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Elution behaviour of polyamic acid and polyamide–imide in size-exclusion chromatography

Yoshiyuki Mukoyama

Goi Works, Hitachi Chemical Co., Ltd., Goi-minami Kaigan, Ichihara, Chiba 290 (Japan)

Naoto Shimizu and To-Ichi Sakata

Ibaraki Research Laboratory, Hitachi Chemical Co., Ltd., Higashi-cho, Hitachi, Ibaraki 317 (Japan)

Sadao Mori*

Faculty of Engineering, Mie University, Tsu, Mie 514 (Japan)

ABSTRACT

The causes of the peculiarities of the elution behaviour of thermoresistant resins, when N,N-dimethylformamide (DMF) is used as the mobile phase were investigated. In order to establish whether the peculiarities are caused by the properties of DMF, by the interactions between the stationary phase and DMF, or by the generation of specific properties of the solutes in DMF, tetrahydrofuran (THF)-soluble polyamic and polyamide–imide resins were prepared. Two stationary phases, hydrophobic polystyrene gel and hydrophilic polymer gel, were used and DMF, THF and a mixture of DMF and THF with or without H_3PO_4 and LiBr were used as the mobile phases. The peculiarities are discussed from the point of dissociation of carboxylic groups of the solutes and of the hydrophilic stationary phase. Adsorption of the resins on the columns or early elution from the columns were prevented by the addition of H_3PO_4 and early elution of the neutral polyamide–imide from the column was prevented by the addition of LiBr. The early elution of the resins was not due to the intramolecular chain expansion of the resins in DMF, but to the interactions between carboxylic groups of the resins and of the hydrophilic polymer gels. The addition of H_3PO_4 suppressed the dissociation of carboxylic groups of the resins. DMF partially controls the dissociation of the carboxylic groups.

INTRODUCTION

Polyamic acid (PAA), which is a precursor of aromatic polyimides, has high heat resistance and is widely used for electronic materials, especially for the surface protection membrane in the production process of integrated circuit (IC). Aromatic polyamide–imide (PAI) is employed as an electrical insulator or in special engineering plastics. These resins are heat resistant and have good film-forming properties. These distinct features are dependent on the monomer type, the composition and the types of end groups and also the molecular weights and molecular weight distributions. However, the deter-mination of molecular weights and molecular weight distributions of these resins by size-exclusion chromatography (SEC) is usually difficult.

As most PAA and PAI are insoluble in tetra-hydrofuran (THF), which is widely used in SEC, N,N-dimethylformamide (DMF) and N,N-di-methylacetamide (DMAc) [1], DMF with 0.01 M LiBr [2], 0.03 M LiBr–0.03 M H_3PO_4–1 vol% THF in DMF [3] and 0.03 M LiBr–0.03 M H_3PO_4–1 vol% THF in DMAc [4] have been reported as mobile phases for the SEC of these resins. Several peculiarities of the elution behaviour of these resins have been observed when DMF or related solvents were used as the mobile phases in SEC.

The objective of this work was to clarify the causes of these peculiarities. In order to establish whether the peculiarities of the elution behaviour of PAA and PAI resins are caused by the properties of DMF itself, by interactions between the stationary phases and DMF, or by the generation of specific properties of the solutes in DMF, THF-soluble PAA and PAI were prepared and the elution behaviour of PAA and PAI resins on two types of stationary phases, hydrophobic polystyrene (PS) gel and hydrophilic polymer gel, was investigated with THF, DMF and a mixture of THF and DMF (1:1) as mobile phases. A column packed with a hydrophilic polymer gel has recently been found to be compatible with several organic solvents such as THF and DMF, in addition to aqueous solvents [5].

EXPERIMENTAL

Samples

PAA was prepared by polycondensation of 2,2-bis[4-(4-aminophenoxy)phenol]propane (BAP) and pyromellitic dianhydride in DMAc. The reaction was continued for 8 h at 25°C and then a portion of water was added to the reaction mixture to precipitate PAA. PAA has two carboxylic groups capable of dissociation and two amide groups in a repeating unit with the following structural formula:
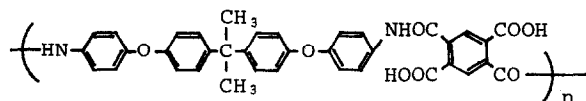
PAI with an acid value of 0 (PAI-A) was prepared by the following procedure. A DMAc solution containing trimellitic anhydride chloride was added dropwise to a DMAc solution containing BAP and triethylamine at 0°C. After 3 h at 0°C, the temperature of the reaction mixture was raised to 20°C, an excess of a mixture of acetic anhydride and pyridine (2:1, v/v) was added, the reaction was continued for 12 h at 20°C and then a portion of water was added to the reaction mixture.

PAI with an acid value of 11 (PAI-B) was obtained by reaction of BAP and trimellitic anhydride with phosphoric acid in N-methyl-2-pyrrolidone (NMP) at 140°C, followed by adding metha-

nol to the reaction mixture to obtain solid PAI-B. The structure of PAI is
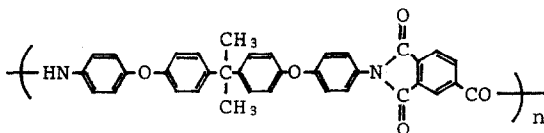
Both PAI-A and PAI-B contain imide and amide groups. PAI-B may contain a certain amount of free carboxylic groups in the chain.

The acid value of PAI was determined by the following procedure. PAI and triethylamine were dissolved in NMP and the solution was titrated with a 0.05 M solution of potassium hydroxide in ethanol. The volume of the titrant (ml) minus the blank was divided by the amount of sample (g) and this ratio (ml/g) is defined as the acid value.

Apparatus

High-performance liquid chromatography (HPLC) was performed with a Hitachi (Tokyo, Japan) Model L6000 liquid chromatograph equipped with a Model L-4000 UV–VIS spectrophotometer. Solvents used as the mobile phase were THF, DMF and a mixture of DMF and THF (1:1, v/v), with and without 0.06 M orthophosphoric acid (H_3PO_4) and 0.03 M lithium bromide (LiBr). The flow-rate of the mobile phase was 1.0 ml/min and the wavelength of the UV detector was 270 nm. The sample concentration was 0.5% (w/v) and a portion of 5 μl of the solution was injected.

Three different types of columns were used. Column A was Gelpack GL-A100MX (30 cm × 7.8 mm I.D.) (Hitachi) packed with PS gel having an exclusion limit of 2 × 10^8 PS molecular weight. This column was used with THF and two columns were connected in series. Column B was Gelpack GL-S300MTDT-5 (30 cm × 7.8 mm I.D.) packed with the same PS gel. This column contained DMF–THF (1:1, v/v) and was used exclusively with this mixture and DMF alone. Two columns were used in series. Column C was Gelpack GL-W550 (30 cm × 10.7 mm I.D.) packed with hydrophilic polymer gel (polyglyceryl methacrylate gel) with an exclusion limit of 2 × 10^6 PS molecular weight. The column was filled with water, but it can be used interchangeably with organic solvents such as DMF, THF–
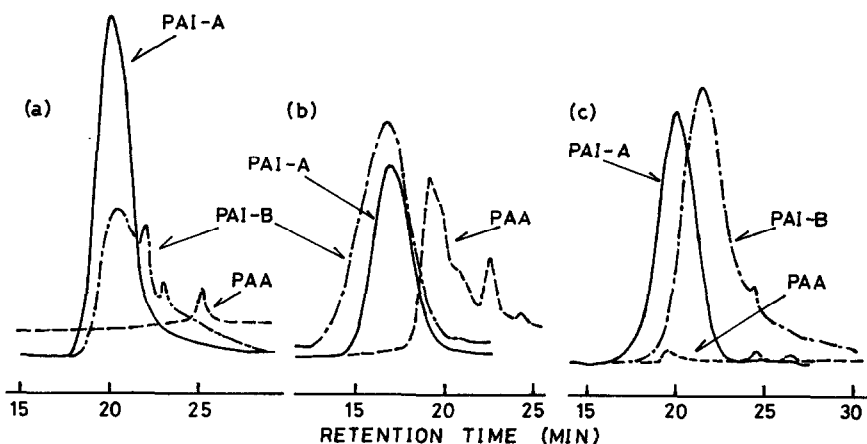
Fig. 1. Chromatograms of PAA and PAI on polystyrene gel columns. Mobile phase and column: (a) THF, column A; (b) DMF, column B; (c) DMF–THF (1:1, v/v), column B.

DMF and alcohols and with aqueous solvents. A single column was used.

RESULTS AND DISCUSSION

Typical chromatograms of PAA, PAI-A and PAI-B in three mobile phases without additives on columns A and B are shown in Fig. 1 and those on column C are shown in Fig. 2. PAI-A which had no free carboxylic groups in the chain showed similar shapes of the chromatograms irrespective of the mobile phase and column. The only difference was in the retention volumes in the different systems of mobile phases and columns: PAI-A eluted at the

exclusion limit of the column in the DMF–column C system (Fig. 2a), whereas it eluted at the normal position of retention volume in other systems. On the other hand, PAA and PAI-B, with free carboxylic groups in the chain, showed different elution profiles in different mobile phases and on different columns. The addition of $0.06\ M\ H_3PO_4$ and $0.03\ M$ LiBr to the mobile phases led to dramatic changes in the elution profiles for these resins and the chromatograms of PAA and PAI-B were almost the same and symmetrical, irrespective of the mobile phase and column. Examples are shown in Fig. 3.
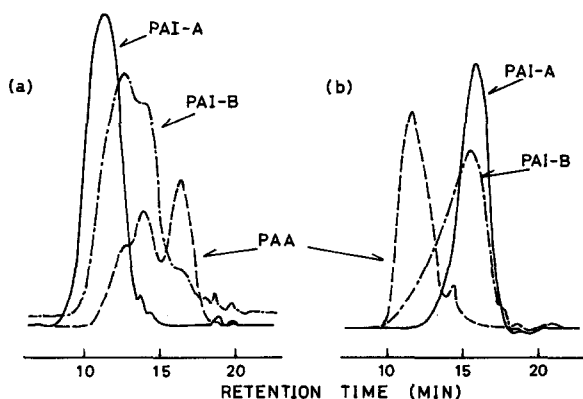

Fig. 2. Chromatograms of PAA and PAI on column C packed with hydrophilic polymer gel. Mobile phase: (a) DMF; (b) DMF–THF (1:1, v/v).
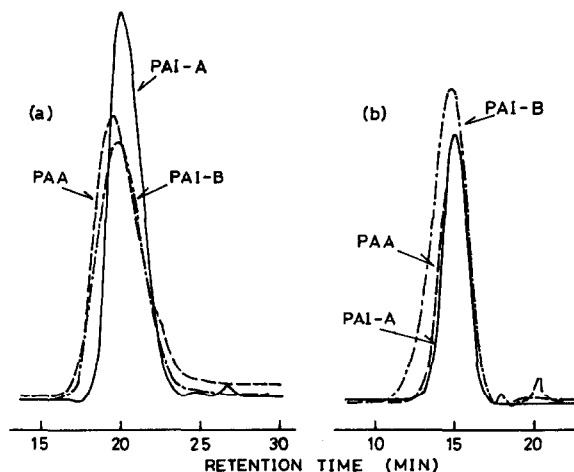

Fig. 3. Chromatograms of PAA and PAI with mobile phases containing H_3PO_4 and LiBr. Mobile phase and column: (a) DMF with $0.06\ M\ H_3PO_4$ + $0.03\ M$ LiBr, column B; (b) DMF–THF with $0.06\ M\ H_3PO_4$ + $0.03\ M$ LiBr, column C.

The elution behaviour of these resins is summarized in Table I. Cha [2] has shown that the elution behaviour of polyacids is profoundly affected by the addition of LiBr to a DMF mobile phase. The chromatogram of polyacid in a 0.1 *M* LiBr–DMF solution had a symmetrical shape and eluted at much higher retention volume than in pure DMF. Nefedov [3] reported the SEC of polyamic acid with a mobile phase consisting of 0.03 *M* LiBr–0.03 *M* H₃PO₄–1 vol% THF in DMF on porous glass and Sephadex columns. He noted that LiBr suppressed polyelectrolyte effects and that the addition of H₃PO₄ improved the solubility of polyamic acid. He also mentioned that the only possible explanation for the anomalous elution behaviour of polyelectrolytes in pure DMF was the expansion of the polyelectrolytes [3].

Although it is possible to consider that the addition of LiBr is effective in suppressing the expansion of polyelectrolytes and in eluting them at the appropriate retention volume [6], it is not sufficient for the elucidation of the elution behavi-

our of the resins in our work. PAI (A and B) eluted at the normal retention volumes in the DMF–PS gel system (Fig. 1b), but at the exclusion limit in the DMF–column C system (Fig. 2a).

In order to interpret the elution behaviour by taking into account the chromatograms and the summary in Table I, the following factors were considered:

(1) The solubility parameters of gels and solvents are as follows: PS gel 18.6, hydrophilic polymer gel such as polyhydroxy methacrylate gel 18.4, THF 18.6 and DMF 24.8 $(J/m^3)^{1/2} \times 10^{-3}$; those with similar solubility parameters were considered to have a greater affinity between them [7].

(2) It is estimated that PS gels have no residual free carboxylic groups, whereas the hydrophilic polymer gels do; the charge of the surface of the hydrophilic polymer gels was negative.

(3) The pH of a 0.5 *M* DMF solution in water is 6.5 [8].

(4) The addition of a small amount of H₃PO₄ to the mobile phase improved the recovery of PAA

TABLE I

ELUTION BEHAVIOUR OF PAA AND PAI IN DIFFERENT MOBILE PHASES

Conditions			Resin		
Column	Mobile phase	Additive[a]	PAA	PAI-A	PAA-B
A	THF	Without	Not eluted	Normal elution	Broad and tailing
		With	Normal elution	Normal elution	Normal elution
B	DMF	Without	Broad and tailing, retardation	Normal elution	Normal elution
		With	Normal elution	Normal elution	Normal elution
B	DMF–THF	Without	Not eluted	Normal elution	Broad and tailing, retardation
		With	Normal elution	Normal elution	Normal elution
C	DMF	Without	Split into two and retardation	Eluted at the exclusion limit with normal shape	Broad and early elution
		With	Normal elution	Normal elution	Normal elution
C	DMF–THF	Without	Eluted at the exclusion limit with normal shape	Normal elution	Leading
		With	Normal elution	Normal elution	Normal elution

[a] 0.06 *M* H₃PO₄ + 0.03 *M* LiBr.

from column A or B, but the addition of LiBr did not improve the recovery.

(5) LiBr is a neutral electrolyte and has two main effects: it reduces the electric double layer on the gel surface to minimize the ion-exclusion or the electrostatic repulsion effects [9], and it decreases the expansion of the resin to elute them at the expected retention volume.

(6) H_3PO_4 is a weak acid and suppresses the dissociation of weakly acidic substances. H_3PO_4 also acts as an electrolyte.

In this paper, the role of H_3PO_4 is mainly discussed from the point of view of the dissociation of the carboxylic groups in the chain of the resins.

Elution behaviour of PAI-A

PAI-A had an acid value of zero and was considered not to have free carboxylic groups in the structure. Only amide and imide groups may interact with gels. The elution of PAI was normal on PS columns, irrespective of the mobile phase with or without the LiBr and H_3PO_4 additives. On the other hand, it eluted at the exclusion limit on column C with DMF (Fig. 2a), and the addition of the additives or THF (Fig. 2b) was effective in eluting it at the expected retention volume. These results suggest that the expansion of PAI-A in DMF, which was pointed out by Nefedov *et al.* [1], was not observed in the DMF–PS gel system (Fig. 1b) and the elution at the exclusion limit in the DMF–column C system is due to the interaction of PAI-A with the stationary phase. It is important to note that the interrelation between the mobile phase and the stationary phase must be taken into account when the elution behaviour of solutes is discussed.

The anomalous elution behaviour of PAI-A in pure DMF on column C is explained as follows. Although DMF has a high basicity parameter [10], the pH of a DMF solution in water is below 7.0 [8]. Therefore, the dissociation of the residual carboxylic groups on the surface of the hydrophilic polymer gel may be substantially suppressed. The surface of the gel is negatively charged owing to a small extent of the dissociation or to the non-dissociated carboxylic groups. The solubility parameter of DMF is far from that of the gel and the solute molecules can approach close to the gel surface, resulting in an electrostatic repulsion between the gel surface and the solute molecules. PAI-A may have a negative

charge on the surface due to n electrons on oxygen and nitrogen atoms on the surface. The addition of LiBr to DMF reduces the electric double layer in the pores of the gel, resulting in the facile approach of the solute molecules to the inside of the gel pores. The addition of THF prevents the access of the solute molecules to the surface of the gel, because the solubility parameter of THF is close to that of the gel and THF molecules are assembled on the surface of the gel much more than DMF molecules.

Elution of PAA

PAA contained two carboxylic groups in a repeating unit and the interaction with the stationary phase is assumed to be higher than that with PAI-A. In the THF–PS gel system (Fig. 1a), the retardation of carboxylic acids is well known because of the adsorption on the gel surface. The situation is similar to PAA molecules and PAA retained in the column in the THF–PS gel system, because of the adsorption of PAA on the gel surface. The addition of H_3PO_4 suppressed the dissociation of the carboxylic groups of PAA and eluted PAA from the column. Although DMF suppressed the dissociation of the carboxylic groups, a small amount of dissociation still caused the adsorption of PAA on the surface of the gel to some extent (Fig. 1b). The addition of THF to DMF (Fig. 1c) increased the dissociation of carboxylic groups due to the decrease in the acidity of the mobile phase, resulting in an increase in adsorption.

The elution behaviour in the DMF–column C system (Fig. 2a) is considered to be the same as that in the DMF–PS gel system. The addition of THF (Fig. 2b) accelerated the dissociation of the carboxylic groups of both PAA and of the gel, and the access of PAA molecules to the gel surface was prevented because of the superior access of THF molecules to the gel surface, resulting in an ion-exclusion effect between them. The addition of H_3PO_4 suppressed the dissociation of the carboxylic groups of both PAA and of the gel and the addition of LiBr reduced the electric double layer of the gel pore.

Elution behaviour of PAI-B

PAI-B has one free carboxylic group per three repeating units, and thus it must have an intermediate behaviour between PAA and PAI-A. A typical

example is shown in chromatograms obtained in the THF–PS gel system (Fig. 1a). In the DMF–PS gel system (Fig. 1b), the dissociation of PAI-B was suppressed and the normal elution behaviour was observed. The addition of THF to the DMF–PS gel system (Fig. 1a) partially accelerated the dissociation of PAI-B and peak broadening was observed as a result of the adsorption effects.

In the DMF–column C system, early elution of PAI-B was observed because of the ion-exclusion effect. The addition of THF caused the chromatogram of PAI-B to be asymmetric. The peak shape indicates that the interphase distribution is characterized by a concave sorption isotherm which is formed as a result of the electrostatic exclusion [1]. The roles of the additives are the same as those for PAA.

CONCLUSIONS

In this paper, the elution behaviour of PAA and PAI has been discussed from the point of view of the dissociation of the carboxylic groups in the chain of the resins and those in the stationary phase of the hydrophilic polymer gel. The addition of H_3PO_4 to the mobile phase suppressed the dissociation of the carboxylic groups and was very effective in preventing the adsorption of the resins to the gel surface or the ion-exclusion effect between them.

DMF controls the dissociation of carboxylic groups of the resins. The early elution of the resins was not due to the intramolecular chain expansion of the resin in DMF, but to the interactions between

carboxylic groups of the resins and of the hydrophilic polymer gels. Although potentiometric titration of the hydrophilic polymer gels showed that the acid value of the gels was zero, it was assumed that the gels have a small amount of the residual carboxylic groups.

The addition of LiBr may be effective in preventing the association of the resins and in eluting them at much higher retention volumes than in pure DMF. It can be concluded that H_3PO_4 acts to suppress the dissociation of the carboxylic groups of the resins and of the hydrophilic polymer gel, and LiBr acts to prevent the association of the non-dissociated resins.

The optimum system for the SEC of these resins was DMF with H_3PO_4 + LiBr and column B or DMF–THF (1:1, v/v) with H_3PO_4 + LiBr and column C. For PAI-A, the system can be used without the additives.

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