

New Conducting Thermoplastic Elastomers. I. Synthesis and Chemical Characterization

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ABSTRACT: In the last 20 years, much interest has been focused on conducting polymers to find new materials to transfer from research to industry. However, in many cases, as for elastomers for which intrinsically conducting materials are unavailable, it is necessary to use conducting particles that are physically mixed with the polymeric matrix to give loaded rubbers. In this work we report the synthesis and the chemical characterization of an intrinsically conducting material with good mechanical and electrical conduction properties. To achieve such a global goal, we covalently linked, by an amidation reaction, the terminal NH_2 of Emeraldine (EB) and sulfonated Emeraldine (SPAN) to a free carboxylic group belonging to the repetitive unit of a functionalized segmented polyurethane. The reaction was carried out by activating such a carboxylic group with *N,N'*-dicyclohexylcarbodiimide and *N*-hydroxysuccinimide. The reaction yields and the chemical properties of the polymers were studied by proton and carbon-13 nuclear magnetic resonance, ultraviolet, and Fourier transform infrared spectroscopy. The average numbers of EB or SPAN aromatic rings per polyether urethane acid (PEUA) repetitive unit, which cannot be assumed to be amidation degree because at this moment the molecular weights of the inserted EB and SPAN chains are unavailable, were 6 in case of the polymer obtained from the pristine Emeraldine and 1 for that obtained from the sulfonated Emeraldine. This result could be because SPAN was used in the acidic form, which depresses the nucleophilicity of the NH_2 group because of the presence of the sulfonic protons. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 857–867, 2002

Key words: polyaniline; sulfonated polyaniline; polyurethanes; elastomers; conducting polymers

INTRODUCTION

The conducting polymers research field has been recently acknowledged as one of the most important with the assignment of the Nobel prize to the major discovery in this field. These materials have features of both polymers and conducting or semi-conducting materials. In many cases, as for elastomers for which intrinsically conducting ma-

terials are unavailable, conducting particles (e.g., carbon black, metallic particles, or conducting polymers¹) are physically mixed with the polymeric matrix to give loaded rubbers. One of the applications of these co-materials is found, for example, in the covering of high tension cables.

In the field of intrinsically conducting polymers, polyaniline is the more studied compound because of its several possible applications; for examples, protection from electromagnetic interference,^{2,3} molecular sensor,⁴ and electrochromic displays.^{5,6} Since 1910, many oxidation states

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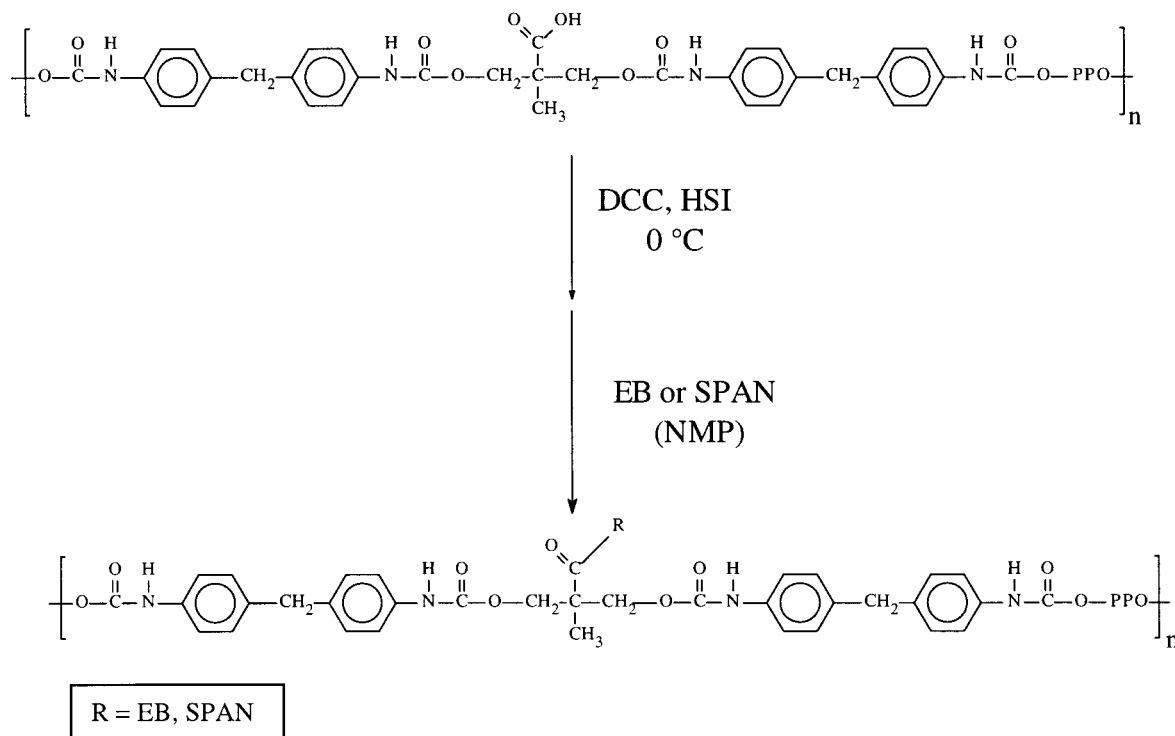


Figure 1 Synthesis scheme of amidated polyurethane.

of this polymer have been studied.^{7,8} The form that exhibits the strongest conducting properties is Emeraldine, especially if doped with a protic acid. The chemically synthesized Emeraldine form has very low solubility in most of the organic solvents. The substitution of a hydrogen atom on the benzene ring increases the polymer solubility.⁹ One of the more interesting substituents is the sulfonic group.¹⁰ Its introduction doesn't involve any modification of the Emeraldine structure but does cause a large increase in the solubility of many organic solvents, such as *N*-methyl-2-pyrrolidone, *N,N*-dimethylformamide, or dimethylsulfoxide. The sulfonic groups, inserted in the "ortho" position, provide the protons necessary to dope the macromolecular chain. For this reason, such a system is called "self-doping".

As far as conventional thermoplastic-elastomeric materials are concerned, one of the more interesting classes is represented by polyurethanes: their technological applications are concerned either with the properties related to the resistance to abrasion and stress or those related to thermal and acoustic isolation, which is typical of plastic materials. In addition, the possibility to obtain these materials in different solid structures or as foams makes these polymers inter-

esting for their durability and versatility. Segmented polyurethanes are thermoplastic elastomers with traditional application in engineering and, nowadays, in the biomedical field¹¹ because of their good hemocompatibility. The chemical structure of segmented polyurethanes is that of block copolymers with alternate "hard" and "soft" segments.¹² The "hard" segment is composed of a diisocyanate group bonded to a low molecular weight diol or diamine, whereas the "soft" segments are typically polyethers, polyesters, or polyalchidloles. The good mechanical properties of these materials are due to the physical interactions among "hard"–"hard" segments, inhibiting the viscous flow of the chains. These hydrogen bond interactions harden the material and are responsible for the elastic deformation due to the "soft" domains.

The aim of our work was to synthesize a polymer combining both the mechanical properties of polyurethanes and the electric and electrochromic properties of Emeraldine. Therefore, we used a polyurethane containing, in the "hard" unit, a free carboxyl group. This group was then amidated, using the free amine of the Emeraldine and sulfonated Emeraldine chains.

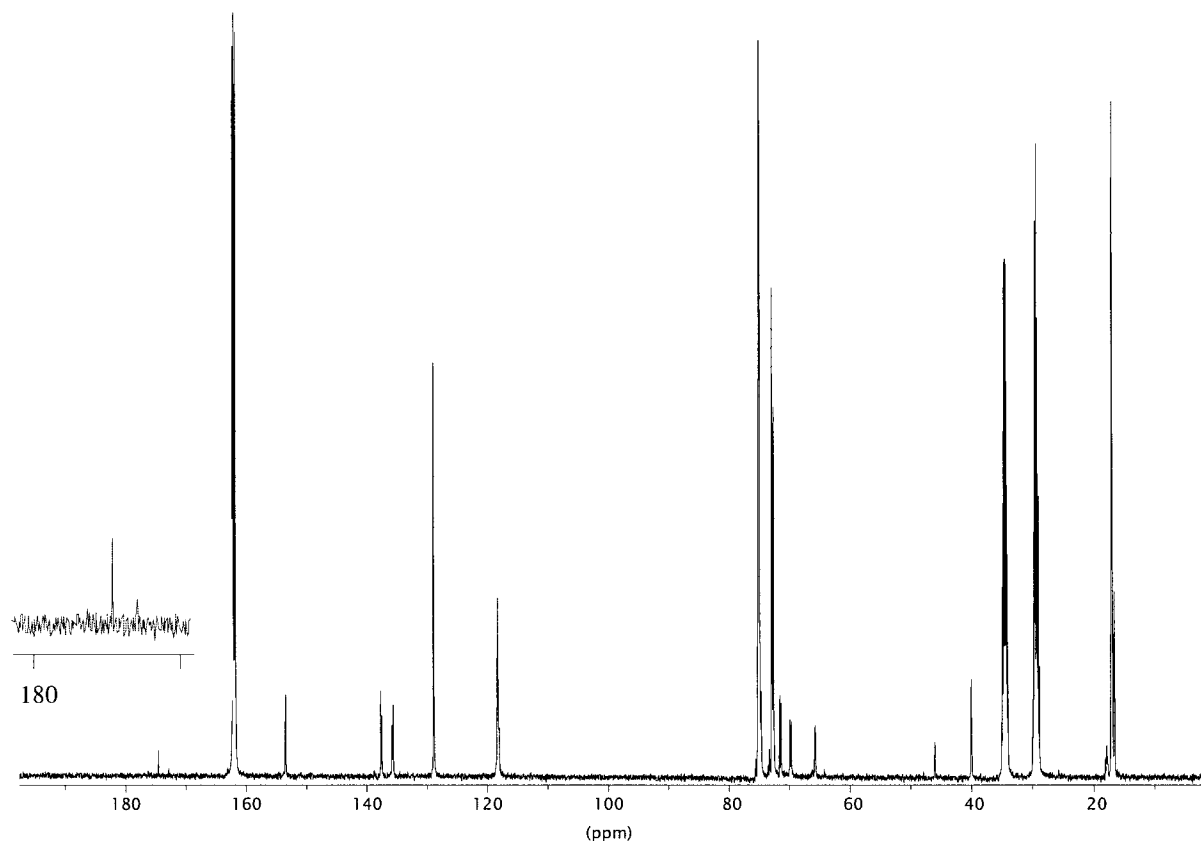


Figure 2 ^{13}C -NMR spectrum (DMF-d_6) of PEUASPAN.

EXPERIMENTAL

Synthesis and Preparation of the Emeraldine Base (EB)

Aniline was previously distilled. KIO_3 (99.5% Aldrich Chemicals) was used as oxidation agent in a hydrochloric acid solution. According to a known method,¹³ the molar ratio of KIO_3 /aniline was determined as 0.38%. The resulting product was washed with water and dried under vacuum. The so obtained polymer was purified from a low molecular weight fraction by treatment in a Soxhlet column with tetrahydrofuran (THF; Carlo Erba). The base form was prepared by stirring the Emeraldine at room temperature in NH_4OH 0.1 M for 60 h.

Synthesis of Sulfonated Polyaniline (SPAN)

A solution in Oleum of 0.5 g of EB, synthesized by the aforementioned procedure, was prepared at 0 °C. Then, the reaction was allowed to proceed for 30 min at room temperature, and a saturated

solution of methanol (Carlo Erba) and NaOH (Carlo Erba) was slowly added until the excess of SO_3 was removed. Finally, SPAN was filtered from the reaction solution.

Synthesis of Polyether Urethane Acid (PEUA)

The polyurethane was synthesized in two steps, as for all segmented polymers, by the method of Marconi and co-workers¹⁴ as modified by us.¹⁵

The first step was the preparation of a prepolymer from the poly(propylene oxide) (PPO; Fluka 1200) and methylene-bis-4,4'-phenyl isocyanate (MDI; Eastman Kodak Company), in a molar ratio of 1:2. The second step was the prepolymer extension by the reaction with dihydroxymethylpropionic acid (DHMPA; Aldrich Chemicals). To increase the molecular weight, the reagent concentration and the temperature of the second step were modified as follows: 8.93 g of MDI and 21.62 g of PPO were dissolved in a mixture of 45 mL of 4-methyl-2-pentanone and 55 mL of dimethylsulfoxide (DMSO; Fluka). The second step was carried out in 24 h at 50 °C.

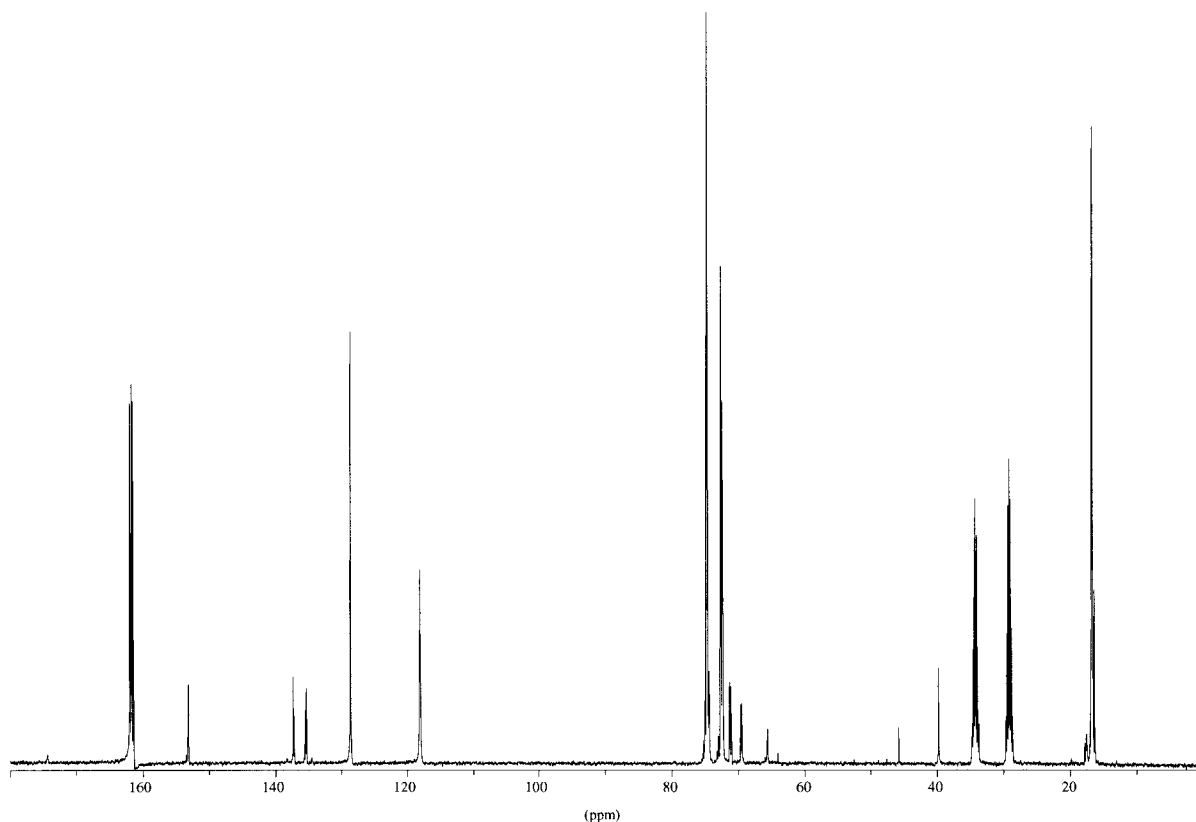


Figure 3 ^{13}C -NMR spectrum (DMF-d_6) of PEUA.

Synthesis of Amidated Polyurethane (PEUAPAN) with EB

First, the carboxylic groups present in the polyurethane chains were activated with *N,N'*-dicyclohexylcarbodiimide (DCC; Fluka) and *N*-hydroxysuccinimide (HSI; Fluka). These reagents were added to *N*-methyl-2-pyrrolidone (NMP; Fluka puriss. p. a.) solutions at 0 °C in equivalent molar quantity to the PEUA carboxylic groups. After 3 h, a solution of EB (0.45 g in 50 mL of NMP) was added. The reaction proceeded for 24 h at room temperature under constant stirring. In Figure 1 a scheme of synthesis is reported.

Then, the high molecular weight fraction of EB, which is insoluble in NMP, was separated by centrifugation. The polymer was then precipitated by pouring the reaction mixture in a NaCl

water solution and washing with water to eliminate the salt. PEUAPAN was finally purified from unreacted DCC and HSI and from dicyclohexylurea (DCU), a secondary product of the reaction, by Soxhlet extraction in methyl alcohol and then in ethyl alcohol. The purified polymer was dried under vacuum at 25 °C for 24 h.

Table I Assignments of ^{13}C NMR Characteristic Peaks of Polyurethane Repetitive Unit

Assignment	ppm
CH_3 (DHMPA, PPO)	17
$\text{Ph-CH}_2\text{-Ph}$ (MDI)	40
Quaternary C (DHMPA)	46
CH_2 (DHMPA)	71
CH_2 (PPO)	72.6–73
CH (PPO)	74.7
MDI- $\text{C}_{(2)}$	118.3
MDI- $\text{C}_{(3)}$	128.9
MDI- $\text{C}_{(1)}$	136
MDI- $\text{C}_{(4)}$	138
Carboxylic C	176

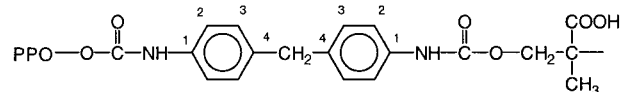


Figure 4 MDI-DHMPA, polyurethane repetitive unit segment.

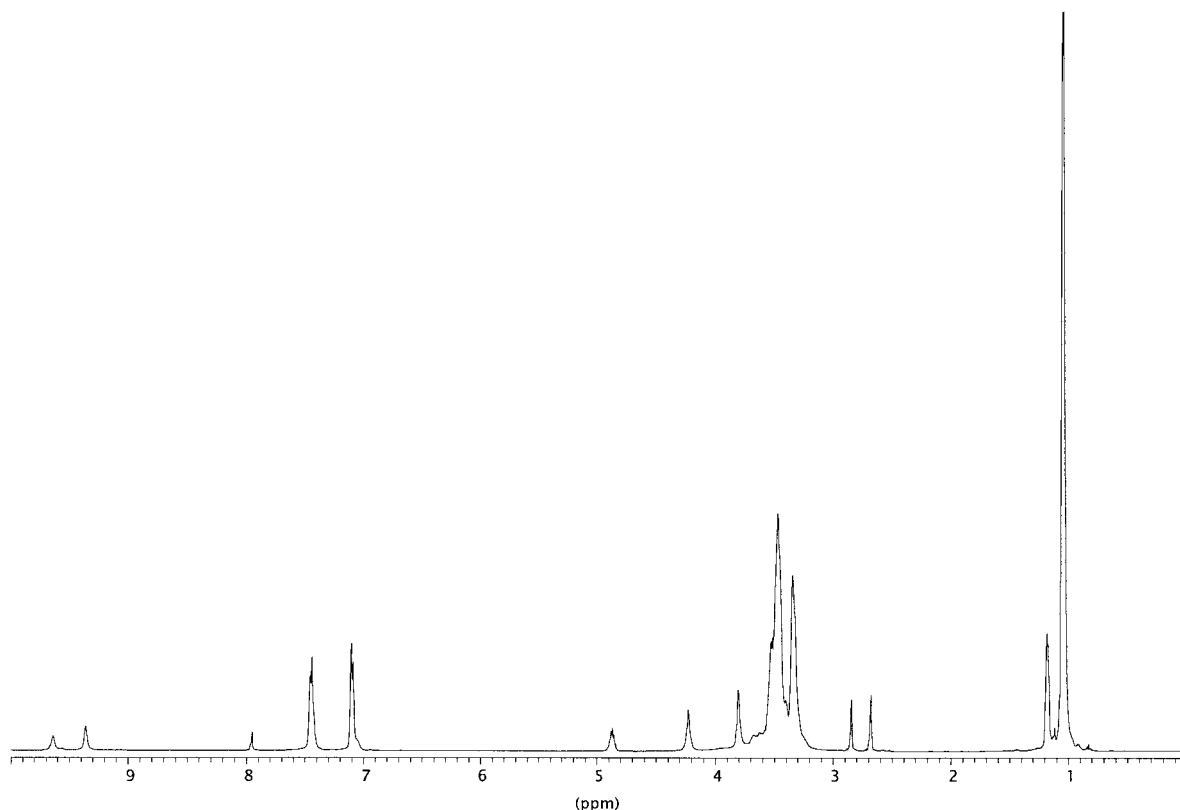


Figure 5 ^1H -NMR spectrum (d_6 -DMF) of PEUA.

Synthesis of Amidated Polyurethane (PEUASPAN) with SPAN

Both the procedures of synthesis and purification were exactly the same as for PEUAPAN, replacing EB with SPAN.

Nuclear Magnetic Resonance (NMR) Spectroscopy

The NMR spectrometer used was a BRUKER 500 MHz. The ^1H - and ^{13}C -NMR spectra were obtained by solubilizing the polymers in deuterated dimethylformamide (d_6 -DMF; 99.5%, Aldrich Chemical) at 50 mg/mL concentration, whenever PEUAPAN was less soluble in DMF than PEUA and PEUASPAN.

Ultraviolet-Visible (UV-vis) Spectroscopy

A Hewlett Packard 8452A diode array single-beam spectrophotometer was used. The investigated range was from 280 to 820 nm, with an accuracy of 4 nm and a resolution of 2 nm. Because of the low solubility of our polymers in

usual organic solvents, the one used for our measurements was NMP.

Infrared (IR) Spectroscopy

A Fourier transform infrared (FTIR) Matson 5020 Interferometer was employed. Transmission spectra were acquired in the range $4000\text{--}400\text{ cm}^{-1}$ by casting the polymer film on a KBr disk. Attenuated total reflection (ATR) spectra were acquired in the range $4000\text{--}650\text{ cm}^{-1}$ using a SeZn crystal at an incidence angle of 60° .

RESULTS AND DISCUSSION

NMR Characterization

The ^{13}C -NMR reveals the amidation of the polymers. Near the peak of the carboxylic acid group at 175 ppm in the spectra of PEUASPAN is a less intense peak at 173 ppm, which can be attributed to the amidic carbon atom.^{16,17} This peak is clearly evident in the inset of Figure 2. This peak, although of a low intensity, is significantly out-

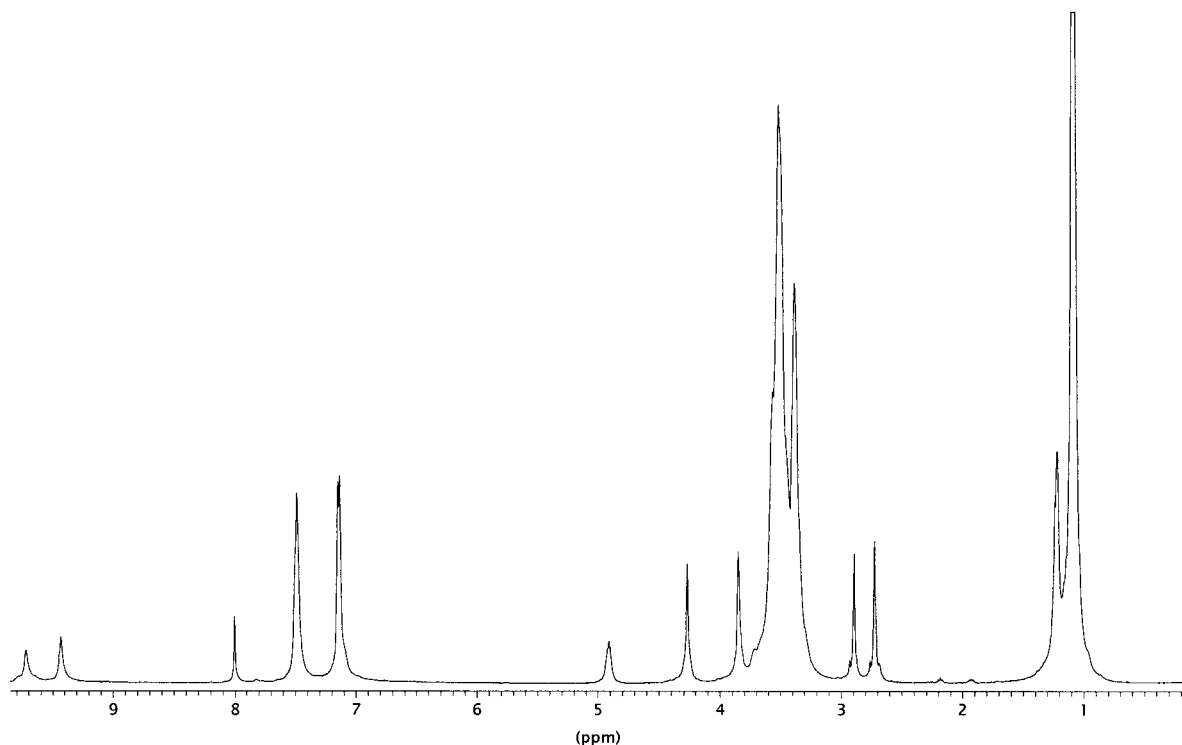


Figure 6 $^1\text{H-NMR}$ spectrum (d_6 -DMF) of PEUASPAN.

side the signal noise. Moreover, it must be stressed that only one carboxylic group for repetitive unit is present in the PEUA and that this unit is very large (~ 1800 amu). This result may explain the low intensity of such a signal. The PEUA spectrum, where all the characteristic peaks of the polyurethane chain can be found, is shown in Figure 3.

The peaks of the PEUA spectrum were assigned to the carbon atoms of the polyurethane repetitive unit segment shown in Figure 4, and the assignments are listed in Table I. These signals are the same for the amidated and non-amidated polyurethanes because the polyaniline aromatic carbon peaks are superimposed on the MDI ones.

The $^1\text{H-NMR}$ spectra of PEUA and PEUASPAN in d_6 -DMF are shown in Figures 5 and 6, respectively. The assignments of the $^1\text{H-NMR}$ characteristic signals of the polyurethane repetitive unit are reported in Table II. In this case, the assignments are also the same for the amidated and non-amidated polymers.

The direct amidation degree measurement was not possible because the amidic proton signal intensity was too low and the molecular weight of the inserted conductive polymers is currently un-

available. However, preliminary results obtained by gel permeation chromatography (GPC) analysis of the THF-soluble Emeraldine extracted fraction indicate that it is due to the oligomers of <5 units.

The attribution of the integral value of one proton was independently carried out by evaluating the integral of the peaks at 3.8 ppm (CH_2 between benzene rings of MDI) or at 4.3 ppm (CH_2 of PPO chain near urethane bond) or at 9.4 and 9.7 ppm (urethane protons). As far as the latter case is concerned, it is known¹⁴ that each urethane signal refers to a couple of protons, with the higher field peak reflecting the hydrogen atoms near the PPO chain and the lower field peak reflecting those hydrogen atoms near the DHMPA. The average number of EB or SPAN aromatic rings per PEUA repetitive units was calculated by the aromatic protons integral. This integral gives three aniline rings per polyurethane repetitive units in the PEUAPAN chain and one in that of PEUASPAN. For this polymer, in fact, the peaks between 7 and 7.5 ppm are due to 20 protons belonging to five aromatic rings that are 1-4 substituted, four of which are in the polyurethane backbone. By such a procedure, one

Table II Assignments of ^1H NMR Characteristic Peaks of Polyurethane Repetitive Unit

Assignment	ppm
CH_3 (PPO) and CH_3 (DHMPA) in chain CH and CH_2 (PPO)	1.08–1.2
CH_2 between the phenyl groups of MDI	3.8
CH_2 (PPO) adjacent to the urethanic bond	4.3
CH (PPO) adjacent to the urethanic bond	4.9
Aromatic hydrogen (MDI)	7.1–7.5
Urethanic NH	9.4–9.7

SPAN ring per polyurethane repetitive unit was found.

Although the PEUAPAN spectrum is less clear than that of PEUASPAN, the same kind of analysis can be used. The low quality of the PEUAPAN spectrum is due to the lower solubility of this polymer compared with that of PEUASPAN. We have calculated that 28 aromatic protons, corresponding to seven benzene rings, must be present in the chain. This result gives an average ratio of 3:1 for Emeraldine and the PEUA repetitive unit.

With the hypothesis that 5 aniline units should be the lower limit for the conducting chains used to carry out the amidation of PEUA in NMP, the amidation degree for the PEUAPAN polymer should be 60% and that for PEUASPAN should be 20%. The PEUAPAN reaction yield is greater than that of PEUASPAN, as it was confirmed by UV-vis and IR spectroscopy.

Both spectra of our amidated polyurethanes show a signal near to 7.8 ppm, which can be

attributed to the amide protons. The intensity of these peaks is quite low because the fraction of amide protons is smaller than the total number of protons in the chain.

The signals of the aromatic amine protons are not easy to identify. They usually fall in a rather wide range (3–5 ppm) for the hydrogen bond effect on the chemical shifts of the signals, which are influenced by temperature, solvent, and concentration. In our case, these signals overlap the CH— and CH_2 — signals of PPO chain (3.5 ppm).

UV-vis Spectroscopy

The spectra of our polymers were obtained with NMP as solvent. However, due to the solvent absorption at 230 nm, only the spectral range from 280 to 800 nm may be investigated. The UV-vis spectra of our amidated polymers (Figure 7) show two absorptions. The first one is near 300 nm and is due to the π – π^* electronic transitions of the benzene rings.^{18,19} The second one is near 600 nm and it is due to the π – π^* transitions of the chinoid rings.^{19,20} The same transition are shown by Emeraldine and its derivative SPAN. Moreover, the 300 nm intensity of the polyurethane spectra is higher than that of Emeraldine because of the presence of the aromatic rings on the polyurethane backbone.

In our materials, both peaks are shifted to a smaller wavelength than in the Emeraldine base spectrum because of the interactions between the urethane protons and aromatic π electrons. The benzene rings show a larger shift than the chinoid ones. In the sulfonated polymer spectra another band near 350 nm appears. It is due to the presence of the sulfonic acid group on the aromatic

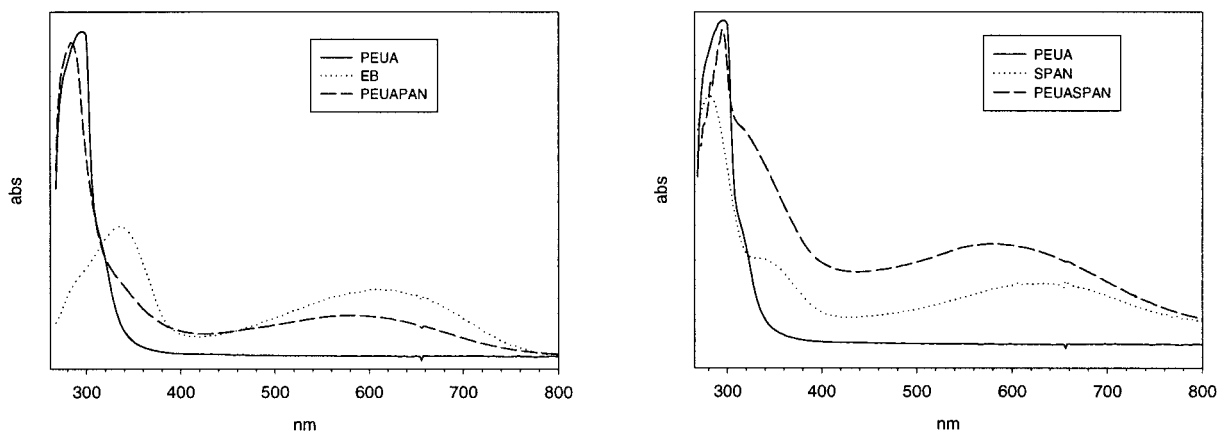


Figure 7 UV-vis spectra of non-amidated polyurethane, conducting polymers and amidated polyurethanes.

rings. Such a substituent has a little doping effect on the conducting polymer, causing a lower energy shift of the UV transition. Such a shift is more evident in the SPAN spectrum than in that of the amidated polymer.

The EB and SPAN amount bonded to our polymers was also confirmed by the quantitative UV-vis determination of Emeraldine and SPAN chains in the synthesized polymers, using the extinction coefficient at 600 nm specific to the chinoid rings that are present only in Emeraldine and its derivatives. The Emeraldine and SPAN specific extinction coefficients (ϵ_{600}^S ; Table III) were calculated by the linear regression of the 600 nm absorbance values as a function of the concentration, expressed as weight/volume (w/v) % (see Figure 8).

The Emeraldine and SPAN quantity bonded to the polyurethane chain was calculated by the Lambert-Beer equation, measuring the absorbance at 600 nm of PEUAPAN and PEUASPAN (0.05 w/v %) solutions. Concentrations of $5.87 \cdot 10^{-3}$ (w/v %) and $1.60 \cdot 10^{-3}$ (w/v %) were obtained for EB and SPAN, respectively.

The number of polyurethane repetitive units present in solution was calculated with eq. 1

$$\frac{((W/V)\%_{\text{AmidatedPolym.}} - (W/V)\%_{\text{Conduct.Pol.}})}{M_{\text{PEUA}}} = \text{Number of polyurethane units} \quad (1)$$

where M_{PEUA} is the PEUA repetitive unit molecular weight (1834 amu). The number of bonded units of conducting polymer were calculated according to eq. 2

$$\frac{((W/V)\%_{\text{Conduct.Pol.}})}{M_{\text{CD}}} = \text{Number of conducting polymer units} \quad (2)$$

where M_{CD} is the conducting polymer repetitive unit molecular weight (EB = 91 amu and SPAN = 107 amu).

Table III Calculated Emeraldine and SPAN Specific Extinction Coefficients

Polymer	ϵ_{600}^S
Emeraldine base	95.41 ± 0.01
SPAN	111.03 ± 0.01

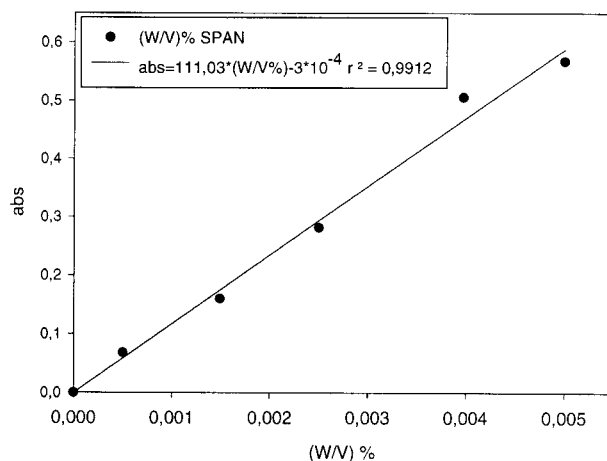
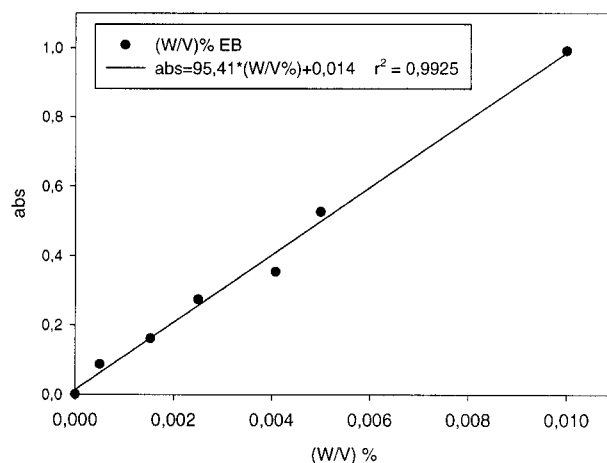


Figure 8 Absorbance values at 600 nm of an EB and SPAN solutions in NMP as a function of the concentration expressed as w/v %.

As far as the SPAN is concerned, according to the results of thermogravimetric experiments, to be discussed in a forthcoming paper, one sulfonic group is present every 4.5 aniline units. It follows that the SPAN unit molecular weight is 107 amu, as already stated.

From the ratio number of conducting polymer units/number of polyurethane units (eq. 2/eq.1) values of 2.7 and 0.6 aniline units per polyurethane repetitive unit in PEUAPAN and in PEUASPAN, respectively, were found. The so obtained values were in good agreement with the $^1\text{H-NMR}$ data.

Infrared Spectroscopy

All the PEUA characteristic bands are present in the spectra of both PEUAPAN and PEUASPAN

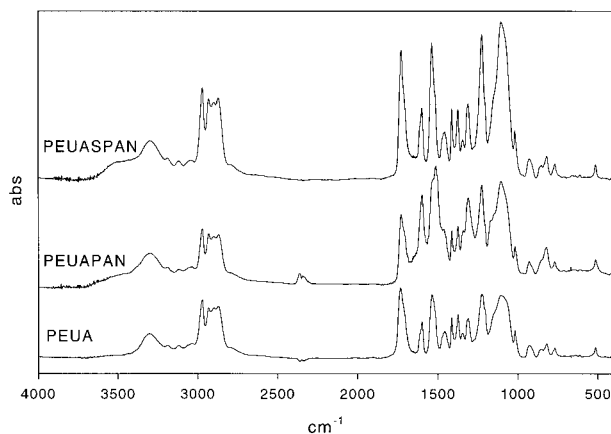


Figure 9 FTIR spectra of the polyurethaneic polymers studied.

(see Figure 9). The polyurethane chain characteristic absorptions are reported in Table IV. The absorption spectra of our polymers in the range 1650–1450 cm^{-1} are reported in Figure 10. All of the spectra show an absorption at 1600 cm^{-1} due to the benzene rings C=C stretching. The modification of the peak at 1530 cm^{-1} of the PEUAPAN and PEUASPAN spectra may be due to the second amide band characteristic of the N-substituted amide. The PEUAPAN spectrum also shows an absorption at 1510 cm^{-1} , which is attributed to the chinoid C=C stretching of Emeraldine. This intense absorption confirms the higher concentration of Emeraldine in PEUAPAN than in PEUASPAN indicated by the NMR data.

The IR surface investigation by the ATR technique was carried out to evidence the phase sep-

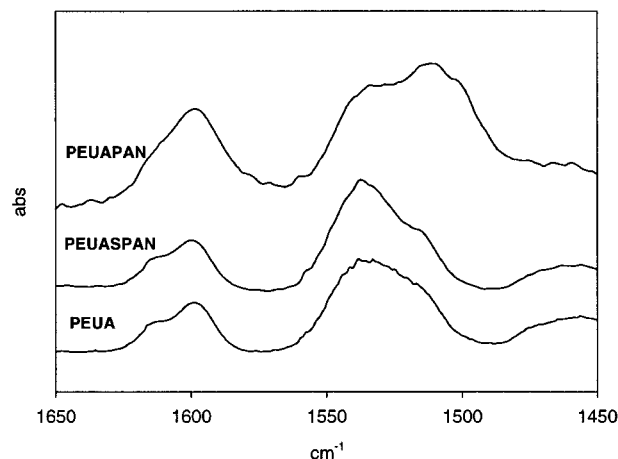


Figure 10 FTIR spectra in the range 1650–1450 cm^{-1} of amidated and non-amidated polyurethanes.

aration effects, if present, and the data were compared with those obtained by transmission measurements carried out on the same materials. To take into account the dependence of the depth penetration on the frequency, the ATR spectra were multiplied for the corresponding wave number.²¹ A comparison of the observed ratio values of the free and hydrogen-bonded carboxylic groups absorbance, recorded by the two techniques, are reported in Table V.

First of all it must be noticed that both the transmission and the ATR techniques indicate that the PEUA polymer is characterized by a higher concentration of hydrogen-bonded carboxylic groups than the amidated materials. This result may be due to the presence in the Emeral-

Table IV Infrared Band Assignments of Polyurethaneic Compound

Compound	Assignment, cm^{-1}
Urethaneic N—H stretching (hydrogen bonded)	3320
Aromatic C—H stretching	3030
CH ₃ asymmetric stretching	2960
CH, CH ₂ asymmetric stretching	2920
CH ₃ symmetric stretching	2885
CH, CH ₂ symmetric stretching	2850
Urethaneic C=O stretching (free)	1730
Urethaneic C=O stretching (hydrogen bonded)	1715
Aromatic C=C stretching	1600
N—H bending + C—N stretching	1530
CH ₂ bending	1500–1435
Aromatic C—C stretching	1410
CH ₂ wagging	1375
COC asymmetric stretching (PPO)	1228
COC stretching of (C=O)OC	1100

dine chains of amine hydrogens, which favorably interact with the oxygen atom of the PEUA backbone carboxylic group. On the other hand, the comparison of the transmission and ATR results evidenced some morphological difference between the bulk and the surface of our polymeric materials. All the spectra were first normalized, with respect to the peak at 1374 cm^{-1} , relative to the CH_2 wagging. In this region, in fact, the spectra are not modified by the different chemical compositions of the polymers. Then the absorbance values of a transmission spectrum were subtracted from a corrected ATR spectrum until this peak went to zero. These measurements indicate a higher concentration of hydrogen-bonded carbonyl groups on the surface than in the bulk of the material.

By observing the difference between ATR and transmission spectra (Figure 11), we can see, for PEUA and PEUASPAN, respectively, a large negative peak near 1740 cm^{-1} due to the free $\text{C}=\text{O}$ stretching and a positive one at 1705 cm^{-1} due to the hydrogen-bonded carbonyl. This evidence indicates a larger presence of bonded $\text{C}=\text{O}$, due to the phase segregation in the surface rather than in the bulk of our materials. Such a difference seems not to be present in the PEUAPAN difference spectrum.

CONCLUSIONS

It is quite difficult to determine the amidation degree of our polymers because of the low solubility of polyanilinic material, which doesn't allow measurement of their molecular weight. However, we can suppose that the conducting chains covalently bonded to the polyurethane should contain at least five repetitive units, as indicated by preliminary results from GPC analysis of the THF-soluble Emeraldine extracted fraction. With

Table V Ratio Values of the Free and Hydrogen-Bonded Carboxylic Groups Absorbance for the Polyurethanic Polymers

Polymer	Method	
	ATR	Transmission
PEUA	1.56	1.88
PEUAPAN	1.30	1.46
PEUASPAN	1.32	1.55

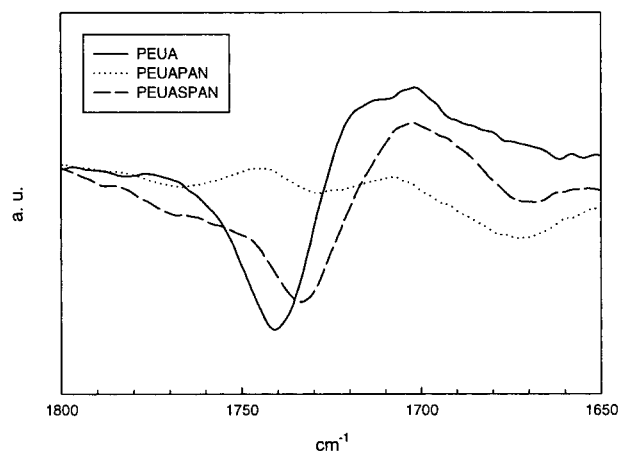


Figure 11 Difference between ATR and transmission spectra for PEUA, PEUAPAN, and PEUASPAN, in the range $1800\text{--}1650\text{ cm}^{-1}$.

such an assumption, the maximum value of the amidation degree for the PEUAPAN polymer should be 60% and that for PEUASPAN should be 20%.

Another important consideration is that PEUASPAN is less amidated than PEUAPAN. This result might be because SPAN was used in the acidic form. The presence of the protons of the sulfonic groups may have depressed the nucleophilicity of the NH_2 group. Indeed, such an effect is very important in molecules with a large delocalization charge, like a conducting polymer.

In conclusion we have been able to synthesize two new conducting thermoplastic elastomers whose physical properties will be investigated in a forthcoming paper.

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