Viscosity behaviour of poly(ether imide) in solution: intramolecular interaction and intermolecular association effects

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Properties of dilute and semi-dilute solutions of a poly(ether imide), used to form asymmetric membranes, are investigated from viscosity measurements. Several solvents are considered. The analysis of experimental results suggests the existence of associated polymer chains in pyridine. Association is found to occur also in a binary *N*-methylpyrrolidone/water solvent with various concentrations of water. Electron donors and electron acceptors are carried by monomeric units; their interactions are supposed to give rise to the association of polymer chains.

(Keywords: viscosity; poly(ether imide); solution properties; association)

INTRODUCTION

It is now well established that the average conformational structure and properties of aromatic polyimides in the condensed state depend strongly on the state of aggregation of polymer chains[1,2]. Molecular aggregation originates in the strong intermolecular interaction that arises from the formation of charge-transfer complexes between electron-donor and electron-acceptor units located on the chain backbone[3]. Polymeric systems that exhibit molecular association effects, like for instance conducting polymers, are generally characterized by a very poor solubility. However, the solubility of polyimides can be improved by the choice of specific monomer structures able to reduce the association between the polymer chains[4]. The poly(ether imide) (PEI) studied here is of this latter type; it is soluble in several common organic solvents. Thus, it is proposed to examine how association effects appear in solution and to investigate the resulting properties of the PEI. More precisely, it is well known that semi-dilute polymer solutions have a statistical structure. The structural domains are characterized by a correlation length, or mesh size, which confers to the system a transient network structure. Association effects are expected to enhance both lifetime and cohesion of such network structures.

It is worth noting that this polymer is used in solution in view of making asymmetric membranes for gas permeation. The membrane formation process is very fast, which suggests that the structure of the initial solution cannot reorganize itself during the process. Consequently, morphologies and permeametric properties of membranes are expected to depend to some extent on the statistical structure of initial solutions. Furthermore, the thermodynamic equilibrium of the chain association–dissociation phenomenon is not reached instantaneously. Time evolution of the solutions has been observed. For instance, PEI/dichloromethane (DCM) solutions become turbid after several weeks[5], suggesting a chain association mechanism leading to aggregation. PEI/*N*-methylpyrrolidone (NMP)/water solutions exhibit other behaviour: freshly made solutions demix when the temperature is lowered below a characteristic temperature, whereas systems of one month of age remain homogeneous at all temperatures[6]. It is therefore of great interest to characterize the state of association of PEI chains in solution.

In this work, the first results of a detailed study currently conducted on PEI solution properties are presented; we report the viscometric behaviour of dilute and semi-dilute solutions of PEI in several solvents and binary solvents. The aim of the present paper is to give evidence for intermolecular and intramolecular interactions, which occur in the range of low concentration.

EXPERIMENTAL

Samples

The poly(ether imide) is commercially available (Ultem 1000 from General Electric). Its structural unit is represented in *Figure 1*. Its number-average molecular weight M_n is equal to 10 000 with a polydispersity index $I_p = 1.6$. It was dried at 150°C for 4 h before use. Solutions were prepared by gentle shaking at 60°C for 3 days in the 0–8% w/w range of concentration. Solutions had to be studied shortly after homogenization was

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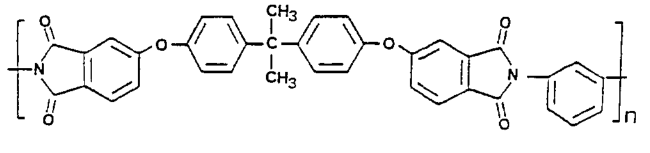

Figure 1 Monomer unit of PEI

achieved because a time evolution of the solutions was observed over several weeks in dichloromethane and in binary NMP/water mixtures.

Viscometry

Viscosity measurements were performed in a Schott Gerate capillary viscometer, which permits easy serial dilutions. All experiments were performed in a water bath regulated at 10, 25 and 50°C ($\pm 0.01°C$).

Data analysis

Intrinsic viscosities were determined from the intercept of the Huggins plot, $(\eta/\eta_s - 1)/c$ *versus* c, and from the plot of $\log(\eta/\eta_s)/c$ *versus* the polymer concentration c ($\mathrm{g\,ml^{-1}}$) in the limit $c = 0$; η_s is the viscosity of the solvent. The resulting plots were linear within a good accuracy for $c < 0.015\ \mathrm{g\,ml^{-1}}$. Huggins constants were derived from the slope of the Huggins plot.

INTRINSIC VISCOSITIES

Figure 2 illustrates the viscometric behaviour of the poly(ether imide) in dichloromethane, NMP and pyridine. In *Figure 3* is reported the viscometric behaviour of the poly(ether imide) in two binary mixtures NMP/water characterized by different water content.

The concentration dependence of the viscosity is usually described by the virial expansion:

$$\eta/\eta_s = 1 + [\eta]c + k_H[\eta]^2c^2 + o(c) \qquad (1)$$

where $[\eta]$ is the intrinsic viscosity and k_H is the Huggins coefficient. At a first glance, experimental curves can be satisfactorily described by formula (1), with the Huggins constants obtained in NMP/water solutions and in pyridine solutions being high, as discussed below (*Figures 4* and *5*). Values obtained for the intrinsic viscosities and for the Huggins constants are listed in *Table 1*.

Nature of solvent

The highest value of intrinsic viscosity is measured in pure NMP. It is slightly smaller in dichloromethane, and the lowest value is observed in pyridine: thus, polymer chains are less expanded in these two solvents than in NMP. The effect of chain contraction is particularly strong in pyridine, where the intrinsic viscosity is reduced by a factor 2 compared to the value obtained in NMP. The effect of chain shrinkage must be primarily associated with the variation of the quality of the various solvents. However, the solubility diagram of the PEI indicates that NMP, dichloromethane and pyridine are good solvents of the polymer[5].

Binary solvent

In the binary solvent NMP/water the intrinsic viscosity is found to decrease on increasing the water content in NMP. This behaviour implies that the macromolecular coils are more compact when water is present in NMP. Contrary to the preceding case concerning the one-component solvents, water is known to be a non-solvent of the polymer. The chains collapse for a polymer concentration equal to 8% w/w and a water content in NMP equal to 6% w/w. Therefore, the quality of the binary solvent NMP/water decreases when the content of water increases in the mixture.

Intramolecular interactions

It is worth emphasizing that the value of the intrinsic viscosity of pyridine is much less than that of NMP though both solvents are good solvents of the PEI. This suggests that the solution properties of PEI cannot be described from the single consideration of the solvent quality. Interactions specific to PEI and to solvents may

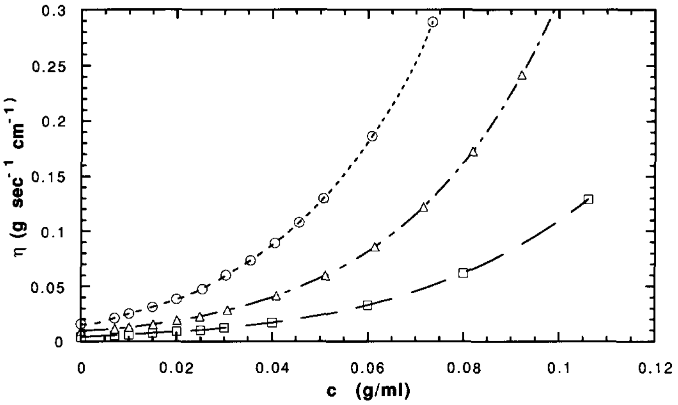

Figure 2 Variation of the viscosity *versus* c: (○) NMP solution; (□) dichloromethane solution; (△) pyridine solution

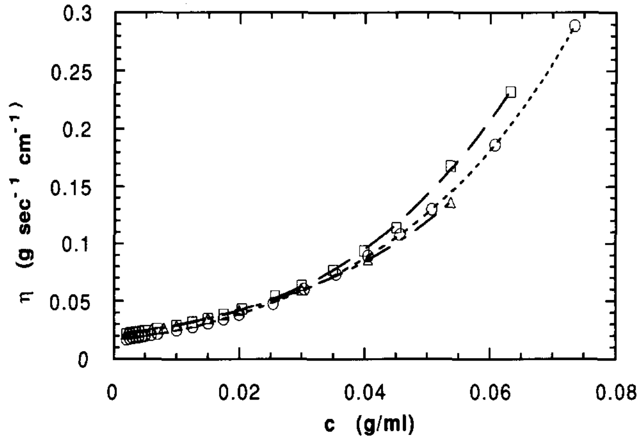

Figure 3 Variation of the viscosity *versus* c in mixed NMP/water solutions: (○) 0% of water; (□) 4% w/w of water; (△) 5% w/w of water

Table 1 Intrinsic viscosity and Huggins constant

	$[\eta]$ (ml g^{-1})			K_H		
	10°C	25°C	50°C	10°C	25°C	50°C
DCM	43	37	–	0.43	0.66	–
Pyridine	25	23	–	2.13	2.44	–
NMP	51	45	–	0.48	0.59	–
NMP/4% H_2O	33	34	29	1.00	0.80	1.16
NMP/5% H_2O	–	25	23	–	1.93	2.23

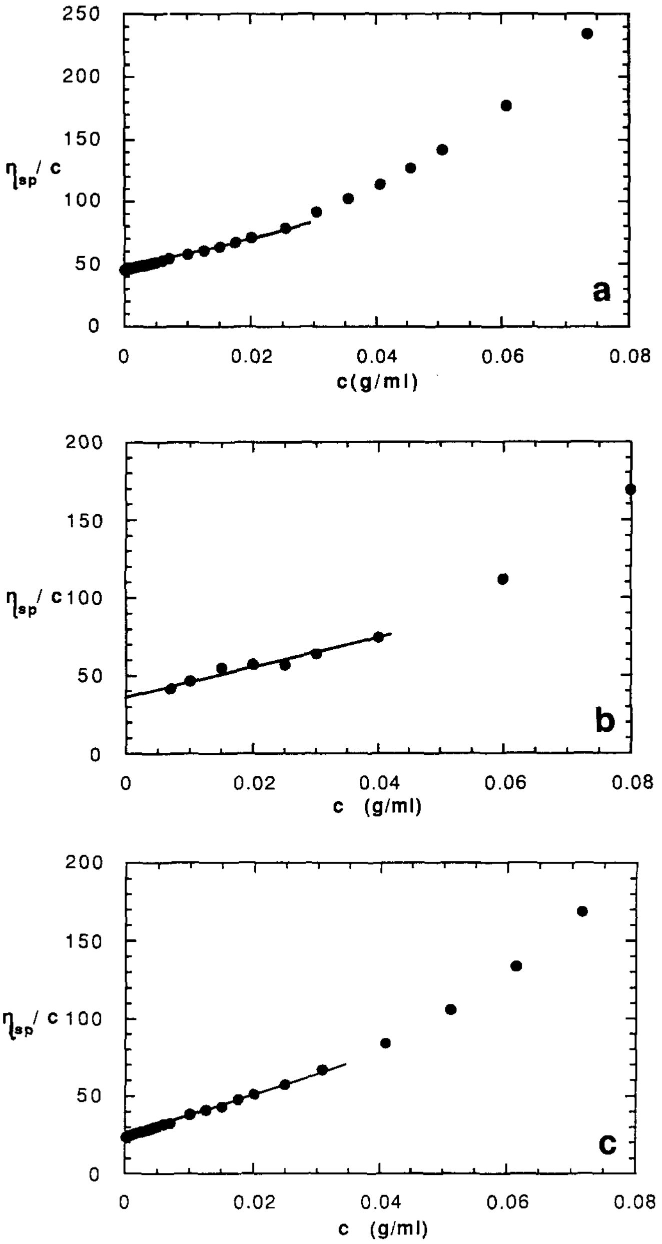

Figure 4 Determination of $[\eta]$ by the Huggins plot: variation of η_{sp}/c *versus c*. The slope of the curve gives the product $k_H[\eta]^2$. (a) NMP solution; (b) dichloromethane solution; (c) pyridine solution

tend to promote the formation of stable associations, which can act as intramolecular aggregates and lead to a reduction of the size of the macrocoils. The existence of attractive interactions in solution has not been shown in this system at this stage. Formation of intramolecular and intermolecular charge-transfer complexes (CTC) has been reported in solution in compounds containing both electron-donor and electron-acceptor groups. In particular, the derivatives of phthalimide are involved in such systems as electron acceptors[7,8]. Intramolecular interaction has also been evidenced in polymeric solutions[9]. Charge-transfer complexes can exist in the PEI studied here, for instance from a π-orbital of the aromatic rings to an orbital of the electron acceptor C=O group. Furthermore, in the systems where the intrinsic viscosity is small, i.e. NMP/water solutions and pyridine solutions, additional interactions exist between monomeric units and solvent molecules (water and pyridine): on the one hand, hydrogen bonds can direct the association between one or two hydrogen atoms of a water molecule with one or two carbonyl groups of the monomeric units into an intramolecular aggregate structure; on the other hand, pyridine and phthalimide groups of monomeric units can form solvent–monomer charge-transfer complexes.

HUGGINS COEFFICIENT

The second quantity to be measured is the Huggins coefficient, which characterizes the effect of pair interactions between chains upon the solution viscosity. The usual experiments show that values of k_H are near 0.8 at the theta temperature and decrease monotonically when excluded-volume effects are less and less screened to reach a limiting value $k_H = 0.3$ in good solvents. Several theories predict the value of the Huggins coefficient under specific limiting conditions. This varies from 0.4 for free-draining coils to 0.76 for non-draining Gaussian coils[10,11].

Nature of solvent

Unlike the intrinsic viscosity, k_H increases on passing from NMP solutions to dichloromethane and pyridine solutions. It is only for NMP and dichloromethane solutions that Huggins coefficients are found to be in the normal range, from 0.4 to 0.6. It is larger than unity for pyridine solution.

Binary solvent

The Huggins coefficient increases also when the water content in NMP increases. Values close to unity are found in the mixed solvents.

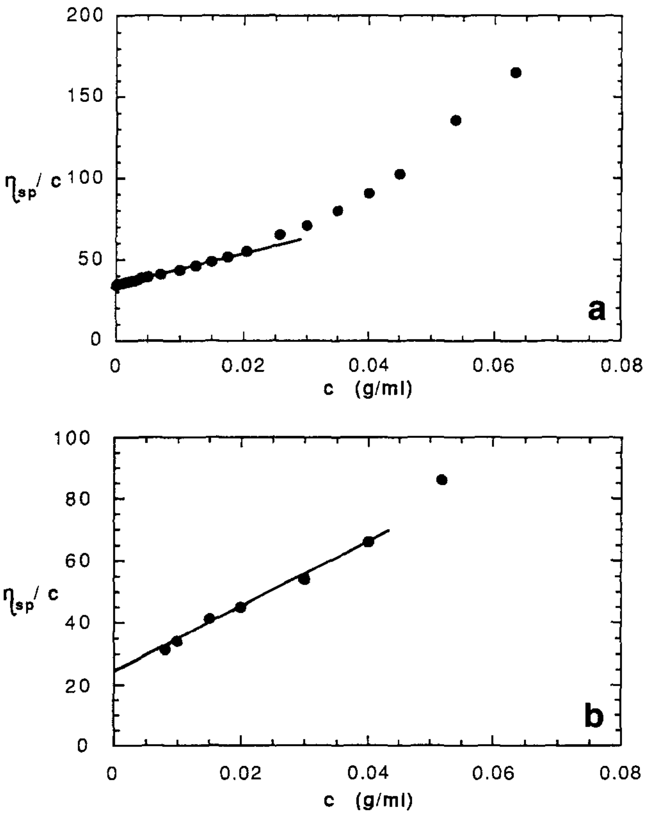

Figure 5 Variation of η_{sp}/c *versus c* in mixed NMP/water solutions: (a) 4% w/w of water; (b) 5% w/w of water

Intermolecular association

This behaviour strongly suggests intermolecular association in NMP/water solutions and in pyridine solutions. The high values of the Huggins constants correspond to small values of the intrinsic viscosities. This is consistent with the presence of molecular association: at low concentration, chain dimensions are reduced due to intramolecular attraction whereas intermolecular aggregation and clustering increase on increasing the polymer concentration. For instance, a similar behaviour is currently observed with ionomers in solution in low-polarity solvents[12]. In this latter case, in dilute solution, the low viscosity is due to dominant intramolecular dipolar association between ion pairs, while at higher polymer concentration, the large values of k_H observed are due to an intermolecular association effect between ion pairs.

In the case of PEI, intermolecular association is very likely due to interactions responsible for intramolecular association in dilute solution. It may be suggested, in agreement with Simionescu's observations[9], that in the semi-dilute regime intermolecular electron donor–acceptor interaction appears, thus inducing the formation of intermolecular charge-transfer complexes similar to those observed in the solid state. CT interactions are not sufficient, however, to induce aggregation in any PEI solution since no association is observed in pure NMP solutions. Hydrogen bonds and CT interactions existing respectively in NMP/water solutions and in pyridine solutions may help the aggregation process. It is not known, however, how these interactions compete with and cooperate with monomer–monomer charge-transfer interaction to determine the aggregate structure.

CTC formation obeys a thermodynamic equilibrium. However, the equilibrium is not reached instantaneously for the following reason: the obtention of an intermolecular charge-transfer complex requires that an electron-donor unit encounters an electron-acceptor unit of another chain with a geometry favourable to a good overlap of their orbitals. This may take a long time for low polymer concentrations. Indeed, time evolution of the solutions was observed over several weeks in dichloromethane and in binary NMP/water mixtures. This would thus support the hypothesis of the presence of charge-transfer interaction in solution. More precisely, it is worth emphasizing that data presented in this work concern freshly made solutions. A subsequent study is devoted to the problem of ageing of these systems.

The solvation of polymeric chains and the stability of association are not greatly influenced by increasing the temperature from 10 to 50°C. Viscometric measurements do not reveal significant variations of $[\eta]$ and k_H.

INTRINSIC VISCOSITY–HUGGINS COEFFICIENT INTERRELATIONSHIP

No theory has been proposed until now to predict the behaviour of the Huggins coefficient when attractive forces between monomers exist in the system. Muthukumar and Freed have recently proposed an approach that applies to the case where the excluded-volume effect is weak[13]. This latter is expressed in terms of a parameter z, proportional to $(1-\theta/T)M^{1/2}$, where M is the molecular weight of the polymer; properties are determined in an asymptotic power-series expansion in z. The coefficient k_H is shown to be expressed as:

$$k_H = k_H(\theta)A([\eta]_\theta/[\eta])^2 - Bz/[\eta]_\theta \qquad (2)$$

where A and B are constants, θ refers to the θ-state and $[\eta]/[\eta]_\theta$ is the viscosity expansion factor. Several appropriate approximations are used in order to obtain the linear variation of k_H with z, which usually is experimentally observed.

In this work, it is proposed to deal with attractive interaction in a manner similar to that used by Muthukumar and Freed. The parameter z thus accounts for the effect of attraction that exists between monomeric units in observed solutions. Values of the expansion coefficient can therefore be less than unity when polymer chains are more contracted than chains in the θ-state, i.e. for solutions characterized by a value of k_H greater than 0.8. The dependence of the Huggins coefficient on the intrinsic viscosity is reported in *Figure 6*. All experimental data, obtained in various solvents and at three different temperatures, fall on a single curve. It is interesting to point out that data referring to solutions that exhibit association effects and data referring to solutions without association effects obey the same law. The Huggins coefficient is found to vary linearly with $1/[\eta]^2$. This is in agreement with the dependence of k_H on $[\eta]$ predicted by formula (2). The term $Az/[\eta]_\theta$ in (2) must be carefully considered since it varies with z. However, it may be considered that z varies in a small interval so that variations of $Az/[\eta]_\theta$ are small and do not affect significantly the law of variation of k_H on $[\eta]$. This behaviour strongly suggests that an attractive force between monomeric units is the main physical phenomenon responsible for the general viscometric behaviour of these systems. When its strength increases, the excluded-volume effect is progressively screened until it is compensated for solutions in the θ-state; stronger attraction further increases the chain contraction effect.

CONCLUSIONS

Poly(ether imides) are known to exhibit association properties in the solid state. A modified PEI can be put into solution in several organic solvents; it may therefore undergo association effects in dilute or semi-dilute solution. This point was addressed in this study from a viscometric approach. The results suggest the existence of an association effect in several systems, depending on

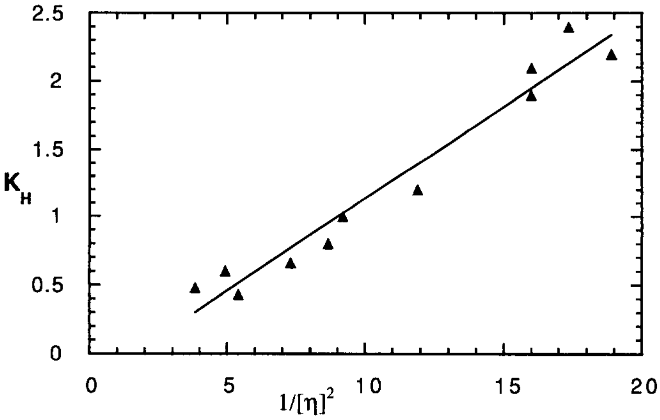

Figure 6 Variation of the Huggins coefficient as a function of $1/[\eta]^2$

the nature of the solvent used in the solutions. It was considered that intrachain association occurred at low concentration and chain aggregation occurred in the semi-dilute regime in the systems where small values of intrinsic viscosities and large values of the Huggins coefficient were observed. The existence of association effects is reinforced by previous observations, which related a time evolution of several solutions and were interpreted on the basis of a slow association–dissociation process.

Formation of charge-transfer complexes may be responsible for the observed behaviour since intramolecular and intermolecular CTC are commonly observed in aromatic polyimides in the solid state. Moreover, additional interactions can exist in solutions, which may help the aggregation process; these can be, for instance, hydrogen bonds or charge-transfer interaction between monomers and solvent molecules.

In closing, it is worth noting that the statistical structure of the solutions then depends both on the nature of solvent and on the age of the solution. This point is of importance because PEI solutions are used to make membranes. The formation process of these membranes is fast, so that it is believed that morphologies and permeametric properties of membranes are correlated to some extent to the state of the initial solution. Mechanisms of chain interaction and time evolution of solutions are currently under investigation and will be reported.

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