Charge-transfer interaction and chain association in poly(ether imide) solutions: a fluorescence spectroscopic study

Annie Viallat*, Ricardo Pedro Bom and Jean Pierre Cohen-Addad
Laboratoire de Spectrométrie Physique, associé au CNRS, BP 87, 38402 Saint Martin d'Hères cedex, France
(Received 28 April 1993; revised 16 September 1993)

The analysis of absorption and fluorescence spectra of poly(ether imide) solutions and related model compounds shows the existence of charge-transfer complexes in poly(ether imide) solutions and in poly(ether imide) solid state. A correlation is established between the fluorescence emission due to charge-transfer complexes and the aggregation state of poly(ether imide) solutions. The kinetics of aggregation of a solution and the aggregate dissociation phenomenon in dilute solution are observed from the study of fluorescence emission of poly(ether imide) solutions.

(Keywords: poly(ether imide); aggregation phenomena; fluorescence spectra)

INTRODUCTION

Aromatic polyimides in the solid state exhibit a microscopic aggregation structure. The degree of molecular aggregation and of chain stacking is strongly influenced by the thermal history and the molecular orientation of polymer chains as well as by the ionization potential and electron affinity of the chain structural units[1,2]. Numerous studies conducted on solid polyimides have been concerned with these effects[3,4]. However, on a more fundamental level, the nature of the strong intermolecular interactions leading to association effects is still speculative. The hypothesis currently put forward is that polymer chains interact via charge-transfer complex (CTC) formation[5–9]. This hypothesis is supported mainly by results obtained from u.v. absorption and fluorescence experiments conducted on solid systems.

Structural properties of polyimide solutions have not been studied so extensively, probably because most polyimides are characterized by a low solubility. However, soluble polyimides have recently been synthesized, and therefore the question arises whether the solvent can disrupt chain interaction and inhibit chain association in solution. It has been shown in previous work that the behaviour of a soluble poly(ether imide) (PEI) strongly suggests the existence of chain association in solution[10]. First, it was observed that solutions made with chlorinated solvents became progressively turbid upon ageing, thus revealing a progressive aggregation process. Secondly, the viscosity behaviour of dilute and semidilute solutions suggested that intrachain association occurred at low concentration while chain aggregation occurred in the semidilute regime.

This work proposes a u.v. absorption and fluorescence study of charge-transfer (CT) interactions in PEI solutions. The main objectives are as follows:

(i) To determine whether the absorption and luminescence behaviour of PEI is consistent with CT formation and whether a relation can be found between the fluorescence emission and the physical state of PEI solutions. For this purpose, u.v. spectroscopy experiments are conducted on PEI solutions and on related monomeric compounds, using two different solvents. These latter compounds serve as models to afford insight into CTC interactions in PEI.

(ii) To study the aggregation phenomenon occurring in dichloromethane–PEI solutions. Kinetics of formation of aggregates and conditions for aggregate dissociation are investigated from the observation of fluorescence emission; the latter point is briefly discussed.

EXPERIMENTAL SECTION

Samples

The polymer Ultem 1000 was obtained from General Electric. Its molecular weight is $M_n = 10\,000$, with a polydispersity index of 1.6. It was dried at 150°C for 4 h prior to use. The two model compounds were commercially available phthalimide and *N*-phenylphthalimide (*Figure 1*).

PEI solutions, prepared at room temperature, were gently stirred until homogenization was completed. PEI solutions were prepared in the 0.1–30 wt% range of concentration (see *Table 1*). The two solvents used were *N*-methylpyrrolidone (NMP) and dichloromethane (DCM).

Dichloromethane–phthalimide solution at concentration equal to 1.4 wt% (6.8×10^{-3} M) was homogeneous, and dichloromethane–*N*-phenylphthalimide solutions were homogeneous for concentrations up to 2.5 wt%

---

* To whom correspondence should be addressed

0032-3861/94/13/2730–07

Table 1 Solutions used in this study

NMP–phthalimide		1 wt% 6.8×10^{-3} M			15 wt% 1.1×10^{-1} M			
NMP–*N*-phenylphthalimide		1.4 wt% 8×10^{-3} M			15 wt% 9.3×10^{-2} M solid phase			
DCM–*N*-phenylphthalimide	0.083 wt% 3.2×10^{-4} M	0.93 wt% 3.6×10^{-3} M	2.46 wt% 9.5×10^{-3} M	9 wt% 3.6×10^{-2} M solid phase	15 wt% 6.3×10^{-2} M solid phase			
DCM–PEI	0.1 wt%	1 wt%	5 wt%	11 wt%	15 wt%	20 wt%	24.8 wt%	30 wt%

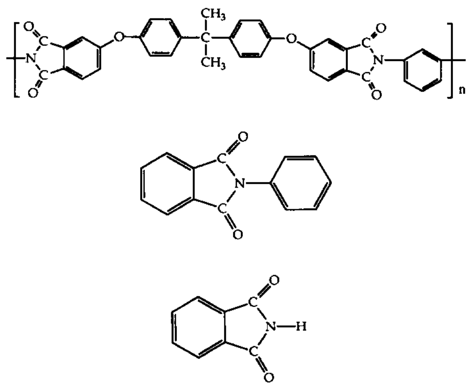

Figure 1 Phthalimide (top), *N*-phenylphthalimide (centre) and PEI monomeric unit (bottom)

(9.5×10^{-3} M). Systems prepared at higher concentrations exhibited two phases: a solid phase at the bottom of the tube and a dilute liquid phase. In the following, experimental results concerning solid phthalimide and solid *N*-phenylphthalimide will refer to the solid phase of concentrated phthalimide and *N*-phenylphthalimide solutions.

Solutions were studied shortly after homogenization was completed. Then, PEI solutions were kept at room temperature for several weeks in order to study the ageing process of PEI solutions.

Film preparation

The 16 wt% dichloromethane–PEI solutions were prepared and cast on a glass plate at room temperature; they were then dried at 45°C. Resulting films were about 50–60 nm thick.

Spectra

Absorption spectra were recorded on a Cary spectrophotometer. Solutions were deposited in a quartz cell (Hellma; diameter 1 mm). Fluorescence emission and excitation spectra were recorded on an ISA Jobin–Yvon Spectrofluo spectrophotometer. Solutions and films were excited in a front-face arrangement to minimize self-absorption.

CHARGE-TRANSFER INTERACTIONS IN POLY(ETHER IMIDE) AND MODEL COMPOUNDS

The PEI studied in this work contains alternate structural elements of different electronic nature: electron-acceptor diimide fragments and electron-donor aromatic units. Donor and acceptor elements can therefore experience mutual CT interactions, which may lead to the formation of either intrachain or interchain CTC. Intrachain CTC are formed between two adjacent electron-donor and electron-acceptor elements along the same molecule or between distant elements belonging to the same polymer chain. Interchain CTC are formed between donor and acceptor elements located on neighbouring molecules or macromolecules. The formation of a stable ground-state CTC gives rise to charge-transfer absorption bands in the absorption spectrum of the system. Excitation into these bands produces excited complexes, which may dissipate their energy either by a radiationless process or by a specific fluorescence emission.

The existence of a CT absorption band in polyimides was evidenced by u.v. absorption and fluorescence experiments[3,4,6,7]. They showed that CT transitions in polyimides were characterized by a broad long-wavelength absorption at $\lambda > 330$ nm. This band is generally assigned to a π–π^* transition characterized by a shift of electron density from the aromatic substituent to the imide unit. An n–π^* transition might also be involved, which red-shifts upon the conjugation that attends aromatic substitution at the nitrogen atom. Such assignments are supported by quantum-chemistry calculations performed on common polyimides like, for instance, the extensively studied pyromellitic dianhydride-oxydianiline (PMDA-ODA)[1]. The identification of CT interactions in the PEI studied here is based on the analogy of the optical behaviour of several polyimides reported in the literature and on the study of the spectra obtained on related model compounds.

Absorption spectra: ground-state complexation

Attention was focused on the long-wavelength tail of the absorption spectra, which is the region of interest in investigating CT transitions.

Spectra obtained on the three compounds, phthalimide, *N*-phenylphthalimide and PEI, are shown in *Figures 2* and *3*. The spectrum of dilute NMP–phthalimide solution (6.8×10^{-3} M) is similar to those reported in the literature[12,13]; the maximum of absorption at 293 nm is assigned to a π–π^* transition and no tail is observed at wavelengths longer than 320 nm. In concentrated NMP–phthalimide solution (1.1×10^{-1} M), however, an absorption tail extends to about 360 nm, which may indicate a very small ground-state association phenomenon via intermolecular CTC formation.

The absorption spectra of dichloromethane–*N*-phenylphthalimide solutions are similar to those recently reported in the literature[13,14]. A long-wavelength absorption tail extending to about 500 nm is observed whose absorbance is proportional to the concentration of the

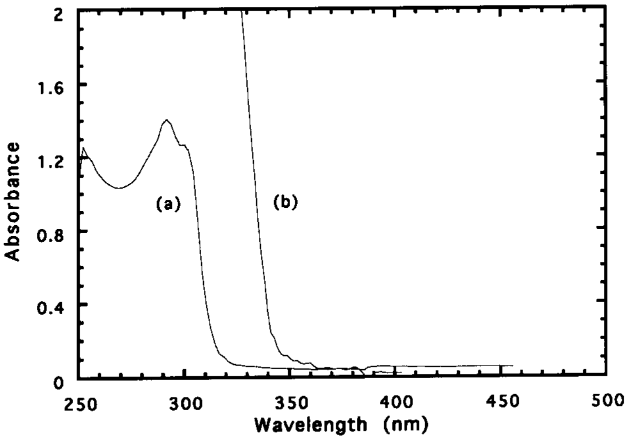

Figure 2 Absorption spectra of NMP–phthalimide solutions: (a) $c = 6.8 \times 10^{-3}$ M, (b) $c = 1.1 \times 10^{-1}$ M

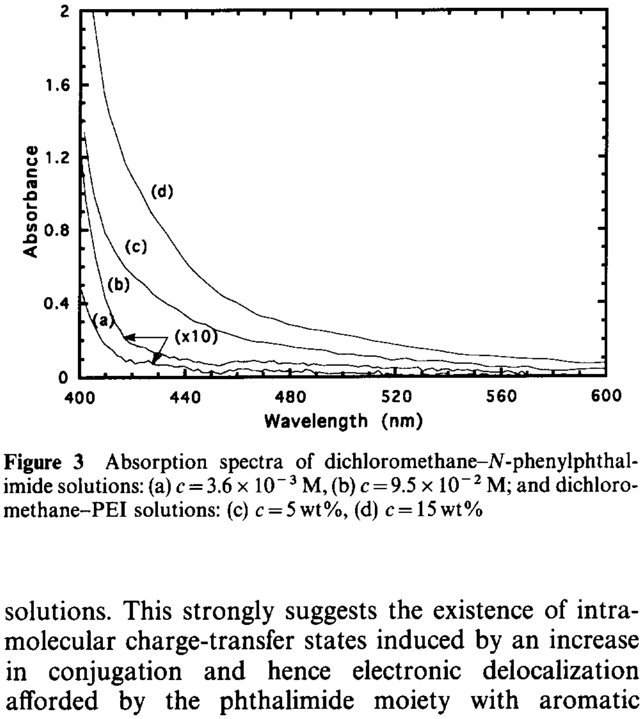

Figure 3 Absorption spectra of dichloromethane–*N*-phenylphthalimide solutions: (a) $c = 3.6 \times 10^{-3}$ M, (b) $c = 9.5 \times 10^{-2}$ M; and dichloromethane–PEI solutions: (c) $c = 5$ wt%, (d) $c = 15$ wt%

solutions. This strongly suggests the existence of intramolecular charge-transfer states induced by an increase in conjugation and hence electronic delocalization afforded by the phthalimide moiety with aromatic substitution.

Absorption spectra of dichloromethane–PEI solutions and of PEI films are characterized by a long-wavelength absorption tail extending to 600 nm, which suggests the existence of transitions with a substantial CT character. By analogy with results obtained on *N*-phenylphthalimide, these CT transitions can be partly attributed to the intramolecular CTC of the *N*-phenylphthalimide moiety present on the polymer chain backbone. However, the red shift of the absorption tail observed in PEI solutions suggests that other CTC may exist in PEI systems, like, for instance, intermolecular CTC, which may be formed concurrently with intramolecular CTC.

Excitation and fluorescence spectra: characterization of intermolecular interaction

A weak fluorescence emission has been detected in all *N*-phenylphthalimide and PEI samples. Dilute NMP–phthalimide solution does not exhibit fluorescence emission, in agreement with results reported in the literature[12,15]. However, solid phthalimide, concentrated NMP–phthalimide solutions and dilute dichloromethane–phthalimide solutions were fluorescent.

Excitation spectra. The excitation spectra characterize the transitions that promote a chromophore from the ground state to an excited singlet state and which are followed by fluorescence emission when the chromophore relaxes back down.

Fluorescence excitation spectra were measured by monitoring the emission intensity at two wavelengths, 530 and 590 nm. The shortest wavelength, $\lambda = 530$ nm, corresponds to an emission band observed in model compounds and PEI solutions. The wavelength $\lambda = 590$ nm was chosen to identify the broad, long-wavelength excitation band responsible for emission of concentrated PEI solutions and of solid samples. The excitation wavelength was scanned from 330 to 570 nm. The excitation spectra of model compounds and PEI solutions are shown in *Figures 4, 5* and *6*. These spectra exhibit two characteristic features. The first one is that the excitation wavelength domain corresponds to the far red CT band of the absorption spectra. The second feature is that two excitation bands are detected:

(i) The first band observed in the wavelength range 350–430 nm is detected in all fluorescent solutions. It is centred at 345 nm in dichloromethane- and NMP–phthalimide solutions. It is progressively red-shifted from 350 nm to 395 nm in dichloromethane–*N*-phenylphthalimide solutions upon increase of the concentration. It is also red-shifted in PEI solutions from 410 nm in dilute solutions to 430 nm in concentrated solutions. The excitation bands of the three systems are broad and structureless. The spectra of *N*-phenylphthalimide solutions have the same shape whatever the wavelength used to monitor the emission intensity. However, specific band shapes are observed for each system. The wavelengths corresponding to emission maxima vary from $\lambda = 500$ nm in PEI solutions to $\lambda = 530$ nm in *N*-phenylphthalimide solutions and to $\lambda = 525$ nm in phthalimide solutions.

(ii) The second band is observed in the wavelength domain 470–580 nm. It is detected in all samples that present a solid phase and in dichloromethane- and NMP–PEI solutions. In this latter case, the intensity of the band increases with polymer concentration. This long-wavelength excitation band is structured: it is composed of a peak at approximately 470 nm and a peak, observed in PEI solutions, at 515 nm. The position of the peaks is constant with respect to PEI concentration over

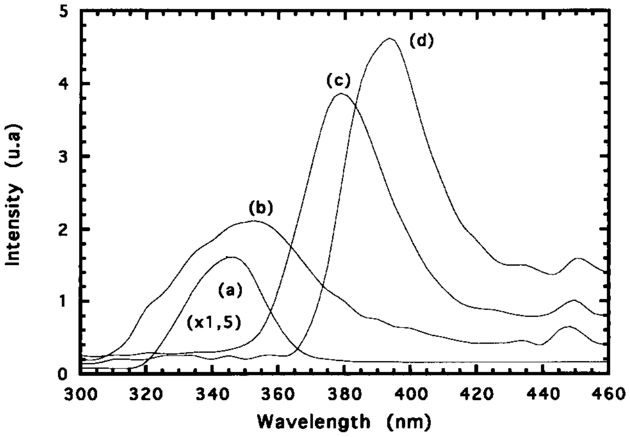

Figure 4 Excitation spectra of dichloromethane–phthalimide solutions: (a) $c = 8 \times 10^{-3}$ M, $\lambda_{obs} = 530$ nm; and dichloromethane–*N*-phenylphthalimide solutions: (b) $c = 3.2 \times 10^{-4}$ M, (c) $c = 9.5 \times 10^{-3}$ M, (d) $c = 8.6 \times 10^{-2}$ M, $\lambda_{obs} = 520$ nm

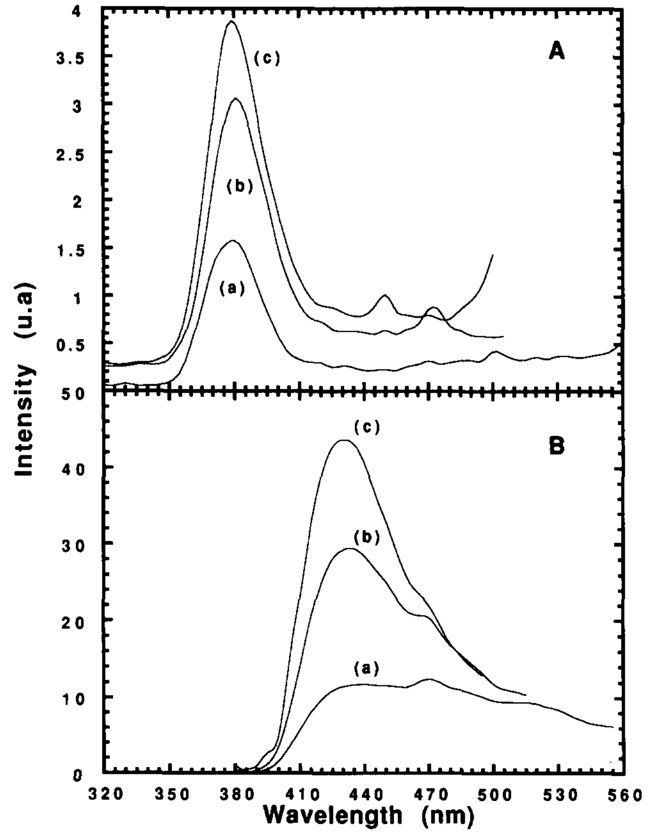

Figure 5 Excitation spectra of dichloromethane–*N*-phenylphthalimide solutions ($c = 9.5 \times 10^{-3}$ M) and a two months aged dichloromethane–PEI solution ($c = 11$ wt%) observed at various wavelengths: (A) *N*-phenylphthalimide solution at (a) $\lambda_{obs} = 520$ nm, (b) $\lambda_{obs} = 550$ nm, (c) $\lambda_{obs} = 590$ nm; (B) PEI solution at (a) $\lambda_{obs} = 530$ nm, (b) $\lambda_{obs} = 550$ nm, (c) $\lambda_{obs} = 590$ nm

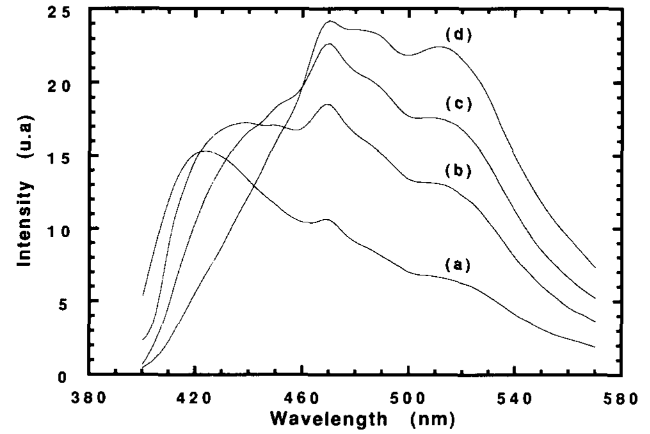

Figure 6 Excitation spectra of dichloromethane–PEI solutions observed at 590 nm: (a) $c = 5$ wt%, (b) $c = 11$ wt%, (c) $c = 15$ wt%, (d) $c = 20$ wt%

the concentration range investigated. The band shape does not depend on the age of the studied PEI solution. In addition, the excitation bands observed on the three compounds containing a solid phase are similar, as clearly seen in *Figure 7*. The corresponding emission maximum, measured for a 20 wt% dichloromethane–PEI solution, was found to be at 585 nm.

Emission spectra. Emission spectra obtained with a short-wavelength excitation (350–430 nm) are shown in *Figure 8* for model compounds and PEI solutions. A broad structureless emission is observed that is blue-shifted from 525 nm for dichloromethane–phthalimide solution to 510 nm for phenylphthalimide solutions and to 500 nm for PEI solutions. The spectra observed for two concentrations of *N*-phenylphthalimide solutions have the same shape, but the emissions of the three compounds studied differ in peak position and half-bandwidth. Similar emission spectra were recently reported in the literature[14].

The emission spectra obtained from excitation wavelengths varying in the long-wavelength band from 460 to 550 nm were measured for a freshly made 20 wt% dichloromethane–PEI solution. As expected from the excitation spectrum, a broad intense structureless band is observed. The intensity of the emission is maximal for an excitation wavelength equal to 475 nm. The emission band is centred at $\lambda = 550$ nm. Another strong emission band centred at $\lambda = 585$ nm is observed after excitation at 520 nm. This suggests that two different chromophores are responsible for the observed emission.

Finally, emission spectra were recorded after excitation at 350 nm (*Figures 9* and *10*). The spectrum of the PEI film is very broad and structureless with an emission maximum at 470 nm, in agreement with results obtained by Hasegawa *et al.*[4,16]. A similar spectrum of weaker intensity is observed in solid *N*-phenylphthalimide. In PEI solutions the emission spectra are broad and the

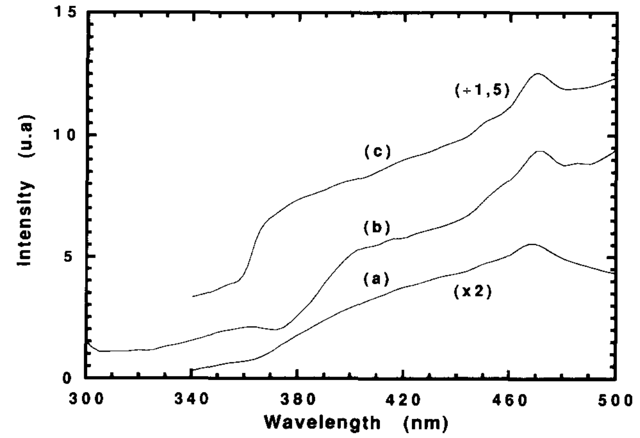

Figure 7 Excitation spectra of systems that present a solid phase: (a) phthalimide, (b) *N*-phenylphthalimide, (c) PEI film; $\lambda_{obs} = 590$ nm

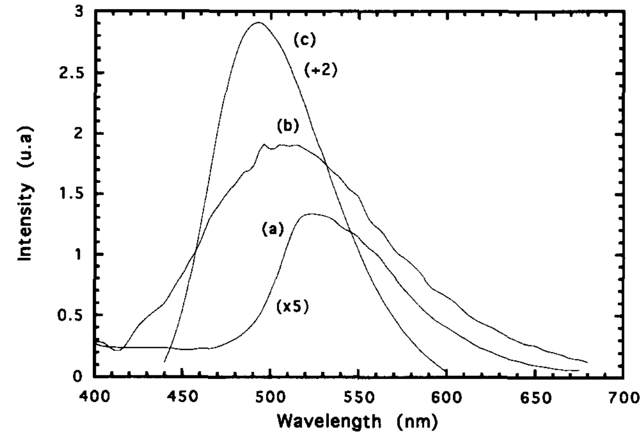

Figure 8 Emission spectra of: (a) dichloromethane–phthalimide solution, $c = 8 \times 10^{-3}$ M, $\lambda_{exc} = 350$ nm; (b) dichloromethane–*N*-phenylphthalimide solution, $c = 9.5 \times 10^{-3}$ M, $\lambda_{exc} = 380$ nm; (c) dichloromethane–PEI solution, $c = 0.1$ wt%, $\lambda_{exc} = 409.5$ nm

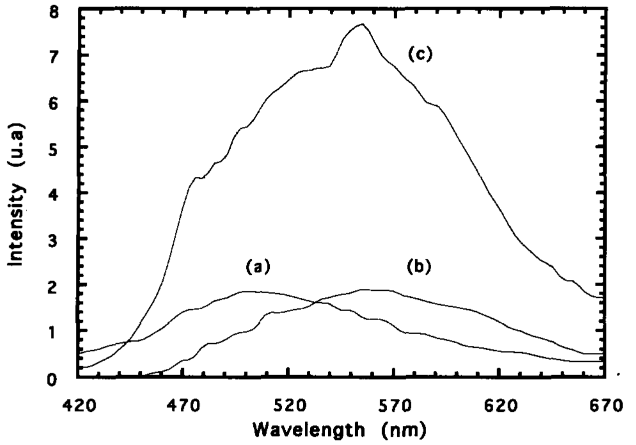

Figure 9 Emission spectra of dichloromethane–PEI solution, $\lambda_{exc} = 350$ nm: (a) $c = 0.1$ wt%, (b) $c = 30$ wt% and (c) two months old solution, $c = 30$ wt%

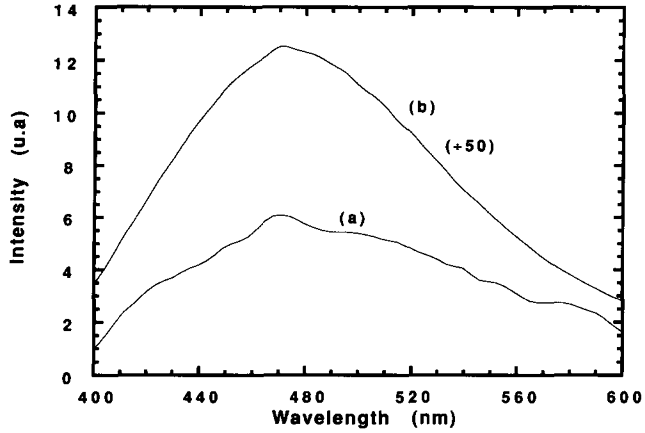

Figure 10 Emission spectra excited at 350 nm: (a) solid *N*-phenylphthalimide, (b) PEI film

intensity is very weak. The fluorescence spectra change upon ageing of the solutions: the overall intensity increases sharply with the age of the solutions, and in old turbid solutions, a shoulder at 470 nm and a peak at 550 nm are clearly observed.

Discussion. The short-wavelength excitation band (350–430 nm) is observed in all solutions of the three compounds studied. The excitation spectra provide broad and structureless emission spectra peaked in the range 500–530 nm due to the existence of charge-transfer states. The sensitivity of the excitation band to the environment of the molecules (concentration of the solutions) observed in this study as well as the sensitivity of the *N*-phenylphthalimide emission spectra with the polarity of solvent reported in ref. 14 strongly suggest the formation of photoexcited CT states of solvated molecules. The large Stokes shift observed in model compounds suggests that the geometry of the emitting CTC is different from that obtained just after excitation. The difference observed in the emission spectra of the three compounds indicates that the steric structures of the excited CTC of the various compounds in solution are different.

More interesting is the second excitation band, which appears in the longer-wavelength domain ($\lambda > 470$ nm). Three features must be noted. First, absorption in the long-wavelength domain suggests direct excitation of a ground-state CTC, since the energy of the lowest excited singlet state of a CTC generally lies below the excited singlet state of either donor or acceptor molecules. Secondly, this band is observed in the spectra of the three compounds studied in the solid state but not in model compounds in solution. Thirdly, the existence of this band in phthalimide spectra suggests that the CTC are of intermolecular nature. Therefore, these features strongly suggest the existence in the solid state of stable CTC among different molecules, thus giving rise to an aggregation microstructure. The existence of CTC in solid phthalimide was also recently evoked by St Clair[9], who proposed that the CTC resulted from the stacking of the electron-rich six-membered rings above the electron-deficient five-membered rings of the phthalimide moiety. This long-wavelength excitation band is also observed in PEI solutions, which suggests the existence of a chain association phenomenon in polymeric solutions.

Finally, the strong long-wavelength fluorescence emission recorded after excitation at 350 nm is observed in solid PEI, solid *N*-phenylphthalimide and turbid aggregated PEI solutions but not in solid phthalimide. This result indicates that the complex mechanisms that lead to this emission require the existence of *N*-phenylphthalimide elements. It also shows that these mechanisms occur specifically in solid or strongly aggregated systems since the emission observed in fresh limpid PEI solutions is very weak. Therefore, this fluorescence emission allows the characterization of a strongly aggregated state of PEI.

An emission spectrum similar to that observed in this study was recently observed in PEI films by Hasegawa *et al.*[16]. The emission maximum at 470 nm was interpreted as being due to CT interactions of intermolecular nature. Their interpretation relied on a series of spectra measured on several commercial polyimides where a red shift of the emission was observed with the increase of electron-donating ability of the imide moiety and electron-accepting ability of the amine moiety. The mechanisms that lead to the observed fluorescence emission and the problem of peak assignments will not be discussed in this work. It will just be concluded from these results that the mechanisms that lead to fluorescence emission at 470–550 nm after excitation at 350 nm reveal the existence of CTC, which involve both diimide electron-acceptor moiety and diamine electron-donor moiety and are characteristic of a solid aggregated state.

Conclusion

The existence of several CT interactions in PEI and model compounds clearly appears from this study. Apart from the formation of photoexcited CT states in solution, the results obtained suggest the existence of an intermolecular ground-state CTC in solid phthalimide and solid *N*-phenylphthalimide and in both PEI solutions and solid PEI. Such CTC can thus be related to an association state of polymer chains in PEI solutions. Lastly, it clearly appears that the study of the fluorescence emission at 470 and 550 nm after excitation at 350 nm is a pertinent method to identify the aggregated state characteristic of old turbid PEI solutions. It is proposed in the following section to use this latter method to observe the time evolution of the physical state of PEI solutions.

TIME EVOLUTION OF POLY(ETHER IMIDE) CONCENTRATED SOLUTIONS

Fresh limpid dichloromethane–PEI solutions kept in sealed tubes at room temperature become progressively turbid. This slow evolution is observed over several weeks. The question arises whether the observed turbidity is due to an irreversible chemical degradation or to a reversible physical effect. This point is addressed in this section: it is proposed to observe the kinetics of aggregation and to investigate the conditions for aggregate dissociation.

Kinetics of aggregation

The kinetics of aggregation of PEI solutions was observed from the observation of the intensity of the emission of fluorescence at 470 and 550 nm after excitation at 350 nm.

The fluorescence emission of a 30 wt% dichloromethane–PEI solution was recorded just after solution homogenization. The sample was then kept at room temperature for nine weeks. The fluorescence emission was recorded every week. The time evolution of the fluorescence spectrum is reported in *Figure 11*. It is observed that the intensity of the fluorescence emission increases sharply with time. Concurrently, the samples become progressively turbid. Roughly spherical particles can be clearly seen using an optical microscope. The size and the number of particles progressively increase upon ageing.

Aggregate dissociation

In order to investigate further the nature of the observed aggregation, a two months old turbid dichloromethane–PEI solution prepared at $c = 24.8$ wt% was dried and then rediluted in dichloromethane at the following concentrations: 5, 10, 15 and 20 wt%. Fluorescence spectra of these rediluted solutions were measured a few hours after the redilution and were compared to those of fresh solutions made directly at each corresponding concentration. These latter solutions are called reference solutions. Results are shown in *Figure 12*. When the concentration is greater than 5 wt%, emission spectra of the aged redilute solutions are very different from those of the corresponding reference solutions. On the one hand, emission spectra of old redilute solutions are more intense than those of reference solutions; and on the other hand, two strong peaks at 470 and 550 nm are observed that do not exist in the spectra of reference solutions. The old redilute solutions are turbid whereas reference solutions are limpid. In contrast, when the concentration of the solutions is equal to 5 wt%, the emission spectrum no longer exhibits peaks at 470 and 550 nm and identical emission spectra are obtained for the reference solution and for the old redilute solution. Concurrently, this latter solution becomes limpid.

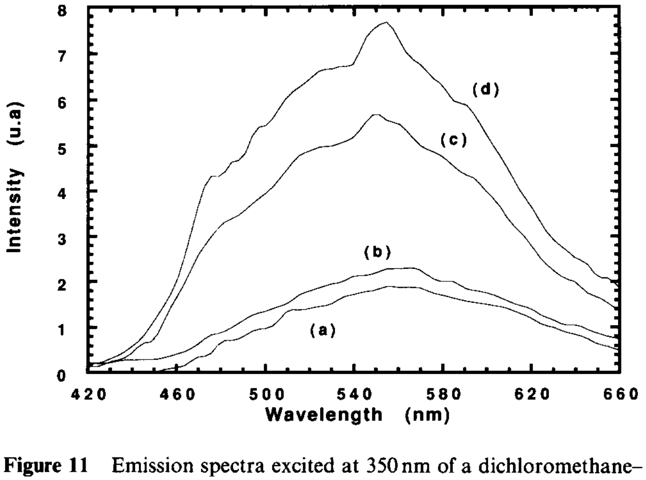

Figure 11 Emission spectra excited at 350 nm of a dichloromethane–PEI solution ($c = 30$ wt%) as a function of the age of the solution: (a) 1–17 days, (b) 24 days, (c) 51 days, (d) 64 days

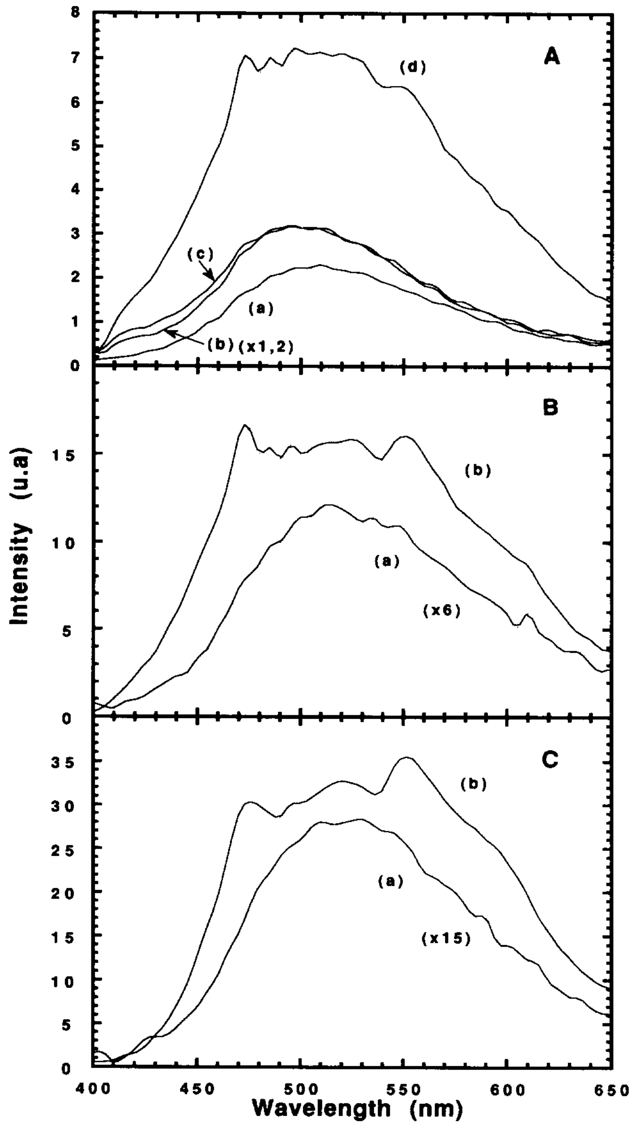

Figure 12 Emission spectra excited at 350 nm of a two months old 24.8 wt% dichloromethane–PEI solution at various redilution concentrations and of corresponding reference solutions (see text): (A) (a) reference solution $c = 11$ wt%, (b) reference solution $c = 5$ wt%, (c) rediluted solution $c = 10$ wt%, (d) rediluted solution $c = 5$ wt%; (B) (a) reference solution $c = 15$ wt%, (b) rediluted solution $c = 15$ wt%; (C) (a) reference solution $c = 20$ wt%, (b) rediluted solution $c = 20$ wt%

Qualitative discussion

There is no detectable irreversible evolution of the PEI concentrated solutions after two months. This fact strongly suggests that no chemical degradation occurs in the system during the ageing process and that aggregation is due to a reversible physical thermodynamic phenomenon: dilution can displace the thermodynamic equilibrium from an aggregated state to a homogeneous soluble state. The fluorescence behaviour suggests that aggregation is induced by formation of CTC among the polymer chains. The formation of CTC is energetically favoured in the system since it lowers the overall energy. However, forcing the macromolecules to be linked together via a CTC reduces the configurational entropy considerably. The time evolution observed on the solutions being slow, it is proposed to describe the physical state of these systems by equilibrium equations. The Flory–Huggins expression for the free enthalpy per site of a homogeneous solution can be used:

$$\Delta G/kT = (1-\phi)\log(1-\phi) + \phi/N \log\phi + \chi\phi(1-\phi) \quad (1)$$

and the free enthalpy per site of a solid aggregate can be written as:

$$\Delta G_{\mathrm{ctc}} = \Delta H_{\mathrm{ctc}} - T\Delta S_{\mathrm{ctc}} \quad (2)$$

where the reference state is the pure melt when no CTC exists among the chains; N is the average number of flexible links of a polymer chain and ϕ is the polymer volume fraction of the solution. The CTC energy and the interfacial energy of the aggregate are accounted for in the term ΔH_{ctc}, and the reduction of entropy due to enhanced local rigidity and link formation between macromolecules are accounted for in the term ΔS_{ctc}. When the two phases are in equilibrium, the chemical potential of chain units in solution:

$$\mu - \mu^{\circ} = -kT[(1-\phi_{\mathrm{d}}) - \chi(1-\phi_{\mathrm{d}})^2] \quad (3)$$

is equal to the chemical potential of chain units in aggregates:

$$\mu_{\mathrm{ctc}} - \mu^{\circ} = \Delta H_{\mathrm{ctc}} - T\Delta S_{\mathrm{ctc}} \quad (4)$$

where the chemical potential per unit of the solution has been derived for polymer of high molecular weight (large value for N); ϕ_{d} is the concentration of the homogeneous part of the solution in turbid solutions (*Figure 13*), which can be calculated from the equality of equations (3) and (4). It can be estimated experimentally: at this concentration the fluorescence spectrum of the turbid solution that has been dried and rediluted is equal to the spectrum of a limpid solution directly prepared at the redilution concentration.

The aggregation process is found to be very slow. This can be understood by considering that a strong free-enthalpy barrier to formation of a CTC between two free chains exists, since crosslink formation considerably reduces the configurational entropy. The formation of CTC likely exhibiting a cooperative aspect, the formation of additive CTC on chains already linked together is expected to induce a smaller loss of configurational entropy and therefore to be faster. When a stable small aggregate is eventually formed, it grows from the progressive sticking of free chains onto the surface of the aggregate.

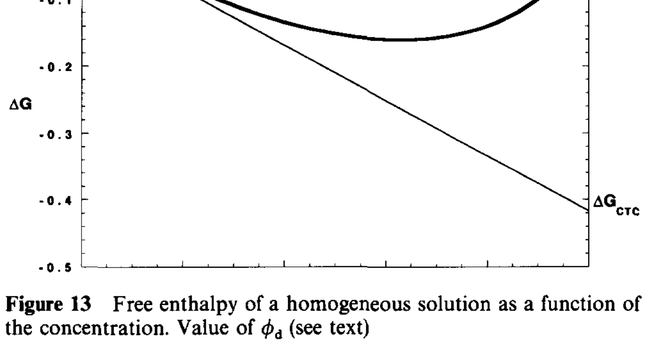

Figure 13 Free enthalpy of a homogeneous solution as a function of the concentration. Value of ϕ_{d} (see text)

CONCLUSION

The study of absorption and fluorescence spectra of PEI clearly showed the existence of CT interactions in solution and in the solid state. The state of aggregation of polymer chains in solution was found to be perceived from fluorescence spectroscopy. More precisely, the observation of the emission peaks at 470 and 550 nm after excitation at 350 nm gave evidence for the existence of a reversible chain association effect related to the formation of CTC in the polymeric solution. In particular, the observation of fluorescence was found to be an appropriate method to study the kinetics of aggregation of solutions and the thermodynamic conditions for aggregate dissociation.

The results show that the microstructure of PEI solutions strongly depends on the age of the solutions. The PEI films obtained from such solutions are expected to exhibit diverse physical properties and microstructures reminiscent of the various aggregation structures of the solutions. It is therefore crucial to characterize the state of aggregation of polyimide solutions. This study shows that the observation of fluorescence emission can provide a control of this aggregation phenomenon.

REFERENCES

1 'Polyimides', Plenum, New York, 1987
2 Wellinghoff, S. T., Ishida, H. and Baer, E. *Macromolecules* 1980, **13**, 834
3 Wachsman, E. D. and Frank, C. W. *Polymer* 1988, **29**, 1191
4 Hasegawa, M., Kochi, M., Mita, I. and Yokota, R. *Eur. Polym. J.* 1989, **25**, 349
5 Dine-Hart, R. A. and Wright, W. W. *Makromol. Chem.* 1971, **143**, 199
6 Kotov, B. V. *Russ. J. Phys. Chem.* 1988, **62**, 1408
7 Ishida, H., Wellinghoff, S. T., Baer, E. and Koenig, J. L. *Macromolecules* 1980, **13**, 826
8 Fryd, M. 'Polyimides' (Ed. K. L. Mittal), Plenum, New York, 1984
9 St Clair, T. L. and St Clair, A. K. *Proc. ACS Div. Polym. Mater.: Sci. Eng.* 1986, **55**, 396
10 Viallat, A., Pedro Bom, R., Cohen-Addad, J. P. and Perez, S. *Polymer* 1992, **33**, 4379
11 Lafemina, J. P., Arjavalingam, G. and Hougham, G. 'Polyimides: Materials, Chemistry and Characterization' (Eds. C. Feger, M. M. Khojastech and J. E. McGrath), Elsevier, Amsterdam, 1989; Arjavalingam, G., Hougham, G. and LaFemina, J. P. *Polymer* 1990, **31**, 840
12 Nurmukhametov, R. N., Belaits, I. L. and Shigoin, D. N. *Russ. J. Phys. Chem.* 1967, **41**, 1032
13 Hoyle, C. E., Creed, D., Nagarojan, R., Subramanian, P. and Anzures, E. T. *Polymer* 1992, **33**, 3162
14 Hoyle, C. E., Anzures, E. T., Subramanian, P., Nagarojan, R. and Creed, D. *Macromolecules* 1992, **25**, 6651
15 Borkent, J. H., Verhreven, J. W. and de Boer, Jh. J. *Tetrahedron Lett.* 1972, **32**, 3363
16 Hasegawa, M., Mita, I., Kochi, M. and Yokota, R. *J. Polym. Sci.* (*C*) 1989, **27**, 263