether it be at the level of molten state reactivity or thermomechanical properties. The first work by Dynes *et al.*<sup>4</sup> involved several telechelic polyimides with variable chain ends, one of which was functionalized with para-aminostyrene. The cross-linking mechanisms proposed for these compounds are cyclotrimerization mechanisms into aromatic structures, as in the case of the arylacetylene compound<sup>5</sup>.

Based on these results, it was decided to examine the mechanism and kinetics of polymerization of the para-aminostyrene (PAS) function. After synthesizing the difunctional model compound PAS-HFDE-PAS, it was investigated by chromatographic, spectroscopic and thermal methods. We then demonstrated the structure of the cross-linking node of the PAS function.

We investigated PAS telechelic polyimides with variable chain structures. After characterizing these macromolecules from a structural and thermomechanical standpoint, we examined the structure/properties relationships of these new telechelic polyimides by varying the type of diamine as well as molar mass.

## EXPERIMENTAL

### Synthesis

Synthesis of PAS-HFDE-PAS. Figure 1 shows the

synthesis path of the bis-styrene compound PAS-HFDE-PAS, resulting from condensation between a dianhydride (HFDA) and two PAS monoamines. A solution of HFDA (4.44 g ( $10^{-2}$  mole) in 25 cm<sup>3</sup> of DMF) was slowly added to a solution of para-aminostyrene (PAS) (2.43 g ( $2 \cdot 10^{-2}$  mole) in 25 cm<sup>3</sup> of DMF). After stirring for 3 h at room temperature, 50 cm<sup>3</sup> of acetone, 10 cm<sup>3</sup> of acetic anhydride and 1.3 g of molten sodium acetate were added to the reaction mixture. The mixture was heated for 5 h at 80°C and was then precipitated in 500 cm<sup>3</sup> of water. The precipitate was filtered and washed with a saturated solution of NaHCO<sub>3</sub>. The product was recrystallized in 300 cm<sup>3</sup> of methanol and dried under vacuum (yield 54%).

*Synthesis of PAS-terminated telechelic polyimides.* Polyimides were synthesized in N-methylpyrrolidone (NMP), a polar, aprotic medium. The polymers were synthesized in a reactor fitted with a condenser, by polycondensation between two dianhydride and diamine monomers, both having an aromatic structure, and a telechelic agent: PAS (Figure 2). The diamine solution was added to the solution of 6-HFDA by slow, dropwise infusion. The mixture was stirred at room temperature for 2 h, adding PAS after 1 h. The reaction mixture was heated for 2 h at 80°C, followed by one plateau at 120°C (2 h) and another at 160°C (3 h).

The solution was then cooled to room temperature, the polymer was precipitated by adding water, was filtered and finally dried in an oven. Residual NMP was removed by redissolving the polymer in acetone and repeating the above process until the complete elimination of NMP.

Using this procedure, we prepared two types of PAS-terminated aromatic polyimides with different macromolecular structure, by varying the nature of the diamine, as well as the polymerization index  $\bar{n}$  ( $\bar{n} = 2, 5, 8$  and 10). The chemical structures of the two polyimides synthesized are

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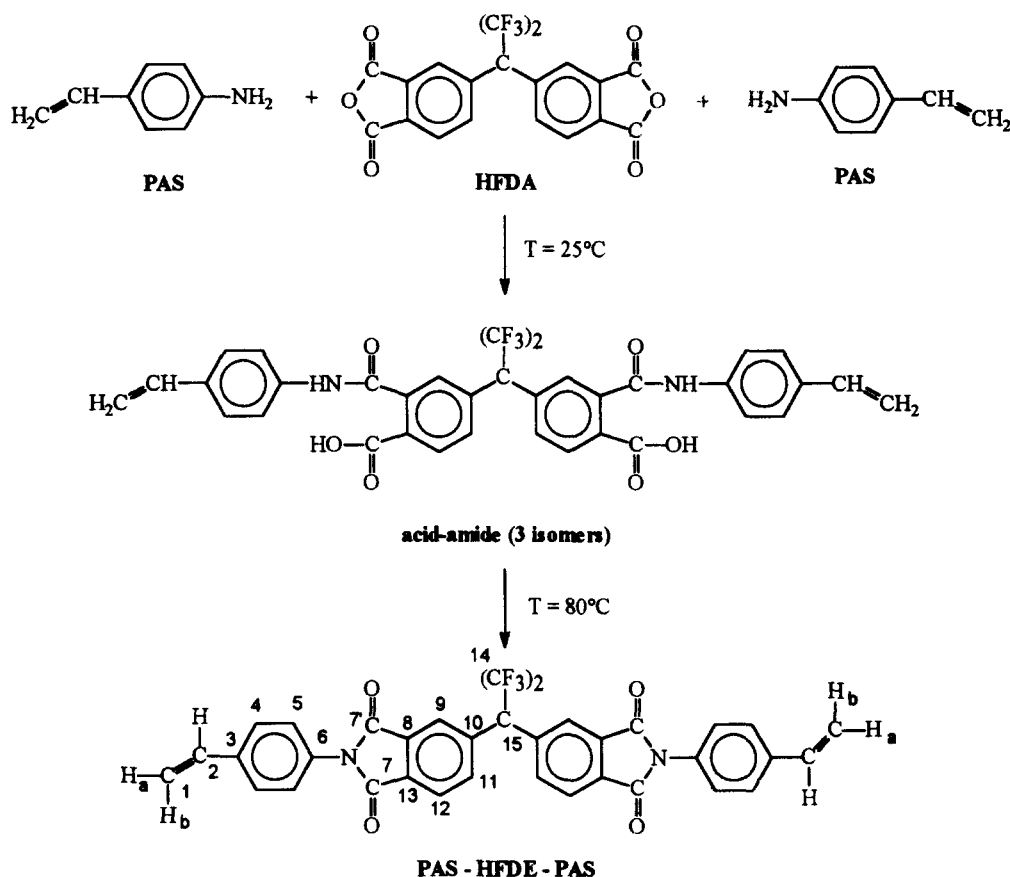


Figure 1 Synthesis path of the bis-styrene compound PAS-HFDE-PAS

shown in Figure 2. In the case of PAS a polyimides, we operated so as to obtain an oligomer soluble in NMP by using 25% mPDA<sup>6</sup>.

#### Equipment

**Fourier transform infrared absorption spectroscopy (FT-i.r.).** FT-i.r. spectra were recorded with a BRUKER IFS 45 spectrometer in the following conditions: spectral width 4000–400 cm<sup>-1</sup>, 32 accumulations, resolution 2 cm<sup>-1</sup> and solid sample (KBr pellet).

**Nuclear magnetic resonance (n.m.r.).** High resolution liquid state <sup>1</sup>H and <sup>13</sup>C n.m.r. spectra were recorded in deuterated dimethylsulfoxide (DMSO) and/or CDCl<sub>3</sub> with a BRUKER AM 400 spectrometer. Recording conditions were: pulse angle 90° (7 μs <sup>1</sup>H and 4.2 μs <sup>13</sup>C), digital resolution 0.122 Hz point<sup>-1</sup> (<sup>1</sup>H) and 0.375 Hz point<sup>-1</sup> (<sup>13</sup>C) corresponding to a spectral width of 4000 Hz (<sup>1</sup>H) and 20 000 Hz (<sup>13</sup>C). Chemical shifts were calculated in the basis of tetramethylsilane (TMS), internal standard.

#### High performance liquid chromatography (HPLC).

Samples were analysed with a VARIAN 5000 high performance liquid chromatograph coupled to an ICS light scattering detector. The column used was apolar ODSC18. The eluent was a water/acetonitrile mixture in which the percentage of acetonitrile was programmed to vary from 50 to 95% in 45 min.

#### Differential scanning calorimetry (DSC).

Thermal measurements were carried out with a SETARAM DSC 111G calorimeter with linear temperature programming at 5°C min<sup>-1</sup> in the temperature range of 50–450°C.

**Rheology.** Since the polyimides used were thermohardening, they had to be used as powders. The thermomechanical properties of a non-meltable powder can be studied only in rectangular torsion. This was done by pelleting the powder with a high pressure press (≈ 40 tons) into a circular plate 1.5–2.5 mm thick. The plate was then machined to obtain a 30 × 10 mm rectangle. Measurements were conducted with a Rheometrics RDA 700 or RDA II (RFIOS environment) instrument in the following conditions: pulse ω = 1 rad s<sup>-1</sup>, deformation 0.01–0.06%, torsion torque ≈ 20 g cm<sup>-1</sup>, temperature range 30–400°C, temperature rise 5°C min<sup>-1</sup>.

## RESULTS AND DISCUSSION

### Physicochemical study of the bis-styrene compound PAS-HFDE-PAS

**Physicochemical characteristics and mechanism of polymerization.** The <sup>1</sup>H n.m.r. study confirmed that PAS-HFDE-PAS was totally difunctionalized by a para-aminostyrene substituent (δ<sub>H<sub>a</sub></sub> = 5.3<sub>4</sub> ppm, δ<sub>H<sub>b</sub></sub> = 5.9<sub>2</sub> ppm, δ<sub>H<sub>2</sub></sub> = 6.8<sub>0</sub> ppm) with coupling constants of <sup>3</sup>J<sub>trans</sub> = 17.6 Hz and <sup>3</sup>J<sub>cis</sub> = 10.9 Hz. This study also demonstrated the stability of the styrene function in solution, whether during synthesis (80°C in dimethylformamide (DMF)) or during recrystallization (65°C in methanol). Integrating the signals obtained also confirmed the cyclic structure of the imide rings at the two extremities by the absence of signals attributable to acid–amide functions.

Liquid- and solid-state <sup>13</sup>C n.m.r. spectra obtained simultaneously (see Figure 3 and Table I) showed that carbon C<sub>1</sub> (vinyl), characteristic of the styrene double bond, was well differentiated from the other resonance lines

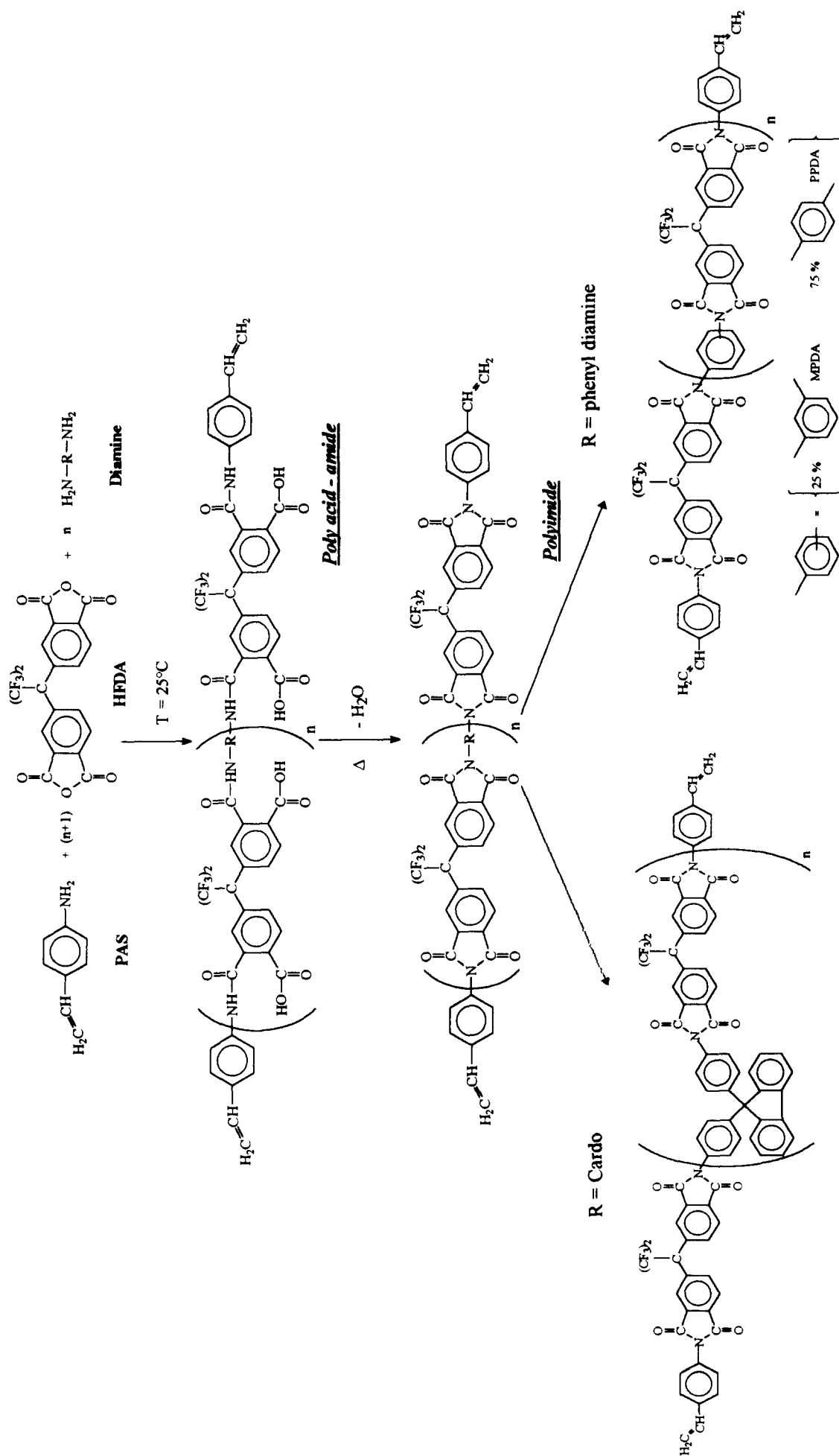


Figure 2 Synthesis path and structure of PAS-terminated polyimides

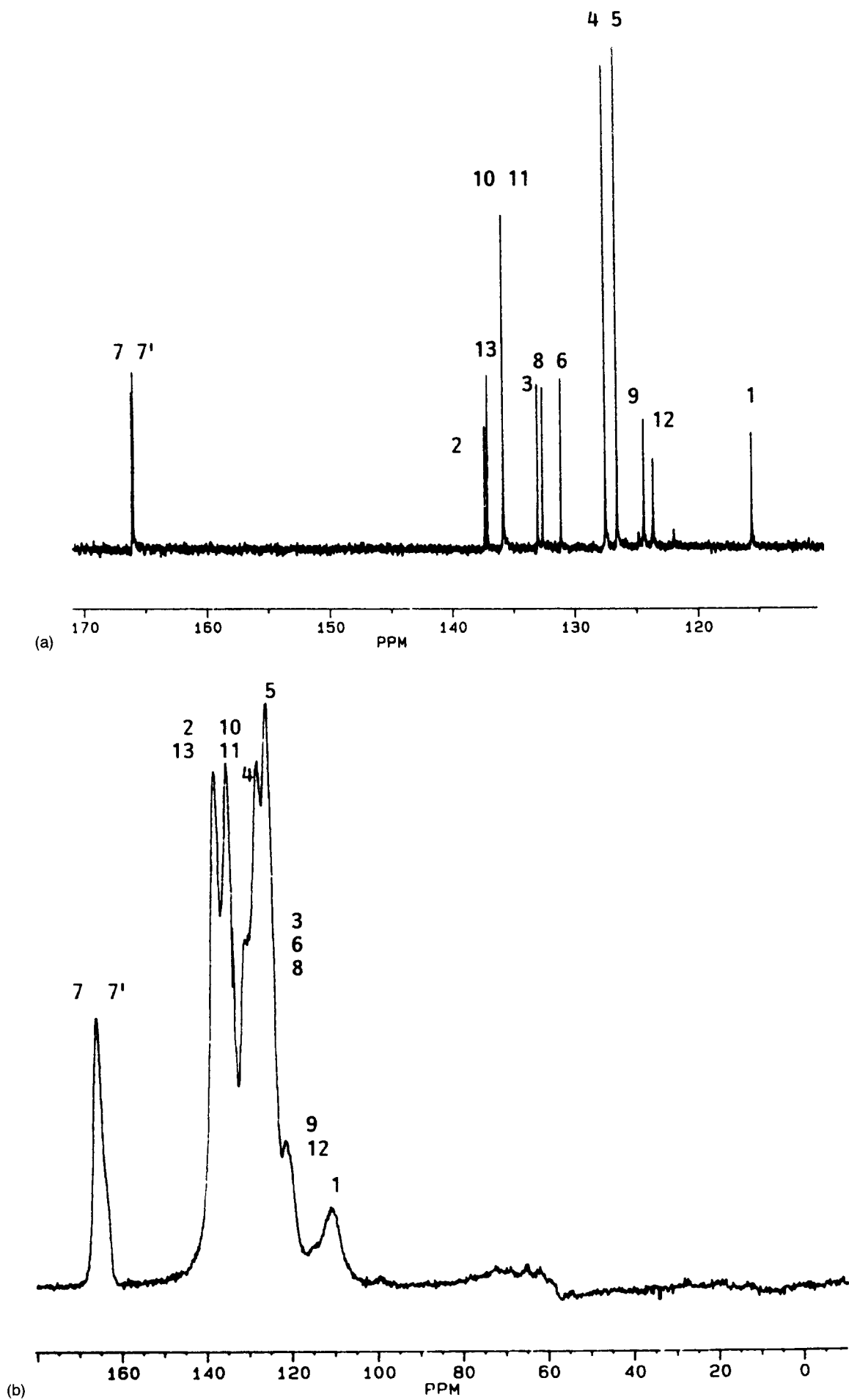


Figure 3 Liquid- and solid-state  $^{13}\text{C}$  n.m.r. spectra of PAS-HFDE-PAS (see Figure 1 for numbering of atoms): (a) liquid; (b) solid

( $\delta = 111.2$  ppm in solid-state  $^{13}\text{C}$  n.m.r.). When the kinetics of the double bond cross-linking reaction was studied, this line could be used as a probe to determine reaction conversion. In addition, the absence of resonance lines in the region characteristic of aliphatic carbons ( $\delta = 0\text{--}60$  ppm) made this a probe region for demonstrating the mechanism involved in the opening of styrene double bonds by thermal priming (formation of an aliphatic bond).

In FT-i.r., vibrations characteristic of the styrene function are well known<sup>7</sup> and can be summarized by given frequency values ( $\nu_{=\text{CH}_2} = 3084\text{ cm}^{-1}$ ,  $\nu_{=\text{CH}} = 3004\text{ cm}^{-1}$ ,  $\nu_{\text{C}=\text{C}} = 1630\text{ cm}^{-1}$ ,  $\gamma_{=\text{CH}} = 990\text{ cm}^{-1}$  and  $\gamma_{=\text{CH}_2} = 910\text{ cm}^{-1}$ ) All these frequencies should normally change with time in the course of a thermal treatment. Considering the vibrations of the other functions of the PAS-HFDE-PAS skeleton, however, only the bands at 3084 and 910  $\text{cm}^{-1}$  can be used in kinetics. In this case, we used as reference vibrations

at 3040  $\text{cm}^{-1}$  (aromatic valence vibration  $\nu_{=\text{CH}}$ ) and at 1515  $\text{cm}^{-1}$  (aromatic valence vibration  $\nu_{\text{C}=\text{C}_{\text{aro}}}$ ), respectively.

The DSC diagram of the PAS-HFDE-PAS bis-styrene compound showed that the system polymerized around 170°C (Figure 4). Since no melting endotherm was observed, however, the two phenomena (exothermal polymerization and endothermal melting) apparently occurred simultaneously and so the overall energy balance of these two modifications is exothermal. The cross-linking exotherm temperature was 190°C ( $T_{\text{onset}}$ ). The exothermal peak characteristic of double bond opening was complex, since there were two maxima ( $T_{\text{max1}} = 202^\circ\text{C}$  and  $T_{\text{max2}} = 212^\circ\text{C}$ ).

There was a second transition beyond this exotherm ( $\approx 300^\circ\text{C}$ ) whose exothermal or endothermal character was difficult to determine. In order to verify the nature of these two transitions, complex by their shape and structure, their nature was examined by dynamic mechanical spectrometry (Figure 5).

The storage modulus  $G'$  revealed the presence of an  $\alpha$  transition around 120°C, characterized by its rupture of slope by a vitreous transition. The modulus then dropped around 190°C, a phenomenon associated with a melting temperature having a maximum  $Tf_{\text{max}} = 205^\circ\text{C}$ . This would tend to confirm the hypothesis formulated in the context of DSC, since the endotherm maximum situated within the cross-linking exotherm would be about 207°C in DSC. Beyond this temperature the three-dimensional network appeared as a result of the opening of the vinyl double bond, characterized by increases in the value of the  $G'$  modulus. At 400°C, there was total destruction of the network with a drop of the values of the storage modulus  $G'$ .

The study of the loss modulus  $G''$  confirmed the existence of a vitreous transition temperature ( $T_g = 120^\circ\text{C}$  maximum of  $G''$ ), followed by fluidization of the system.  $G''$  decreased starting at 290°C, corresponding to the transition not identified in DSC.

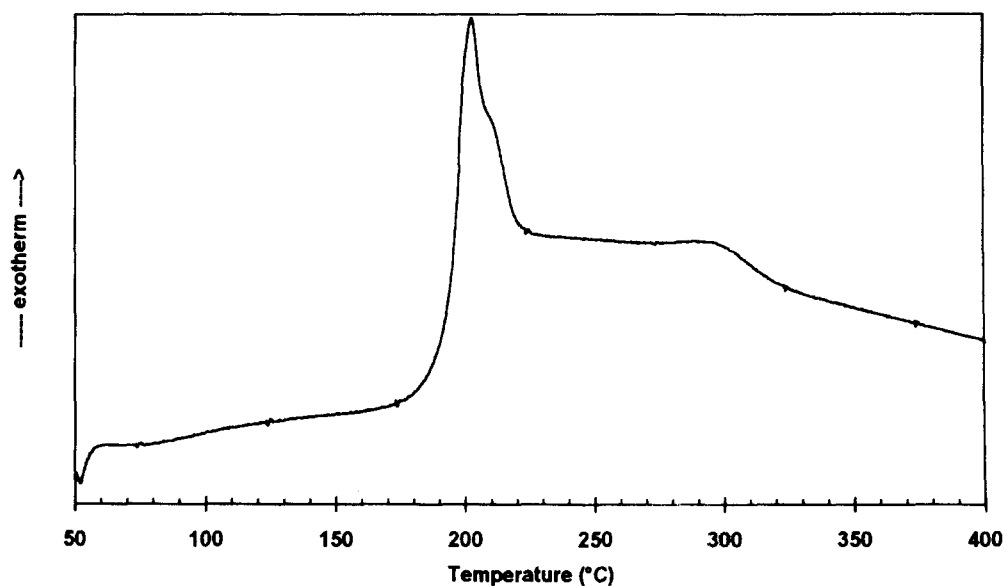
This is consistent with the hypothesis of a thermal oxidation of the network formed from PAS functions, since the measurements were made in air. Following this thermal oxidation of the network, there would be total destruction ( $T = 400^\circ\text{C}$ ). Furthermore, at the end of the experiment,

**Table 1** Chemical shifts of the compound PAS-HFDE-PAS in liquid- and solid-state  $^1\text{H}$  and  $^{13}\text{C}$  n.m.r. (see Figure 1 for numbering of atoms)

Squeleton	Assignments	Chemical shifts		
		Liquid		Solid
		$^1\text{H}$ n.m.r. <sup>a</sup>	$^{13}\text{C}$ n.m.r.	$^{13}\text{C}$ n.m.r.
PAS	1a	5.3 <sub>4</sub> (d)	116.1	111.2
	1b	5.9 <sub>2</sub> (d)	116.1	111.2
	2	6.8 <sub>6</sub> (q)	137.9	137.7
	3		133.6	134.8
	4	7.4 <sub>3</sub> (d)	128.1	125.2
	5	7.6 <sub>3</sub> (d)	127.1	127.4
	6		131.7	130.5
H	7		166.7–166.5	165.8
	7'		166.7–166.5	165.8
F	8		133.2	133.6
D	9	7.7 <sub>5</sub> (s)	124.9	125.2
	10		136.4	137.7
E	11	7.9 <sub>7</sub> (d)	136.4	133.6
	12	8.1 <sub>8</sub> (d)	124.2	125.2
	13		137.7	133.6
	14		128.9	125.2
	15		65.1	67.4

(s) = singulet, (d) = doublet; (q) = quadruplet.

<sup>a</sup> Coupling constants:  $^2J_{\text{gem}} = -6.6\text{ Hz}$ ;  $^3J_{\text{trans}} = 10.9\text{ Hz}$ ;  $^3J_{4-5} = 8.3\text{ Hz}$ ;  $^3J_{11-12} = 8\text{ Hz}$ .



**Figure 4** DSC diagram of the bis-styrene compound PAS-HFDE-PAS

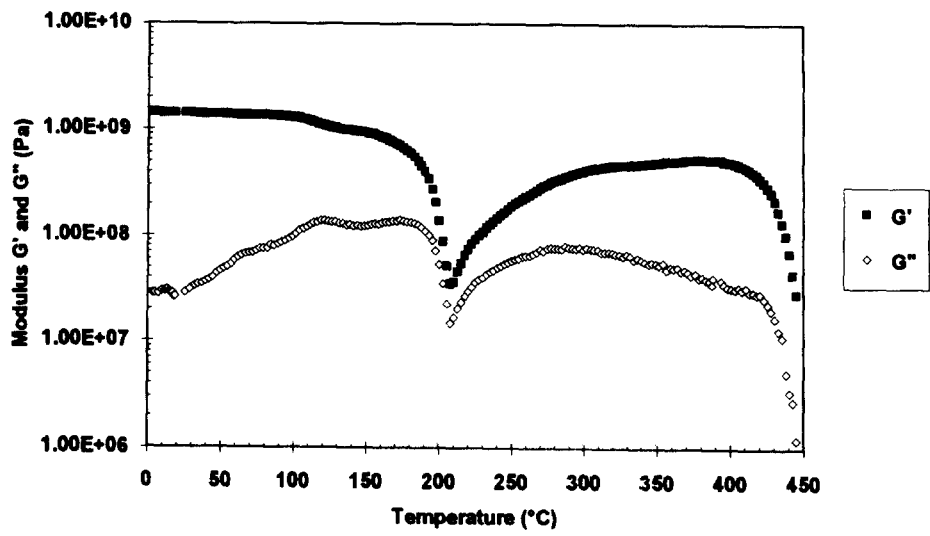


Figure 5 Rheology curve of PAS-HFDE-PAS

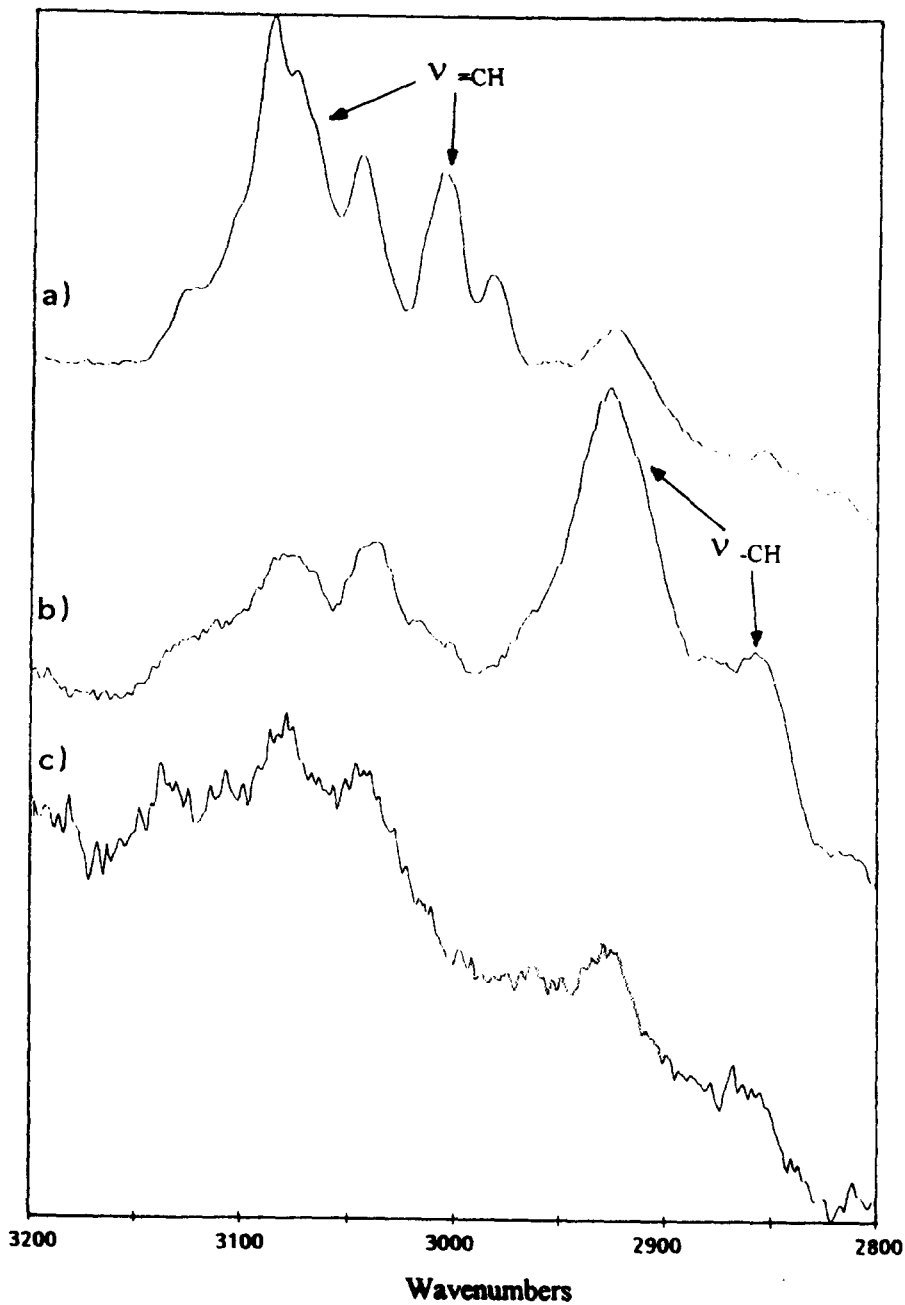


Figure 6 Demonstration of the degradation of the network by FT-i.r. (3200–2800 cm<sup>-1</sup>): (a) PAS/HFDE/PAS; (b) DSC (50–350°C); (c) DSC (50–450°C)

the plate had lost its initial shape with a collapse of the structure and deterioration of the material.

The loss modulus  $G''$  showed the presence of a low intensity sub-vitreous  $\beta$ -relaxation, whose maximum was at 64°C. In light of these results, it is seen that the PAS system reacted starting at 190°C, but that the network formed was not stable beyond 400°C. This phenomenon can be explained by excessive densification of the network, creating considerable internal strain leading to its degradation during heat treatment.

We thus examined PAS-HFDE-PAS after different heat treatments: two temperature rises at 5°C min<sup>-1</sup> were programmed, from 50 to 350 and to 450°C, and we then characterized the adduct formed by FT-i.r. (Figure 6). Following heat treatment up to 350°C, the vinyl double bond ( $\nu_{\text{C-H}} \approx 3050\text{--}3100\text{ cm}^{-1}$ ) opened to form a three-dimensional network built around aliphatic links ( $\nu \approx 2930$  and  $2850\text{ cm}^{-1}$ ) according to the mechanism shown in Figure 7(a).

The infrared absorption spectrum of the sample treated up to 450°C showed that the vibrations associated with these linkages disappeared. These spectroscopic data would indicate that the PAS-HFDE-PAS based network becomes unstable before reaching 450°C. The drop of moduli  $G'$  and  $G''$  observed in rheology is thus due to the deterioration of the network resulting from high temperature heat treatment.

The FT-i.r. study indicated that the vinyl double-bond polymerized to form aliphatic cross-linking nodes. We attempted to confirm this result by solid-state <sup>13</sup>C n.m.r., by examination of a sample heat treated at 200°C for 12 h (Figure 8). The pre-polymerization spectrum of the compound showed that carbon C<sub>1</sub> of the vinyl function was well individualized ( $\delta = 111.2\text{ ppm}$ ) with reference to the other carbons of the aromatic ring. Its disappearance with time should thus be easy to follow, which is what is observed in the spectrum of the product heat treated for 12 h at 200°C. New signals appeared in the region of aliphatic

(20–40 ppm:  $\delta\text{C}_{1'}$  and C<sub>2'</sub> around 41.2 ppm) and aromatic carbons (100–150 ppm:  $\delta\text{C}_{3'} = 145.7\text{ ppm}$ ). In addition, the intensity of the signal from carbon C<sub>1</sub> of the initial monomer decreased. These data are characteristic of the formation of aliphatic links resulting from the opening of styrene functions during heat treatment [Figure 7(b)]. The signal from the region of aliphatic carbons was spread over about 20 ppm and so it is probable that there was a non-selectivity of addition of styrene functions among themselves, i.e. there were head–head, head–tail and tail–tail linkages, or the formation of aliphatic–atactic linkages. Some publications showed that styrene did not polymerize irregularly, but yielded only *head to tail* linkages<sup>8–10</sup>. This regularity would be due to the delocalization of the radical on the aromatic ring. The spectral width of the solid-state n.m.r. signal for the most stereosensitive aliphatic carbons would thus result from the atacticity of the macromolecule formed. These results are consistent with the appearance of an unshielded signal in solid-state, around  $\delta = 145.7\text{ ppm}$ , characteristic of an aromatic carbon C<sub>3'</sub> bound to a tertiary aliphatic carbon, as described in Figure 7(b) ( $\delta_{\text{theoretical}} = 145.8\text{ ppm}$  obtained by incremental calculation).

The physicochemical characterization of PAS-HFDE-PAS, a side product expected during the synthesis of polymers by polycondensation, is very important for the fate of the polymers. Because of its presence in the medium, the determination of its structure and thermal behaviour should lead to a better understanding of the phenomena observed with the prepolymers synthesized.

#### Polymerization kinetics of the PAS function by FT-i.r.

The polymerization kinetics of PAS-HFDE-PAS (99% purity) were obtained via the vibrations characteristic of PAS at  $3084\text{ cm}^{-1}$  ( $\nu_{\text{=CH}_2}$ ) and  $910\text{ cm}^{-1}$  ( $\gamma_{\text{CH}_2}$ ). The reference  $s$  adopted were frequencies around  $3040\text{ cm}^{-1}$  ( $\nu_{\text{=CH aro}}$ ) and  $1515\text{ cm}^{-1}$  ( $\nu_{\text{C=C aro}}$ ), associated with structures unaffected by the polymerization process.

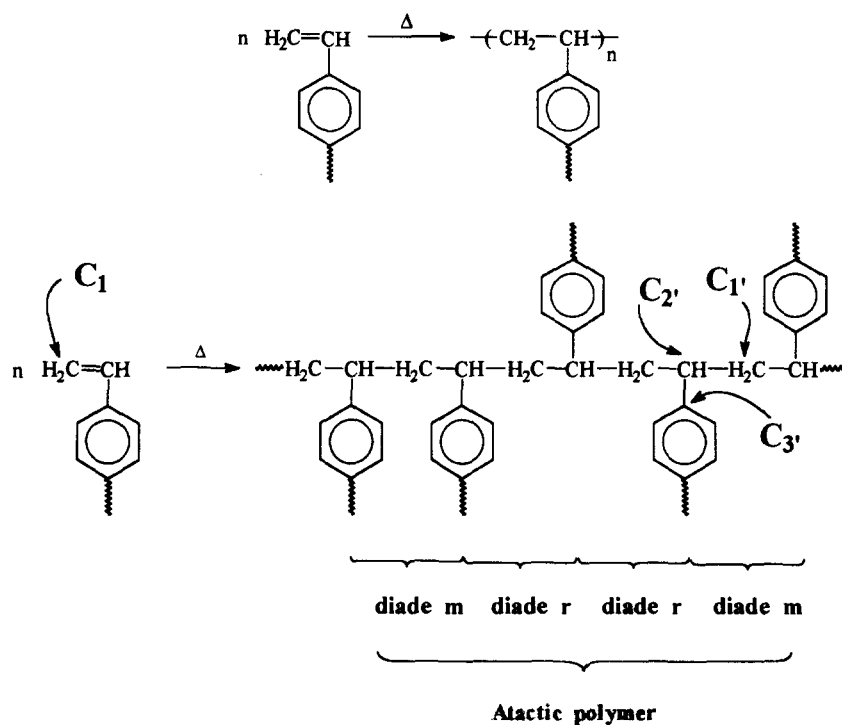


Figure 7 (a) Mechanism of opening of the styrene double bond by thermal excitation. (b) Polymerization mechanism proposed for the vinyl functions of the bisstyrene compound PAS-HFDE-PAS

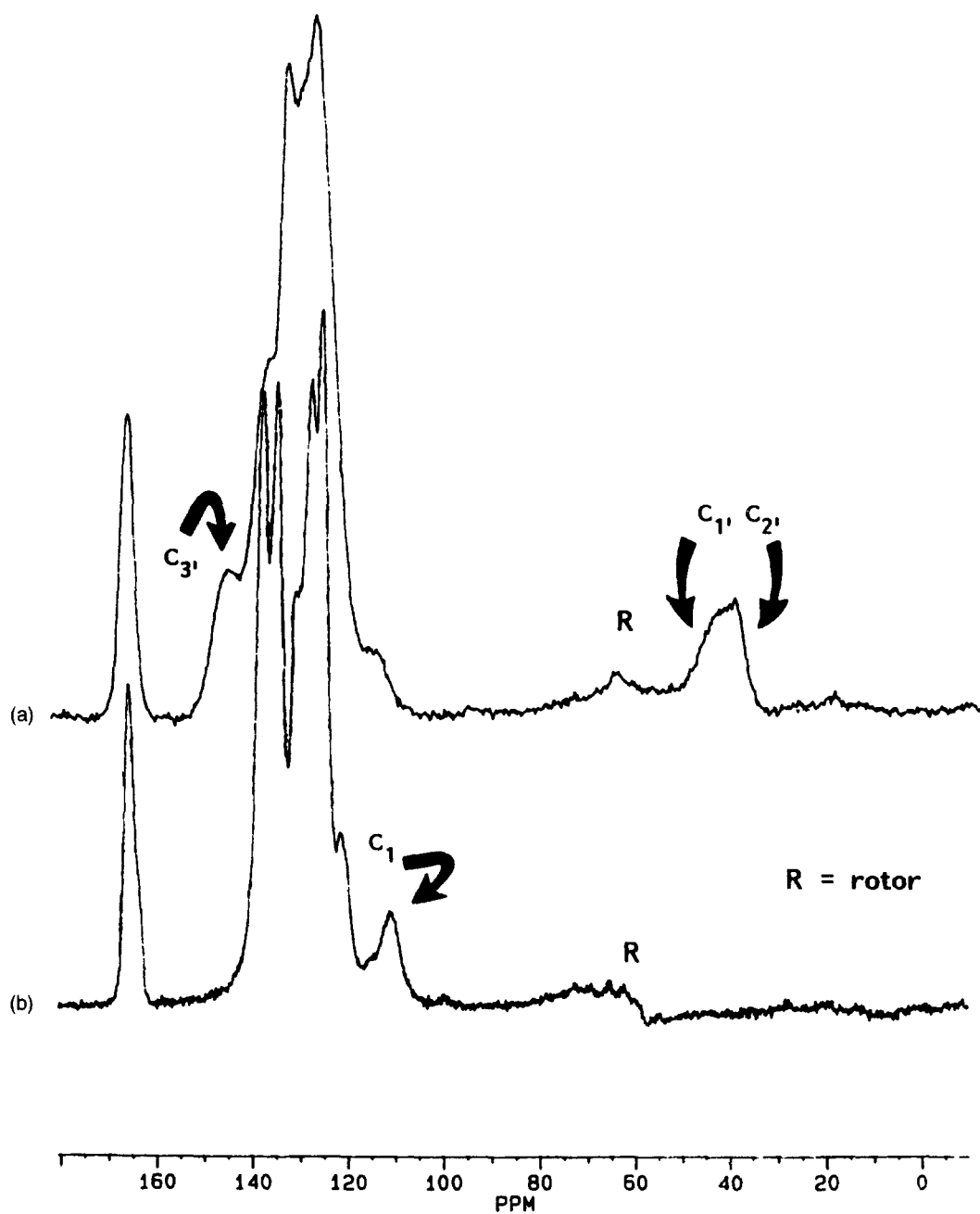


Figure 8 Solid-state  $^{13}\text{C}$  n.m.r. spectra of PAS-HFDE-PAS before and after thermal treatment (200°C, 12 h): (a) before polymerization; (b) after polymerization

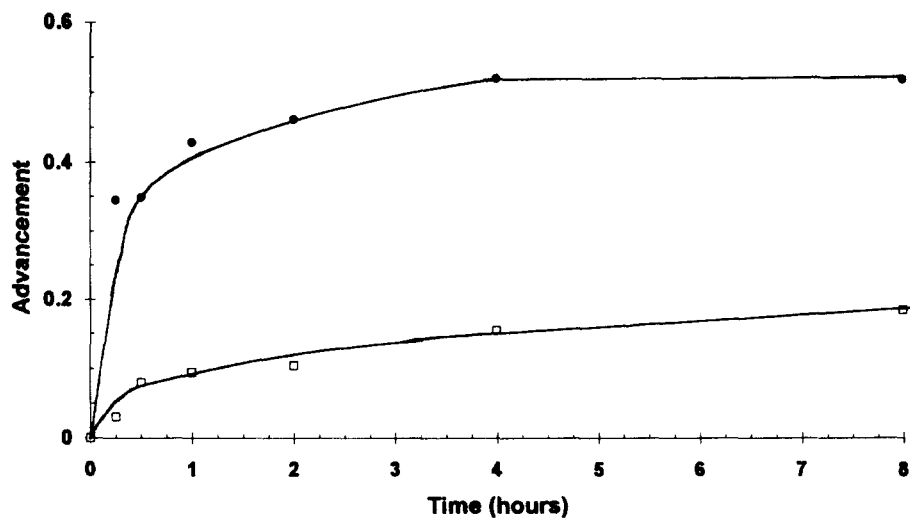


Figure 9 Kinetic curves of the polymerization of the para-aminostyrene (PAS) function: (●) 191°C; (□) 173°C



. Since the exotherm attributed to the opening of vinyl bonds was situated around 170°C in DSC (5°C min<sup>-1</sup>), the bis-styrene compound was subjected to a heat treatment at 173 and at 191°C for 8 h. The kinetic curves obtained at these two temperatures are shown in Figure 9 (the results obtained at the two frequencies used were similar and so the figure shows the mean value of reaction conversion in moles of bis-styrene compound).

Polymerization kinetics at 173°C were slow, with an conversion of about 20% after 8 h of heat treatment. The shape of the curve indicated that at this temperature, cross-linking was continuing and that the system was not static: molecules could still diffuse in the medium to polymerize. Kinetics at 191°C were much more rapid: conversion was about 35% after only 15 min, was 52% after 8 h and appeared to cease after 4 h of treatment. Thus, after 4 h of heat treatment densification of the system was such that molecules could no longer diffuse.

Changes in these systems were also followed by differential scanning calorimetry according to the method of Kissinger<sup>11</sup>. Two batches of PAS-BFDE-PAS were synthesized in the course of the study of this compound. The purity of each batch was controlled with HPLC and the energies of activation were calculated from the DSC diagram obtained with temperature gradients of 2, 5, 10 and 20°C min<sup>-1</sup> (Table 2). These data show that the purity of the initial monomer played an important role in polymerization kinetics: the higher the purity of the compound the greater is the thermal excitation required. Side products (monofunctionalized compound detected by n.m.r. and HPLC) thus apparently favoured both the opening of the double bond at low temperature and the autocatalyzed polymerization of the PAS function. This can be clearly seen in Figure 10, a plot of the

variation of the rate constant  $k$  ( $k = k_0 e^{-E_a/RT}$ ) as a function of temperature.

The curves thus show that polymerization of monomer with purities higher than 95% started around 160°C, and when purity was 85%, the PAS function apparently reacted starting at 110°C, i.e. a gain of 50°C. These curves show that the rate of polymerization of PAS functions varied in the same way as a function of purity, but that the reaction onset temperature was considerably lowered as purity decreased. It is sensible to attribute this enhanced reactivity in the presence of impurities which should initiate polymerization.

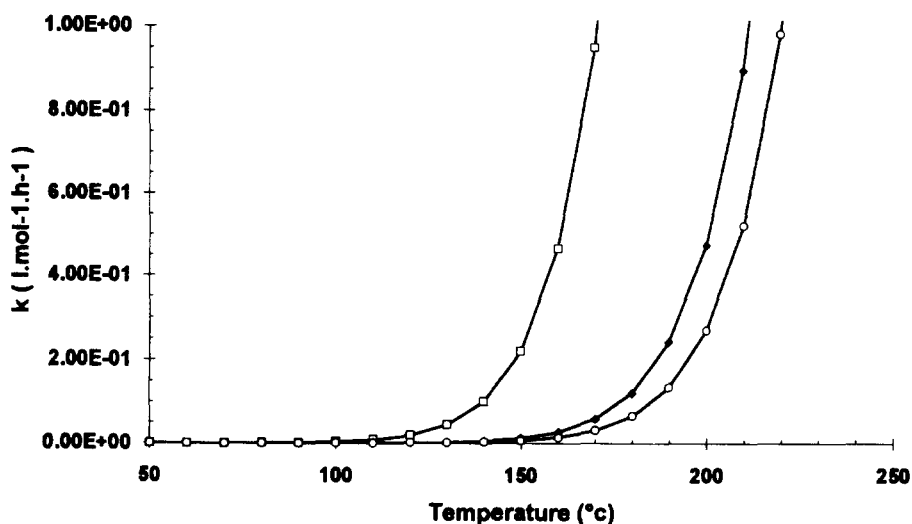
*Study of the thermodegradation exotherm.* In the physicochemical study of PAS-HFDE-PAS, we detected an exothermal transition attributed to the thermal oxidation of the system around 300°C (99% purity, temperature rise 5°C min<sup>-1</sup>). Using the same DSC method as before<sup>11</sup>, we determined the energy of activation of the process (Figure 11). Depending on the batches of compound studied, there was considerable disparity in the energy required to degrade the system by thermal oxidation (Table 2).

As above, purity of the product had a considerable influence on network thermostability: increasing purity of the starting batch would lead to the formation of a denser network and thus the energy required for its oxidation and its degradation will be greater. In the case of the product with 85% purity, the presence of impurities (monofunctionalized compound) should favour the thermal oxidation of the more flexible and less dense network, since it had fewer cross-linking nodes.

In conclusion, this study of the reactivity of the *para*-aminostyrene function on a model compound has shown that during molten state heat treatment, the function could

**Table 2** Values of the energy of activation ( $E_a$ ) of PAS-HFDE-PAS polymerization and thermal oxidation of the network formed from the bis-styrene PAS-HFDE-PAS

PAS-HFDE-PAS	Purity (%)	Polymerization		Thermo-oxidation
		$E_a$ (kJ mol <sup>-1</sup> )	$k_0$ (h <sup>-1</sup> )	$E_a$ (kJ mol <sup>-1</sup> )
Lot 1	85	113	$2.36 \times 10^{13}$	29
Lot 1 purified	< 99	125	$1.89 \times 10^{13}$	87
Lot 2	< 95	121	$1.10 \times 10^{13}$	63



**Figure 10** Variation of the rate constant  $k$  of PAS-HFDE-PAS polymerization: (□) 85% purity; (◆) 95% purity; (○) 99% purity

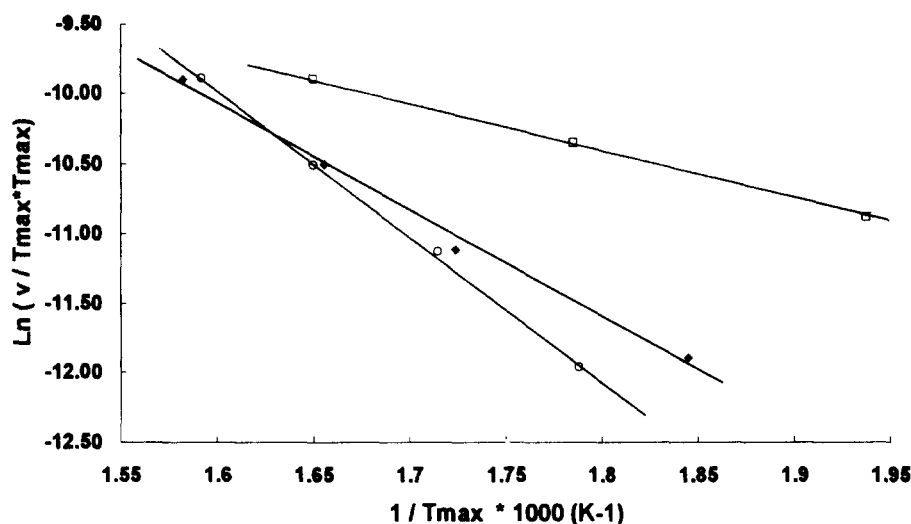


Figure 11 Determination of the energy of activation ( $E_a$ ) of thermal oxidation of the network formed by bis-styrene PAS-HFDE-PAS: (□) 85% purity; (◆) 95% purity; (○) 99% purity

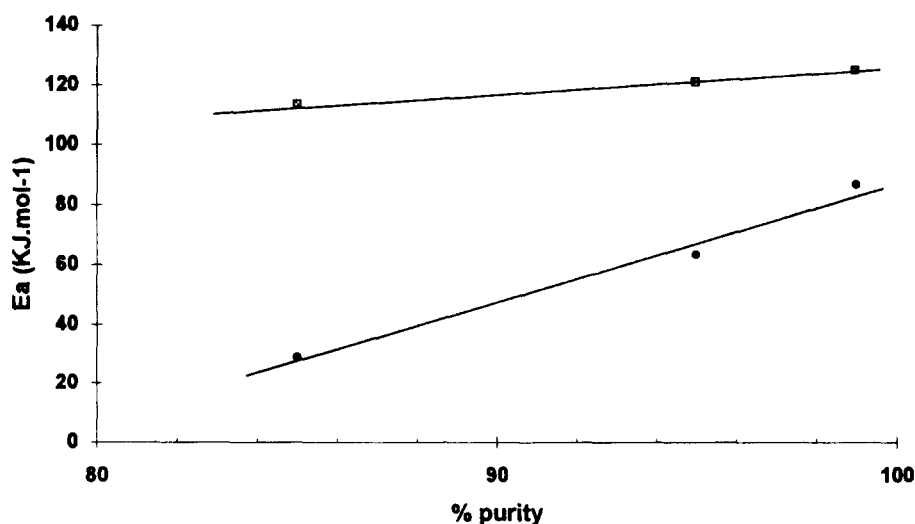


Figure 12 Variation of the energy of activation ( $E_a$ ) as a function of PAS-HFDE-PAS: (□) polymerization; (●) thermal oxidation

lead to the formation of a three-dimensional network built around aliphatic linkages. We have also shown that the purity of the product has a considerable influence on the energy of activation of formation and degradation of the network (Figure 12).

#### Study of PAS and PAS a polyimide prepolymers

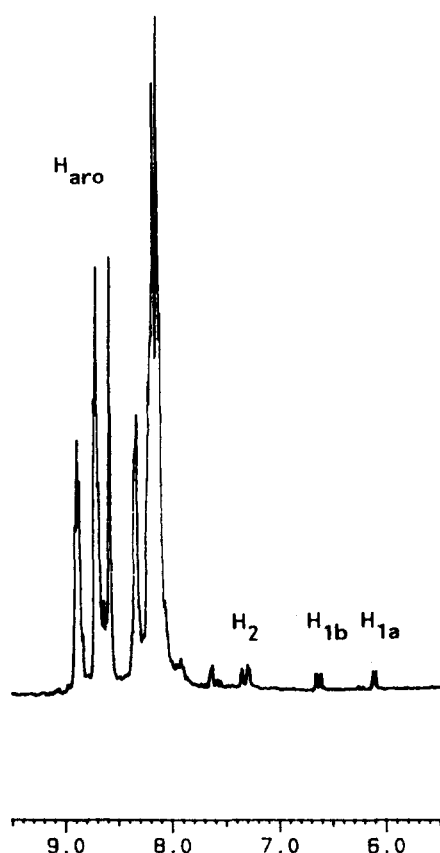
##### Microstructural characterization of styrene-terminated telechelic polyimides

*Cardo diamine-based polyimides (PAS polyimide).* The para-aminostyrene function (PAS) was not studied with this type of prepolymer from a structural, mechanistic and kinetic standpoint, which is why we utilized physico-chemical results obtained with the bis-styrene compound PAS-HFDE-PAS. In this study we synthesized four polyimides with theoretical polymerization indices of  $\bar{n} = 2, 5, 8$  and 10.

In spite of suitable solubilization of the polymers in DMSO  $d_6$ , it was difficult to acquire n.m.r. spectra in solution. At room temperature there was no resonance signal from the carbons in the macromolecular structure. It was necessary to record spectra at high temperature (120°C) to obtain an interpretable spectrum and characterize the

different signals from the main chain skeleton and from PAS chain ends. The  $^{13}\text{C}$  n.m.r. spectra of polyimides (region of carbonyl groups) shows that the carbonyl function was very slightly stereosensitive to changes in the environment brought about by the presence of the cardo diamine or by paraaminostyrene, which prohibited them from being used. The spectral zone  $\delta = 64\text{--}66$  ppm (quaternary carbon of the cardo diamine), however, was interesting in order to verify the presence of the free amine and/or acceptable intramolecular ring formation during the imidization step. All the spectra examined presented a sole and unique signal around  $\delta = 64.7$ , ppm (DMSO  $d_6$ ) that was associated with HFDE-cardo-HFDE linkages. The presence of this signal is synonymous with good imidization of the macromolecular chain in the final step of polycondensation at 160°C.

In the  $^1\text{H}$  n.m.r. study of the bis-styrene model compound, however, we showed that protons characteristic of the PAS function were shielded in comparison to aromatic protons. This observation on the model compound PAS-HFDE-PAS should enable us to precisely determine the value of mean molar mass  $\bar{M}_n$  of the polyimide PAS, since the same phenomena were observed in the spectra of



**Figure 13** Liquid-state  $^1\text{H}$  n.m.r. spectrum of PAS polyimide ( $\bar{n} = 5$ ) ( $\delta = 5.5\text{--}9.5$  ppm, solvent:  $\text{DMSO } d_6$ ,  $T = 120^\circ\text{C}$ )

the prepolymers (Figure 13). Three signals were present, associated with the three styrene protons of the PAS function resonating at strong field ( $\delta = 6\text{--}7.5$  ppm) in comparison to the aromatic protons of the skeleton ( $\delta = 7.5\text{--}9$  ppm). The  $^1\text{H}$  chemical shifts were slightly different from those obtained with the model compound. This result is not aberrant, since the spectra of polymers were recorded in DMSO and at high temperature; these two parameters (solvent, temperature) modify the values of chemical shifts of the stereosensitive protons of the PAS function.

Integration of the six styrene protons at macromolecule chain ends enabled us to calculate the mean mass of the oligomer. Taking into account the chemical structure of the polyimides (Figure 2), there are six styrene protons per macromolecular chain, 22 aromatic protons in the repeat group and 14 aromatic protons not in this group. The following equation can thus be used to determine the polymerization index  $\bar{n}$ :

$$\bar{n} = \frac{\text{Total number of aromatic protons of groups}}{\text{Number of aromatic protons in one group}}$$

Integration of the signals from styrene protons ( $x$ ) enabled the value of one proton to be determined ( $x/6$ ). Integrating all aromatic protons ( $y$ ) led to the total number of aromatic protons ( $N_{\text{aro}} = 6y/x$ ). The total number of protons in the group is thus

$$N_{\text{group}} = N_{\text{aro}} - N_{\text{out}} = \frac{6y}{x} - 14$$

with  $N_{\text{out}}$  the number of protons out of the group (14 protons). The mean polymerization index  $\bar{n}$  is

$$\bar{n} = \frac{6y - 14x}{22x} \text{ or } \overline{Mn} = 756\bar{n} + 643 \text{ g mol}^{-1}$$

where 22 is the number of aromatic protons in one repeat group. The experimental results obtained with the four prepolymers studied are listed in Table 3. The values found in  $^1\text{H}$  n.m.r. are close to the theoretical molar masses of synthesis and indicate an increase in molar mass according to the expected tendency. This  $^1\text{H}$  n.m.r. study easily provided the values of mean molar mass. The disadvantage of this technique is that it does not furnish the possibility of detecting the presence of bis-styrene type parasite molecules.

In a  $^{19}\text{F}$  n.m.r. study, we showed that the flexible linkage  $(\text{CF}_3)_2$  of the HFDE diester was stereochemical changes in the environment (ester, acid-amide and imide)<sup>12</sup>. Thus, in order to determine the molar mass and quantify the presence of certain chemical entities (in particular the PAS-HFDE-PAS molecule), we conducted a detailed study of the  $^{19}\text{F}$  n.m.r. spectra of the four prepolymers of variable mass (Figure 14). The n.m.r. spectra of fluorine show the presence of two signals, around  $\delta = -62.4$  and  $-62.5$  ppm. In order to determine the type of bonds associated with these signals, we first added a HFDE diester and cardo diamine-based linear polyimide, and in a second series added the side product from the PAS/HFDE/PAS polycondensation. In both cases, only the signal at  $-62.4$  ppm appeared to be modified. Cardo-Cardo and PAS-PAS linkages thus apparently have the same effect on fluorine atoms of the flexible linkage  $(\text{CF}_3)_2$  and the signal at  $-62.5$  ppm is associated with chain ends (PAS-HFDE-cardo linkages).

A third signal was obtained by deconvolution of the spectra ( $\delta = -62.35$  and  $-62.40$  ppm) that was unshielded in comparison to the previous two signals (Figure 15). This signal with a lower intensity is apparently associated with the PAS-HFDE-PAS side product, but since its resonance peak was slightly differentiated from the cardo-cardo linkages ( $\Delta\delta = 0\text{--}0.05$  ppm), it emerged in the base of the peak characteristic of the latter. Based on these attributions, we were able to calculate the mean molar mass  $\overline{Mn}$  and the percentage of PAS-HFDE-PAS present in the polymer (Table 3).

**Table 3** Physicochemical characteristics of PAS and PAS *a* polyimides by  $^1\text{H}$  and  $^{19}\text{F}$  n.m.r.

	Polyimide PAS				Polyimide PASa		
	PAS 2	PAS 5	PAS 8	PAS 10	PAS 2a	PAS 5a	PAS 10a
$\overline{Mn}$ theoretical <sup>a</sup>	2150	4400	6700	8200	1700	3200	5800
$\overline{Mn}$ ( $^1\text{H}$ n.m.r.) <sup>a</sup>	2100	4100	7100	8500	1900	3300	6100
$\overline{Mn}$ ( $^{19}\text{F}$ n.m.r.) <sup>a</sup>	3500	3700	7100	8750	1500	3300	5900
%PAS-HFDE-PAS	62	48	31	26	60	25	24

<sup>a</sup> Molar masses in  $\text{g mol}^{-1}$ .

**Table 4**  $\alpha$  and  $\beta$  relaxation temperatures of PAS and PAS *a* polyimides

	Polyimide PAS				Polyimide PAS <i>a</i>		
	PAS 2	PAS 5	PAS 8	PAS 10	PAS 2a	PAS 5a	PAS 10a
$\bar{n}$ ( $^1\text{H}$ n.m.r.) <sup>a</sup>	1.9	4.6	8.5	10.4	2.4	5.1	10.6
$T_g$ (°C) <sup>b</sup>	296	322	361	356	319	329	334
$T_\beta$ (°C) <sup>c</sup>	84	103	117	122	77	82	93

<sup>a</sup> Index polymerization.<sup>b</sup>  $T_g$  = glass transition.<sup>c</sup>  $T_\beta$  = temperature of relaxation  $\beta$ .

The experimental molar masses of the prepolymers synthesized are in agreement with the initial theoretical values and confirm the data obtained with  $^1\text{H}$  n.m.r. (comparison of *Tables 3 and 4*). In addition, these data enabled us to assay polycondensation side product molecules. In the case of PAS polyimides, the concentration of bis-styrene decreased from 60 to 25% as the molar mass of the macromolecule increased. This decrease resulted from the increase in the [HFDE]/[cardo] ratio when the molar mass increased. It also appears that the terminal agent PAS is more reactive towards HFDE than the cardo

diamine, thereby creating large quantities of secondary molecule PAS-HFDE-PAS in the polymer.

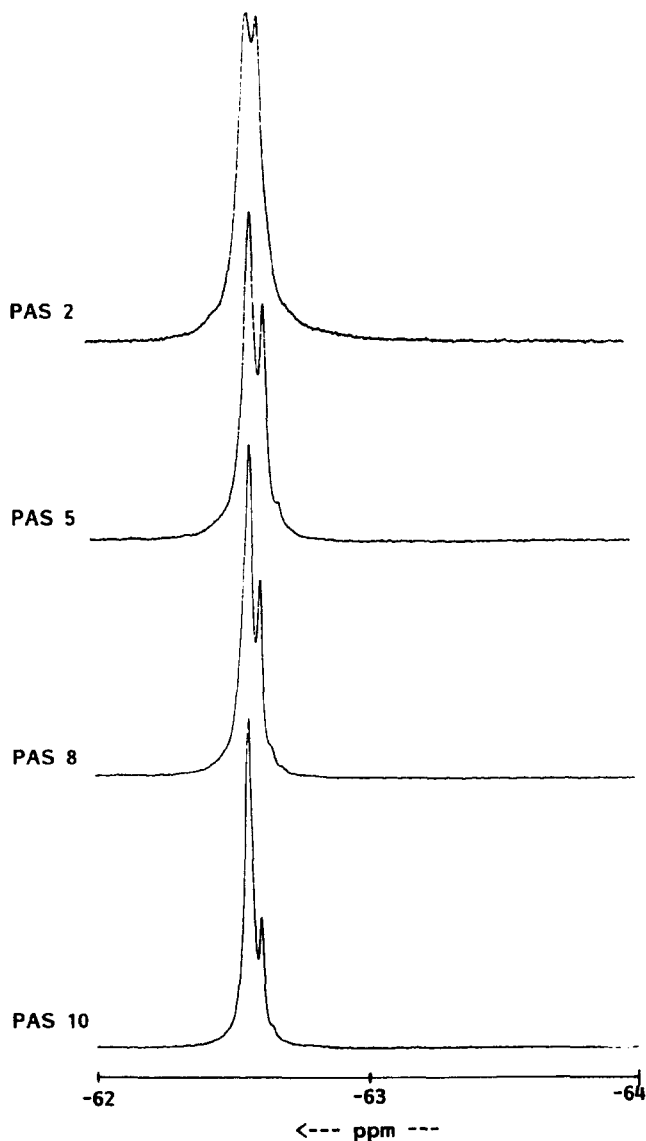
*mPDA and pPDA based (polyimides (PAS *a* polyimide).* A similar study was conducted on PAS-terminated polyimides whose main chain structure is theoretically 25% *mPDA* and 75% *pPDA*. As in the case of PAS polyimides, liquid chromatographies (SEC or HPLC) were impossible because of the presence of aggregates in the medium. We thus used the same procedure as described above for PAS polyimides.

As before,  $^1\text{H}$  and  $^{19}\text{F}$  n.m.r. enabled us to calculate the molar mass and the percentage of bis-styrene compound. The following equation was used for the  $^1\text{H}$  n.m.r. calculation:

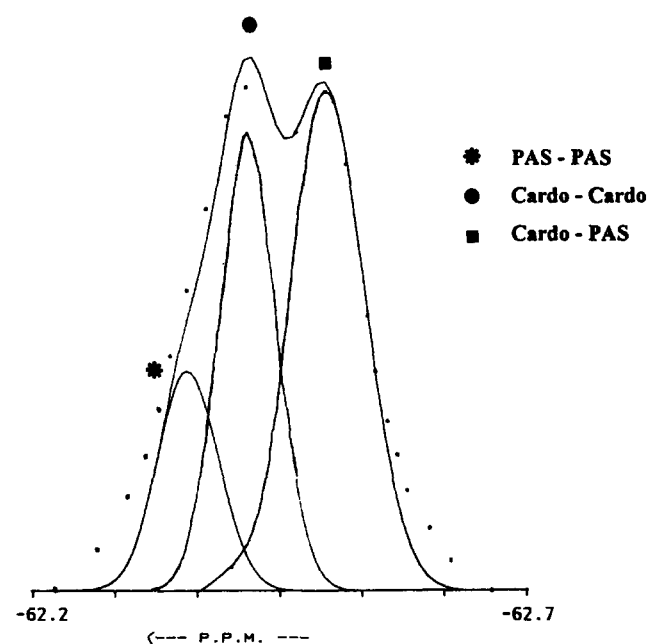
$$\bar{n} = \frac{6y - 14x}{10x} \text{ or } \overline{Mn} = 518\bar{n} + 643 \text{ g mol}^{-1}$$

whereas in fluorine n.m.r. the method used was that applied to PAS polyimides (*Table 3*).

These results show good agreement between experimental and theoretical values. In addition, and in comparison to PAS polyimides (*Table 3*), for the same molar mass PAS *a* polyimide contains a smaller quantity of the bis-styrene compound. This result is consistent with the study of monomer reactivity carried out in the laboratory<sup>12</sup>, where it was shown that the rate constant of polycondensation of diamines *mPDA* and *pPDA* towards the HFDE diester was higher than that of the cardo diamine (leading to a lower proportion of PAS-HFDE-PAS).



**Figure 14**  $^{19}\text{F}$  n.m.r. spectra of PAS-terminated polyimides (reference  $\text{CFCl}_3$ ,  $\delta = -62; -64$  ppm, solvent:  $\text{DMSO } d_6$ )



**Figure 15** Deconvolution of the liquid-state  $^{19}\text{F}$  n.m.r. spectrum of PAS 5 polyimide: (···) experimental band; (---) deconvolution into basic lines

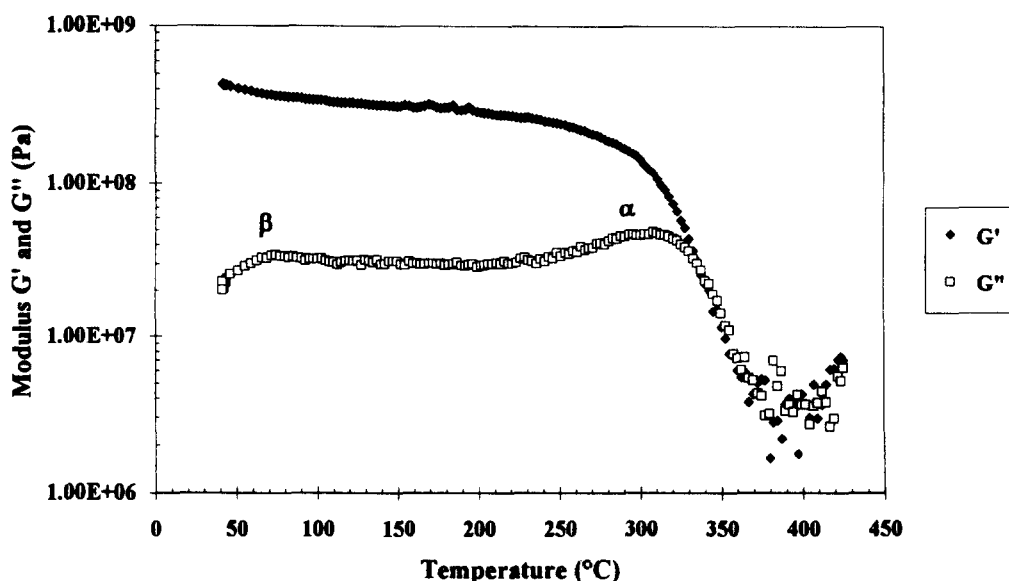


Figure 16 Thermomechanical curve of PAS 5 polyimide

#### Thermomechanical characterization of PAS and PAS *a* polyimides: analysis of the results

The rheological curves represent changes in the moduli of conservation  $G'$  and loss  $G''$  in the course of a temperature rise. For a PAS polyimide with molar mass  $\overline{Mn} \approx 4000 \text{ g mol}^{-1}$  (PAS 5), the study of the storage modulus  $G'$  revealed a vitreous plateau ( $G' \approx 3\text{--}4.0^8 \text{ Pa}$ ) followed by an  $\alpha$  transition at  $322^\circ\text{C}$ , corresponding to the vitreous transition temperature  $T_g$  (Figure 16). This phenomenon was immediately followed by a 'fluidization' ( $T \approx 340^\circ\text{C}$ ) where the modulus  $G''$ , characteristic of the viscous state, was over the storage modulus  $G'$ . Amorphous oligomers of low molar mass ( $\overline{Mn} < 10000 \text{ g mol}^{-1}$ ) do not possess a rubbery state, going directly from the vitreous state (elastic zone) to the viscous state (zone of flow) without passing through the rubbery state (the length of the rubbery plateau is a function of the molar mass of the polymer). This softening can be attributed to the zone of flow of the polymer, containing 48 mol.% bis-styrene compound PAS-HFDE-PAS ( $T_f \approx 210^\circ\text{C}$ ).

Beyond  $400^\circ\text{C}$ , the values of the storage modulus  $G'$  again increased, attributed to the homopolymerization of styrene extremities, thereby forming a three-dimensional network.

The loss modulus  $G''$  confirmed the presence of a vitreous transition temperature, polyimide cross-linking, and also showed a sub-vitreous  $\beta$ -relaxation between 30 and  $150^\circ\text{C}$ . Based on published data<sup>15,16</sup>, this secondary transition is associated with the rotation and/or oscillation of BFDE of para-phenylene-benzimide structures around the flexible  $\text{C}(\text{CF}_3)_2$  linkage in polyimides. The semi-rigid character of the N-phenyl ( $\Phi$ ) bond would assure the cooperative oscillation of these structures.

The thermomechanical study of PAS *a* polyimides with an HFDE/phenylenediamine structure, shows that the same phase transitions occurred within these oligomers (Figure 17). The  $\alpha$  and  $\beta$  transitions shifted with temperature depending on the nature of the diamine used, in the range of  $30\text{--}450^\circ\text{C}$ .

#### Structure/properties relationships of para-aminostyrene functional polyimides

The results (Table 4), analysed with reference to the

structures of the polyimides and their molar mass  $\overline{Mn}$ , show that the temperature values of each transition increased with increasing molar mass of the oligomer. In addition, it is generally observed that the vitreous transition temperatures of phenylenediamine-based PAS *a* polyimides are higher than those of PAS polyimides. This can be explained by the greater free volume occupied by the cardo diamine, thereby lowering the vitreous transition temperature.

*Study of  $\alpha$  relaxation: vitreous transition.* Based on the relationship of Fox and Flory the value of the vitreous transition temperature can be related to the mean molar mass of the polymer according to the equation

$$T_g = T_g^0 - \frac{K}{\overline{Mn}}$$

where  $T_g^0$  represents the vitreous transition temperature for a polymer of infinite molar mass and  $K$  the constant related to the structure of the polymer. Increasing the molar mass results in an increase of the value of the vitreous transition temperature. The influence of chain ends is lower in the case of a larger macromolecule: excess free volume of chain ends decreases in comparison to the free volume occupied by the chain itself. This law was verified with the  $^1\text{H}$  n.m.r. molar mass values, correlated with vitreous transition temperatures  $T_g$  (Table 4).

The study of these two series of polyimides should enable the influence of the nature of the diamine of the main chain on the vitreous transition temperature values of PAS-functionalized oligomers to be determined (Figure 18). The vitreous transition temperature exhibited a linear variation inversely proportional to mean molar mass  $\overline{Mn}$ . In this range of molar masses ( $\overline{Mn} < 10000 \text{ g mol}^{-1}$ ), PAS and PAS *a* polyimides simulated the Fox-Flory law well. Starting with a molar mass  $\overline{Mn} = 4500 \text{ g mol}^{-1}$  ( $1/\overline{Mn} \approx 2.2 \times 10^{-4}$ ) the vitreous transition temperature of PAS polyimides became higher than that of PAS *a* polyimides. This can be explained by better cohesion and rigidity of PAS *a* polyimides of small molecular size. As the size of the macromolecule increases, the system becomes disordered (amorphous polymer), composed of rigid molecules leading to the loss of intermolecular cohesion and as a result a lower vitreous transition temperature.

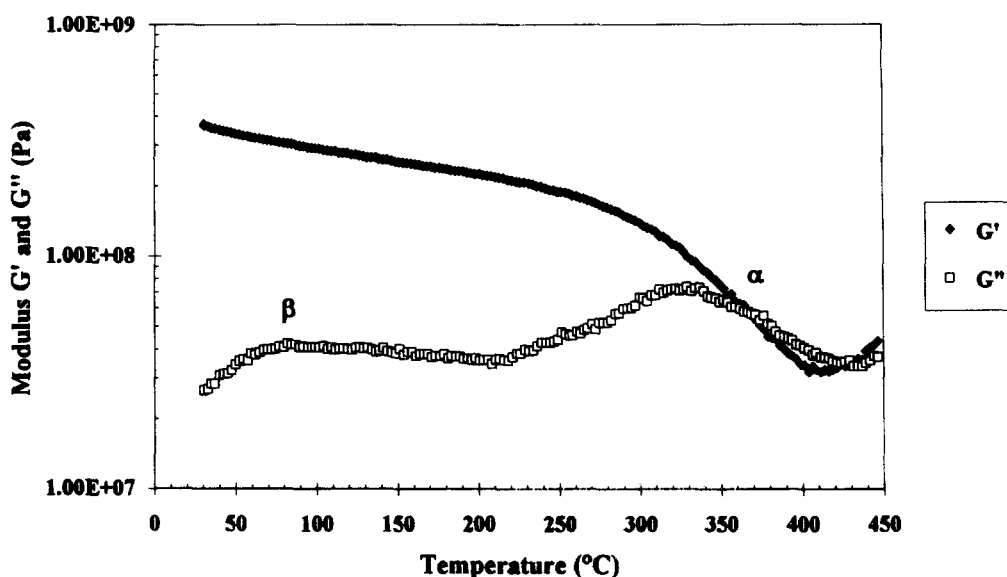


Figure 17 Thermomechanical curve of PAS 5a polyimide

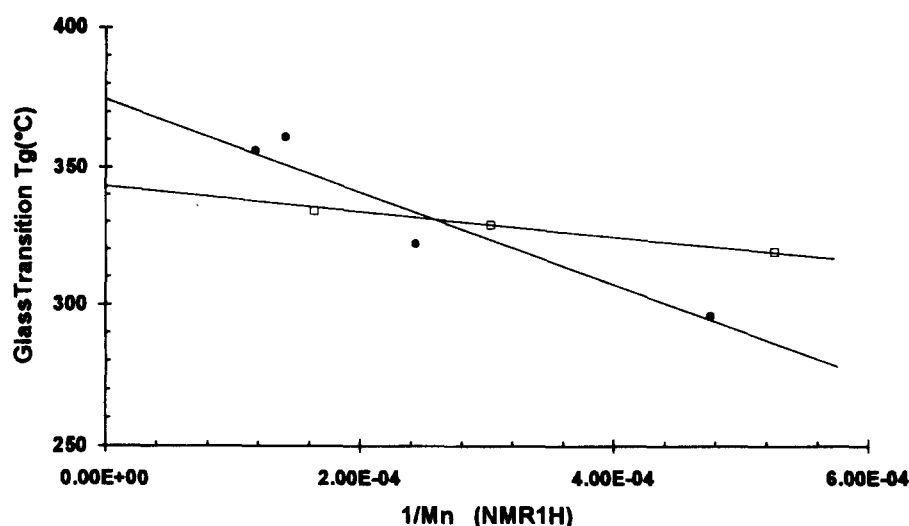
Figure 18 Variation of temperature of  $\alpha$  relaxation according to the Fox-Flory law: (●) PAS; (□) PAS *a*

Table 5 Parameters of the Fox-Flory equation for PAS-functionalized polyimides

Polyimide	$T_g^0$ (°C)	$K \times 10^{-5}$	$r^a$
PAS	377	1.79	0.958
PAS <i>a</i>	350	0.62	0.978

<sup>a</sup> Linear regression coefficient.

Using these curves, we calculated parameters  $T_g^0$  and  $K$ , characteristic of the influence of the molecular structure of the oligomer chain (Table 5). The results show that the vitreous transition temperature of PAS polyimides with high molar mass should be about 30°C higher than those of PAS *a* polyimides. It is also noted that the constant  $K$  related to the structure of the oligomer, is three times higher for PAS polyimides.

In conclusion, this study of the influence of molar mass on thermomechanical properties has shown that functionalized polyimides obey the Fox-Flory relationship for mean molar masses  $\overline{Mn} < 10\,000$  g mol<sup>-1</sup>. Based on the values of the parameters of this equation, mPDA and pPDA-based oligomers of low molar masses

( $\overline{Mn} < 4500$  g mol<sup>-1</sup>) provide rigidity to the chain, conferring on it a higher value of  $T_g$  for the same molar mass. For molar masses higher than this value, the constant  $K$  of cardo diamine-based polyimides is three times higher and so there is an inversion of this tendency (Figure 18).

*Study of  $\beta$  relaxation: sub-vitreous transition.* In work on this series of polymers, we have also shown the existence of a sub-vitreous  $\beta$  transition. These sub-vitreous transitions are generally due to local molecular movements within the macromolecular chain, involving small size groups. The origin of this relaxation remains poorly understood in spite of considerable research<sup>13-16</sup>, although there are two major opposing thoughts on the type of molecular movements responsible for  $\beta$ -relaxation in aromatic polyimides.

The first is that it results from the movement of phenylene groups of the diamines constituting the main chain of polyimides<sup>13,14</sup>. Sub-vitreous relaxation would involve localized non-cooperative movements<sup>14</sup> that dissipate with increasing crystallinity and orientation of

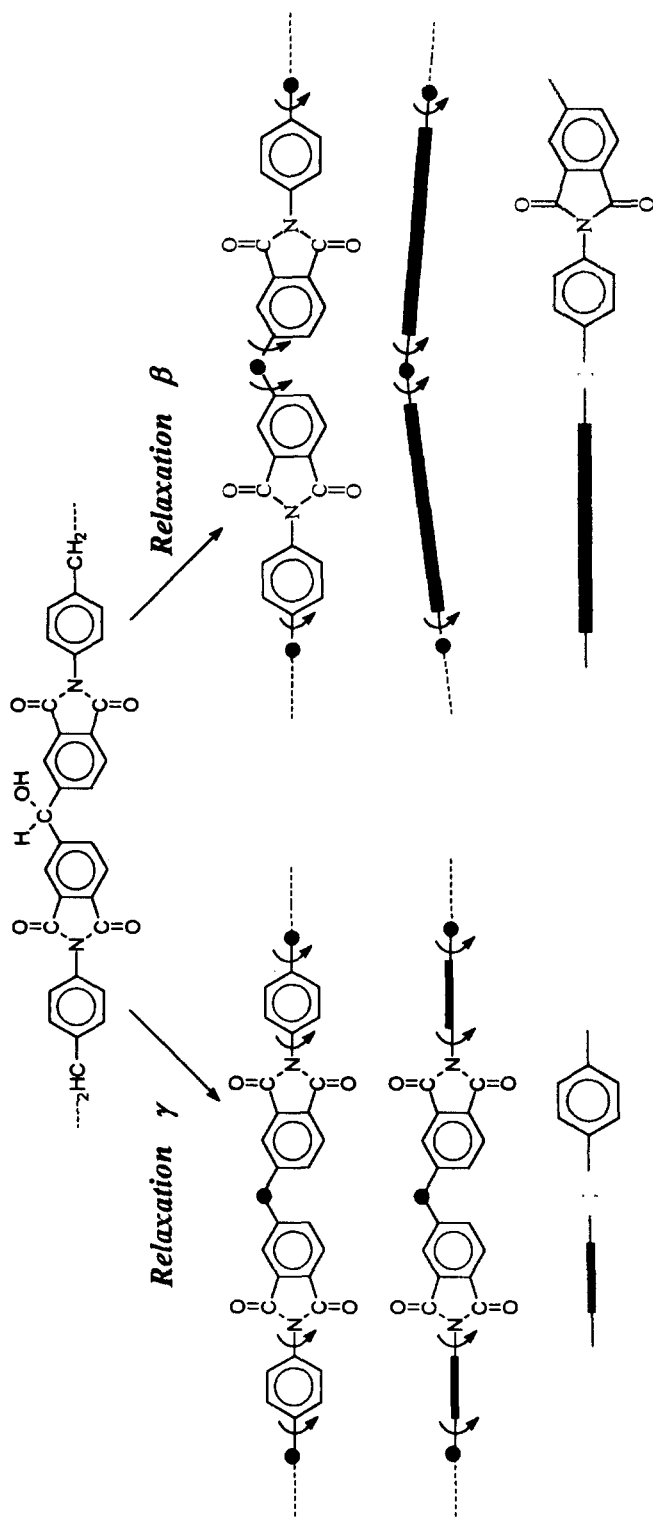


Figure 19 Local movements responsible for  $\gamma$  and  $\beta$  sub-vitreous relaxations<sup>13</sup>: (●) flexible linkage:  $\text{CH}_2$ , O, C=O, CHO,  $\text{C}(\text{CF}_3)_2$ , etc

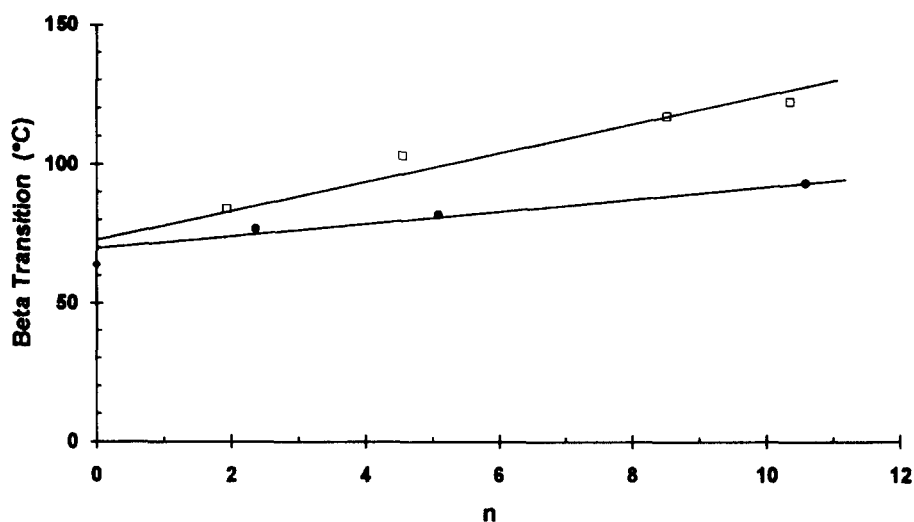


Figure 20 Variation of  $\beta$ -relaxation as a function of the polymerization index of PAS and PAS *a* polyimides determined by  $^1\text{H}$  n.m.r.: (□) PAS; (●) PAS *a*; (◆) PAS-HFDE-PAS

the macromolecular chains<sup>13</sup>. These authors based their hypothesis on the low energies of activation of sub-vitreous relaxation ( $E_a \approx 150 \text{ kJ mol}^{-1}$ ), which would correspond to isolated movements of aromatic rings of diamines.

The second hypothesis attributes this relaxation to cooperative movement between *para*-phenylenes of diamines and imide rings<sup>15,16</sup>. The simultaneous movements of these *para*-phenylene/benzimide structures around flexible linkages ( $\text{CH}_2$ , O, C=O,  $\text{C}(\text{CF}_3)_2$ , etc.) would result from the semi-rigid character of the N-phenyl ( $\phi$ ) bond. Whereas Sun *et al.*<sup>16</sup> considered this bond to be totally double (electronic delocalization of the aromatic ring and the non-bonding doublet of the nitrogen atom), Habas *et al.*<sup>15</sup> discussed an intermediate type between the double and single bond: a 'partially double bond'. This distinction enables it to combine the  $\gamma$ -relaxation situated below the  $\beta$ -relaxation with the movement of aromatic rings of diamines according to the mechanism shown in Figure 19<sup>15</sup>.

We decided to determine the impact of the size of molecules on the molecular movements involved in the sub-vitreous relaxation. To this end, we investigated the variation in the maximum of the  $\beta$ -relaxation temperature as a function of the polymerization index  $\bar{n}$  ( $T_\beta = f(\bar{n})$ ) in order to determine the temperature  $T_\beta^0$ . This temperature is characteristic of  $\beta$ -relaxation for a polymerization index equal to zero, i.e. the relaxation temperature of the side product resulting from PAS-HFDE-PAS polycondensation. The temperature values obtained in the thermo-mechanical study (Table 4) show that the maximum of the  $\beta$ -relaxation varied for the same polymerization index. It was also found that this transition shifted as a function of the molar mass of the polyimide. This result shows that the nature of the diamine affects the movements responsible for  $\beta$ -relaxation.

The results (Figure 20) show good linearity (coefficient of linear regression  $r = 0.980$  for PAS polyimide and  $0.999$  for PAS *a* polyimide) between the maximum of the  $\beta$ -relaxation and the value of the corresponding polymerization index. This would suggest that the energy required to impart movement to a group responsible for the sub-vitreous relaxation is additive within the macromolecule. This result implies that the chemical structures responsible for this relaxation in the polyimide and in the side product are of the same type. Based on the  $T_\beta^0$  results obtained,

the temperatures characteristic of local movements are apparently identical from both an experimental ( $T_\beta^0 = 71^\circ\text{C}$  for the PAS polyimide and  $T_\beta^0 = 67^\circ\text{C}$  for the PAS *a* polyimide) and theoretical point of view ( $T_\beta^0 = 64^\circ\text{C}$  for the bis-styrene compound) within experimental errors.

These data enable us to better understand the groups responsible for the subvitreous  $\beta$ -relaxation. In particular, sub-vitreous relaxation depends on the nature of the diamine used, and the local movements in the side product and the macromolecule are of the same type and are additive.

Considering the structures of the polyimides and of their side products, it is seen that the structure common to all these molecules is the presence of disubstituted aromatic rings (*meta* or *para*) bound to benzimide rings. The movement of this group would be responsible for the mechanical relaxation secondary to the vitreous state, as described in the literature<sup>15</sup>.

## CONCLUSION

The aim of this study was to better understand the thermal reactivity of the bis-styrene compound in order to elucidate its behaviour in the prepolymer. Thus, we initially synthesized, then structurally and thermally characterized the difunctionalized product (polycondensation side product). The structural study utilizing spectroscopic techniques (*FT*-i.r. and n.m.r.) led to the determination of several vibrations or resonance lines specific to the vinyl function, used to kinetically monitor the opening of the styrene function. This approach showed that the *para*-aminostyrene function polymerized starting at  $170^\circ\text{C}$ , forming aliphatic linkages. The network that forms is stable up to about  $400^\circ\text{C}$ , beyond which it undergoes thermo-oxidative degradation in air. We have shown that purity has an important effect on the energies of activation of polymerization and of degradation of the aliphatic network.

Once the physicochemical characteristics of the bis-styrene compound were determined, we were able to carry out the structural and thermomechanical study of telechelic prepolymers in order to establish structure/properties relationships as a function of molar mass and the nature of the diamine. In subsequent work, the spectroscopic study of the PAS function was of fundamental importance



for characterizing *para*-aminostyrene-terminated telechelic macromolecules, since until the present this type of reactive chain end had never been studied in the context of thermostable polymers. Because of the difficulties inherent in liquid-state studies (presence of solute-solvent interactions), only high temperature proton and fluorine nuclear magnetic resonance spectrometry enabled the molar mass and the percentage of bis-styrene compound present in the prepolymer to be calculated. Caution is nonetheless the watchword in terms of the experimental values found because of poor signal separation that required several treatments ( $^{19}\text{F}$  n.m.r.). Following this part of the work, we were able to determine the molar mass of the oligomers synthesized, as well as the molar percentage of the polycondensation side product, the bis-styrene compound PAS-HFDE-PAS present in high concentration in the prepolymer. These results were related to thermo-mechanical properties. The rheology study showed the presence of two transitions,  $\alpha$  and  $\beta$ , associated with the phenomenon of vitreous transition and with local molecular movements, respectively.  $\beta$ -Relaxation was due to the oscillation of the phenylene-benzimide structure as a result of the semi-rigid character of the N- $\phi$  bond, around the flexible C(CF<sub>3</sub>)<sub>2</sub> linkage of HFDE. These two mechanical relaxations varied as a function of the nature of the diamine and above all in relation to the molar mass of the polyimide.

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