Dynamic mechanical behaviour and thermal degradation of undoped polyaniline

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Summary

Dynamical mechanical spectrometry experiments were performed on undoped polyaniline films to provide some information on the microstructure by the analysis of the molecular motions. A mechanical relaxation located at around 200°C has been related to the polyaniline glass transition. At higher temperature, evidence is given for a thermal degradation which is attributed to crosslinking reactions as confirmed by thermogravimetry and FT-IR experiments.

Introduction

Intrinsically conducting polymers have been intensively studied since the last decade due to their potential applications. Among this class of polymers, polyaniline is one of the most promising candidate due to its easy synthesis and good conductivity.
However, thermal stability remains a major drawback for using polyaniline in practical applications. Moreover, the microstructure of polyaniline is still quite unknown because it largely depends on the synthesis parameters and on the dopant nature. Even in the case of the simplest form of polyaniline, namely undoped polyaniline or emeraldine base (EB), the glass transition temperature is still discussed (1, 2, 3). This could result from the relative inefficiency of differential scanning calorimetry (DSC) for this class of polymers (1, 4, 5).
In this work, it is proposed to investigate the microstructure of undoped polyaniline films by dynamic mechanical spectrometry, an original technique which has already proved its efficiency on many polymer whether conducting (2, 5) or not (6).

Experimental

The undoped polyaniline films used in the study were chemically synthesized and supplied by the "Atelier d'Interface Industrielle" (A2I) from the French "Commissariat à l'Energie Atomique" (CEA). The EB used to make our films was synthesized using a procedure described by Angelopoulos (7).
Briefly, aniline hydrochloride was oxidised using ammonium persulphate to yield emeraldine salt (ES) powder. After careful washing, this powder was neutralised and dissolved in mCresol. The resultant solution containing 1.5% of EB was cast onto glass plates, and after subsequent removal of solvent (typically 100 hours at 60°C), free standing films of undoped polyaniline could be removed from the glass substrates. The thickness is ca. 30µm ± 5µm. The molecular formula of undoped polyaniline as proposed in literature (8) is reported figure 1 :
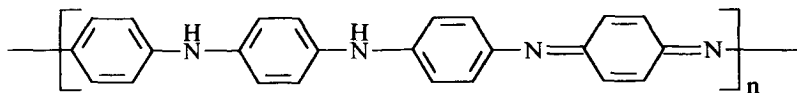
Figure 1 : Molecular formula of undoped polyaniline.

Dynamical Mechanical Analysis (DMA) was performed using a Rheometric Scientific DMTA MkIII spectrometer operating in the tensile mode. This apparatus provides the real and imaginary parts of the dynamic stress modulus so called the storage modulus E' and the loss modulus E" respectively. The loss factor $\tan\delta$ = E"/E' is also calculated. E', E" and $\tan\delta$ are displayed as a function of the temperature for one or several frequencies under isochronal conditions. The isochronal scans were recorded from 50 to 300°C at a heating rate of 1°C/min in a flowing atmosphere of nitrogen and at three frequencies i.e. 0.3, 1 and 5 Hz. Sample dimensions, typically 10x5x0.03 mm were kept constant to ensure reproducibility. A reducing force mode was engaged which adjusts the static force during the test to minimize creep.

Thermogravimetry experiments were conducted with a DuPont 951 thermogravimetry analyser from 50 to 600°C at a heating rate of 10°C/min in a flowing atmosphere of nitrogen.

The FT-IR spectra of polyaniline films were taken by transmittance spectroscopy with a Perkin Elmer 2000 spectrometer.

Results and discussion

Dynamic mechanical behaviour

The plots of dynamic modulus E' and loss factor $\tan\delta$ at 0.3, 1 and 5 Hz versus temperature are shown in figure 2 for the undoped polyaniline film.
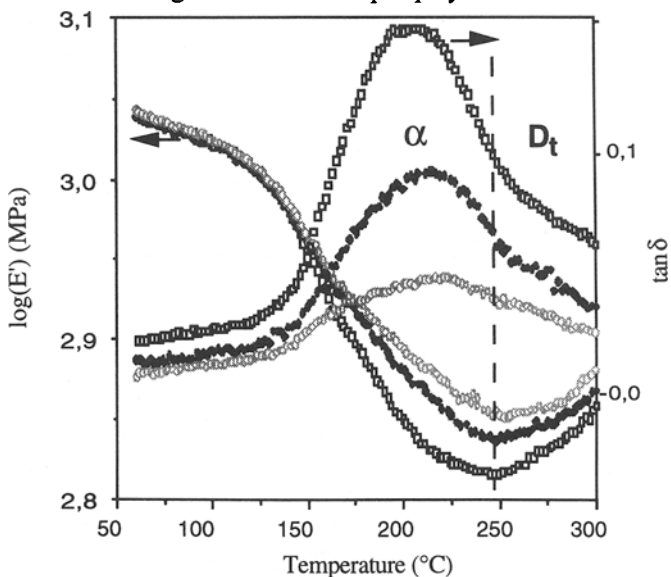

Figure 2 : Plots of the storage modulus E' and internal friction $\tan\delta$ versus temperature at 0.3 Hz(□), 1 Hz (♦) and 5 Hz (○) for the undoped polyaniline film.

With increasing temperature from 50°C to 300°C, two transitions are detected. First, the α transition which is a reversible mechanical relaxation i.e., both magnitude and temperature location depend on the frequency is detected between 100°C and 250°C. The tanδ maxima accompanied by important decreases of E' are located at 204, 215 and 215°C at 0.3, 1 and 5 Hz, respectively. The α relaxation has been analysed in first approximation through the Arrhenius law (eq.1):

$$f = f_0 \cdot \exp(-E_a/RT) \quad (1)$$

where f is the solicitation frequency (Hz),

f_0 is the pre exponential factor (Hz),

E_a is the apparent activation energy (J.mol^{-1}),

T is the absolute temperature (K) and R = 8.32 J.K^{-1}.mol^{-1}.

The frequency dependence of a mechanical relaxation obeys the Arrhenius law when the related molecular motions are equivalent to those of a molecule lifting over a potential barrier from one minimum of potential energy into another one. In the simplest case, considering molecules undergoing rotational oscillations, the frequency f of oscillations is near the Debye frequency i.e. near 10^{13} Hz (9).

The calculation of E_a for tanδ maxima of the α relaxation provides a value of around 400 kJ/mol. The pre exponential factor f_0 is around 10^{47} Hz which is higher than the Debye frequency. This value of f_0 indicates that the frequency dependence of the α relaxation does not obey the Arrhenius law and that related molecular motions are not elementary oscillations. Thus, it can be suggested that the polyaniline α relaxation originates from complex and correlated molecular motions and is related to the glass transition of polyaniline.

Second, the D_t transition, beginning at about 240°C and characterized by an irreversible increase in the real part of the modulus is detected. The D_t transition characteristics are not frequency dependent. Such a transition which has already been evoked for polypyrrole (5) or other usual polymers (11, 12) is significant of a crosslinking process associated with a thermal degradation.

Thermal degradation of undoped polyaniline

To investigate the thermal stability of the film, thermogravimetric measurements were conducted between 50 and 600°C in a flowing atmosphere of nitrogen. The weight loss is plotted versus temperature in figure 3. With increasing temperature, the following three steps in weight loss are detected :

- A first step located between 50 and 100°C which might originate in residual moisture as already described for polyaniline (1, 3, 10).

- A second step ranging between 100 and 200°C which could result from evaporation of residual solvent (mCresol) (2).

- A dramatic weight loss beginning around 350°C which is related to the thermal decomposition of polyaniline macromolecules (13, 14, 15).

No significant weight loss can be observed between 225 and 350°C. This could confirm that in the temperature range where the D_t transition is detected by DMA, thermal degradation of polyaniline is governed by a crosslinking process.
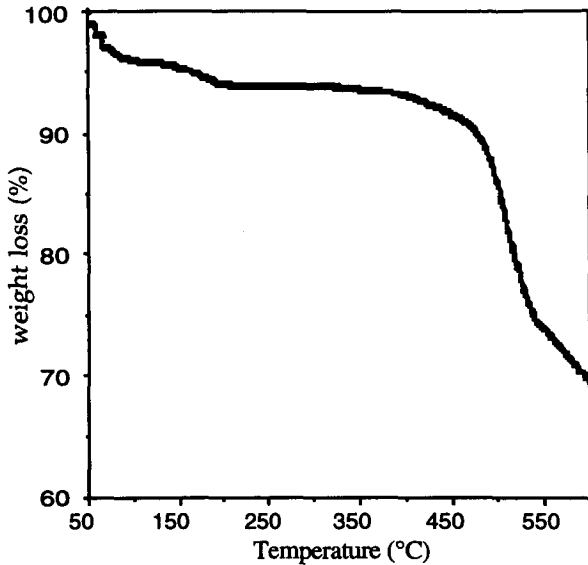
Figure 3 : Thermogravimetry trace for undoped polyaniline.

Analysis of as received and heated polyaniline

To investigate chemical changes induced by thermal degradation, FT-IR analysis was performed to compare the chemical structure of as received (see figure 4) and heated polyaniline samples.
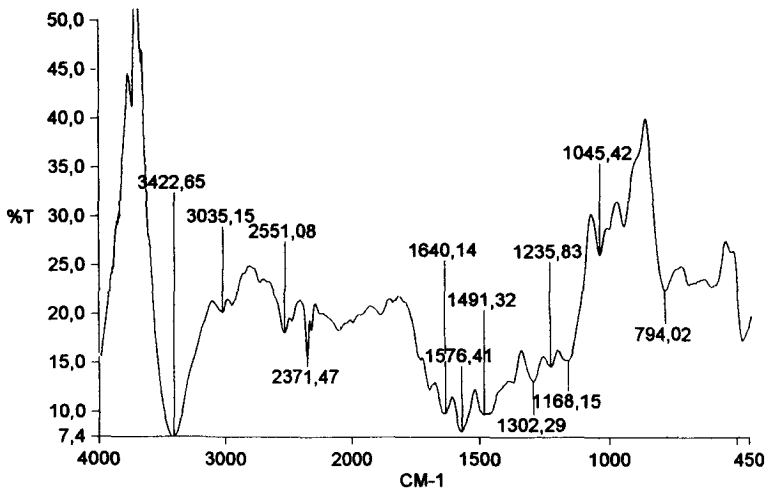

Figure 4 : FT-IR spectrum of as received undoped polyaniline.

The characteristic absorptions observed in figure 3 for are received polyaniline are listed in Table 1.

IR BAND (cm^{-1})	ASSIGNMENT	COMMENT
3422	N-H	2° amine
3035, 1168, 1045, 794	C-H	aromatic, paradisubstitution
2551	N-H	3° amine
2371	CO_2	atmospheric CO_2
1640, 1491	C-C	aromatic
1576	C-N	iminoquinone
1302	C-N	2° aryl amine
1235	C-N	3° aryl amine

Table 1 : FT-IR peak assignments for as received polyaniline

Most of these vibrational bands are in excellent agreement with previously published values (7, 16, 17, 18). However, although the vibrational band at 2551 cm^{-1} has already been detected (7, 17, 19), it has never been assigned. It could be related to hydrogen bond between a nitrogen atom of iminoquinone rings and a secondary amine function of an adjacent macromolecule (20).

After progressive heating up to 150°C, 250°C, 350°C, 450°C and 550°C, the relative intensity of the vibrational band at 2551 cm^{-1} is decreased by 33%, 37%, 45%, 50%, 55% respectively. These changes remain the only noticeable modification of heated samples spectra in comparison with the original spectrum and could be assigned for chemical crosslinking between nitrogen and carbon atoms of iminoquinone functions of two adjacent polymeric chains as mentioned elsewhere (21).

According to this hypothesis, the thermal degradation of polyaniline in the temperature range where D_t transition is detected could follow the crosslinking process as proposed in the following schemes 1 and 2 :
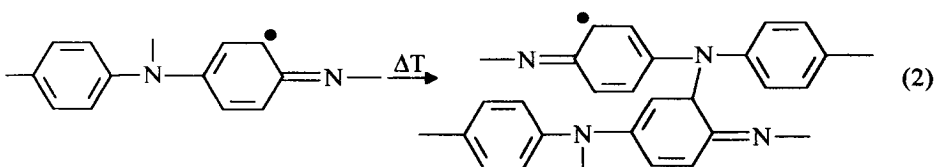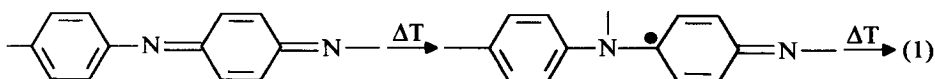
As the crosslinking reaction occurs, the conjugation becomes lower. This reaction could be responsible for the weak stability of doped polyaniline conductivity versus temperature or time.

Conclusion

A method based on the mechanical dynamical spectrometry is proposed to investigate the microstructure of undoped polyaniline films.

By increasing the temperature, the microstructure of polyaniline films is characterized by the two following transitions :

- A mechanical relaxation defined as α transition is related to the glass transition of polyaniline.

- A transition defined as D_t, occurs at temperature above 250°C and is accompanied by an increase in the storage elastic modulus. Such a transition is attributed to the thermal

degradation of the polymer, leading to a crosslinking effect of the macromolecular chains involving imine functions of polyaniline.

Further experiments are in progress to investigate the microstructure and the thermal stability of the doped form of polyaniline.

References

1. Wei Y, Jang GW, Hsueh KF, Scherr EM, MacDiarmid AG, Epstein AJ (1992) Polymer 33: 314.
2. Milton AJ, Monkman AP (1993) Synth Met 55: 3571.
3. Chen SA, Lee HT (1995) Macromol 28: 2858.
4. Truong VT, Ennis BC, Turner TG, Jenden CM (1992) Polym Int 27: 187.
5. Lesueur D, Albérola ND (1997) Synth Met 88: 133.
6. Bas C, Albérola ND (1996) Polym Eng Sci 36: 244.
7. Angelopoulos M, Asturier CE, Ermer SP, Ray E, Scherr EM, MacDiarmid AG, Akhtar MA, Kiss Z, Epstein AJ (1988) Mol Cryst Liq Cryst 160: 151.
8. Huang WS, Humphrey BD, MacDiarmid AG (1986) J Chem Soc Commun Faraday Trans 1 82: 2385.
9. Debye P (1945) Polar Molecules. Dover Publications, New York.
10. Kulkarni VG, Campbell LD Mathew WR (1989) Synth Met 30: 321.
11. Prime RB (1981) Thermosets. In : Turi EA (ed) Thermal characterisation of polymeric materials. Academic press, London.
12. Ferry JD (1983) Viscoelastic properties of polymers. Wiley J (ed), New York.
13. Boyle A, Penneau JF, Geniès E, Riekel C (1992) J of Polymer Science: Part B: Polymer Physics 30: 265.
14. Traore MK, Stevenson WTK, McCormick BJ, Dorey RC, Wen S, Meyers D (1991) Synth Met 40: 137.
15. Amano K, Ishikawa H, Kabayashi A, Satoh M, Hasegawa E (1994) Synth Met 62: 229.
16. Harada I, Furukawa Y, Ueda F (1989) Synth Met 29: E103.
17. Monkman AP, Adams P (1991) Synth Met 41: 891.
18. Quillard S, Louarn G, Lafrant S, MacDiarmid AG (1994) Phys Rev B 50: 12496.
19. Zheng W, Angelopoulos M, Epstein AJ, MacDiarmid AG (1997) Macromol 30: 2953.
20. Socrates G (1994) Infrared characteristic group frequencies. Tables and charts. Wiley J (ed), New York.
21. Lee HT, Liao CS, Chen SA (1993) Makromol Chem 194: 2443.