

# Change in the molecular weight distribution of poly(ethylene oxide) caused by the complexation with poly(acrylic acid)

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The complexation between poly(ethylene oxide) (PEO) and poly(acrylic acid) (PAA) was made by using double the molar quantity of either polymer component at pH 2 where the resulting complex completely precipitates. After the removal of the precipitate, PEO or PAA remaining in the supernatant was subjected to gel permeation chromatography to investigate the change in the molecular weight distribution (*MWD*) caused by the complexation. No remarkable difference is observed in the *MWD* curves for PEO[1] ( $M_w = 1.37 \times 10^4$ ) before and after the complexation with PAA[1] ( $M_w = 1.10 \times 10^3$ ) and PAA[2] ( $M_w = 4.16 \times 10^5$ ). However, the *MWD* curves of PEO[2] ( $M_w = 1.26 \times 10^5$ ) and PAA[2] become shortened and shift to the low molecular weight side after the complexation with PAA[1] or [2] and PEO[2], respectively. This tendency is enhanced by increasing the complexation temperature. From these results, it is indicated that the complexation between PEO and PAA deals with an equilibrium reaction, and the equilibrium constant is dependent on the chain length of both polymer components and also on the complexation temperature.

**Keywords** Poly(ethylene oxide); poly(acrylic acid); molecular association complex; equilibrium reaction; gel permeation chromatography; molecular weight distribution

## INTRODUCTION

Molecular association complexes or polymer-polymer complexes result from mixing aqueous solutions of poly(ethylene oxide) (PEO) and a polycarboxylic acid such as poly(acrylic acid) (PAA). Bailey *et al.*<sup>1</sup> have reported that the complexation is promoted through hydrogen bonding affinity of the ether oxygens in PEO to the carboxyl groups in PAA. Osada *et al.*<sup>2-5</sup> further showed that PEO undergoes reversible association-dissociation in an aqueous medium with poly(methacrylic acid) (PMAA) and the equilibrium varies with molecular weight of PEO, temperature and other things. On the basis of these results, they pointed out that hydrophobic interaction is a significant factor in the stabilization of the complex between PEO and PMAA<sup>5</sup>. Taking these facts into account, it is possible to expect that the change in the molecular weight distribution (*MWD*) for the polyether and/or polycarboxylic acid takes place during the course of the complexation. However, until recently no information about the change of *MWD* during the complexation has been available, although this is an important problem to understand directly the molecular association mechanism. The purpose of this paper is to present some data on the *MWD* curves of PEO and PAA before and after the complexation and to reinvestigate the complexation mechanism.

## EXPERIMENTAL

### Materials

PEO was commercially obtained from Aldrich Chemical Co. Inc. PAA was also of commercial origin (Toa Gosei Kagaku Co.). The purification and molecular weight determination were made in the same manner as described previously<sup>6,7</sup>. The weight-average molecular weights for both sample polymers are: PEO[1],  $1.37 \times 10^4$ ; PEO[2],  $1.26 \times 10^5$ ; PAA[1],  $1.10 \times 10^3$ ; and PAA[2],  $4.16 \times 10^5$ .

### Complexation

The sample was dissolved in distilled water in the concentration of  $0.005-0.0005 \text{ mol l}^{-1}$  (in terms of monomer units), and then the pH of the sample solutions was adjusted to  $\text{pH } 2.0 \pm 0.1$  with 1 N HCl. A mixture of PEO and PAA solutions (2:1 or 1:2 v/v) was stirred at 20° and 50°C for 10 h and was then allowed to stand for about 14 h to precipitate the resulting complex. To avoid change in temperature which might have caused re-equilibration during filtration, the precipitated complex was isothermally separated through a 0.1  $\mu\text{m}$  filter. The composition of the complex was determined by measuring the residual polymer concentration of the supernatant using a Beckman total organic carbon analyser (model 915-B). The analytical technique was reported previously<sup>6</sup>.

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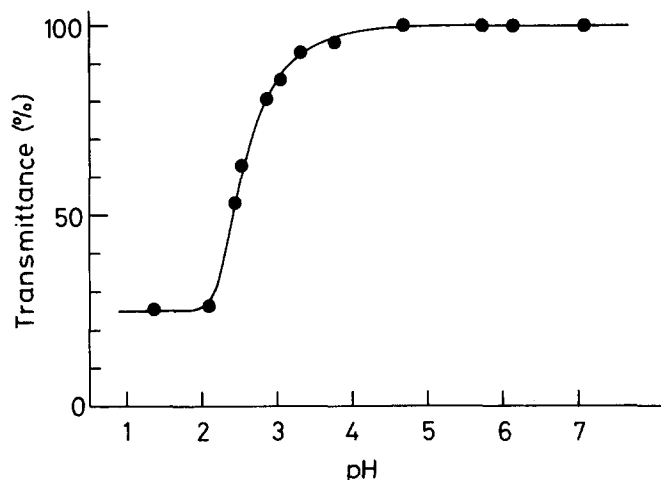


Figure 1 Change of transmittance for a 2:1 molar mixture of PEO[2] and PAA[2] as a function of pH. The sample was prepared by mixing PEO and PAA solutions ( $0.005 \text{ mol l}^{-1}$ ) in a volume ratio of 2:1. The measurement was made at  $420 \text{ nm}$  with a cell having light path  $1 \text{ cm}$

#### Gel permeation chromatography

The *MWD* for PEO or PAA remaining in the supernatant liquid was determined by gel permeation chromatography (g.p.c.). However, the supernatant is so dilute that it cannot be directly subjected to the g.p.c. measurement. Thus, the sample solution was prepared by lyophilizing the supernatant, followed by dissolving the polymer obtained in  $0.1 \text{ N NaCl}$  solution in the concentration of about  $0.045 \text{ mol l}^{-1}$ . The g.p.c. analysis was carried out by using a Hitachi 633A liquid chromatograph equipped with a Shodex RI detector (model SE-11). The g.p.c. curve for PEO was measured by making connection through a Shodex OH pack B-806 column to a Shodex OH pack B-804 column (polymer concentration =  $0.045 \text{ mol l}^{-1}$ ; sample size =  $400 \mu\text{l}$ ; flow rate =  $1 \text{ mol/min}$ ; pressure =  $20 \text{ kg cm}^{-2}$ ). PAA was analysed only with the B-806 column.  $\text{NaCl}$  solution ( $0.1 \text{ N}$ ) was used as the effluent. The  $M_w/M_n$  ratio, which is an indication of *MWD*, was determined from the g.p.c. data by the method of Cazes<sup>8</sup>. A calibration curve, expressed as the relationship between the elution volume ( $V$ ) and the molecular weight ( $W$ ), was obtained by using standard PEO samples. The results are represented by  $\log M = -0.25V + 11.3$ .

## RESULTS AND DISCUSSION

The g.p.c. analysis for excess PEO remaining in the system after the complexation with PAA is a useful method for obtaining information about the change in *MWD* caused by the complexation. As shown in Figure 1, a precipitate or turbidity develops when PAA was mixed with double the molar quantity of PEO in the acidic region below pH 4. This is in fair agreement with the result of viscometric measurement for an equimolar mixture of PEO and PAA<sup>1</sup>, and indicates that the PEO-PAA complex forms as a precipitate from aqueous solution below pH 4 even when an excess of PEO is mixed with PAA. Thus, the PEO sample for g.p.c. measurement can be obtained by separating the precipitated complex, if uncomplexed PAA does not remain in the system.

To determine whether the uncomplexed PAA remains or not, the i.r. spectrum was measured for the sample obtained by lyophilizing the supernatant liquid from

which the precipitated complex has been removed. The investigation was at first carried out for the system composed of the high molecular weight polymers: PAA[2] was complexed with double the molar quantity of PEO[2] at  $20^\circ$  and  $50^\circ\text{C}$  in aqueous medium adjusted to pH 2 where the carboxyl group in PAA is protonated completely<sup>7</sup>. No strong absorption at  $1720 \text{ cm}^{-1}$ , which is assigned to the carboxyl group, was observed in the spectrum for the lyophilized sample. In addition, the pattern of the spectrum completely agreed with that of PEO. It is thus evident that the uncomplexed PAA does not remain in the system after the complexation with PEO. The composition of the resulting complex, expressed as molar ratio of the monomer units, was PAA:PEO = 1:1.1 ( $20^\circ\text{C}$ ) and 1:1.3 ( $50^\circ\text{C}$ ), as determined from the residual amount of PEO in the supernatant. Figure 2 shows the g.p.c. curves of PEO[2] before and after the complexation. It is observed that a broad elution pattern of the original PEO is shortened and shifted to the low molecular weight side caused by the complexation with PAA. Furthermore, the increase in the complexation temperature enhances the change in the elution pattern after the complexation. Similar results were obtained even when the complexation was made by using more dilute polymer solutions ( $0.001\text{--}0.0005 \text{ mol l}^{-1}$ ). It has been found by a control experiment that the g.p.c. curve of PEO[2] is unchanged by the operating conditions for the g.p.c. and complexation. Therefore, the results obtained

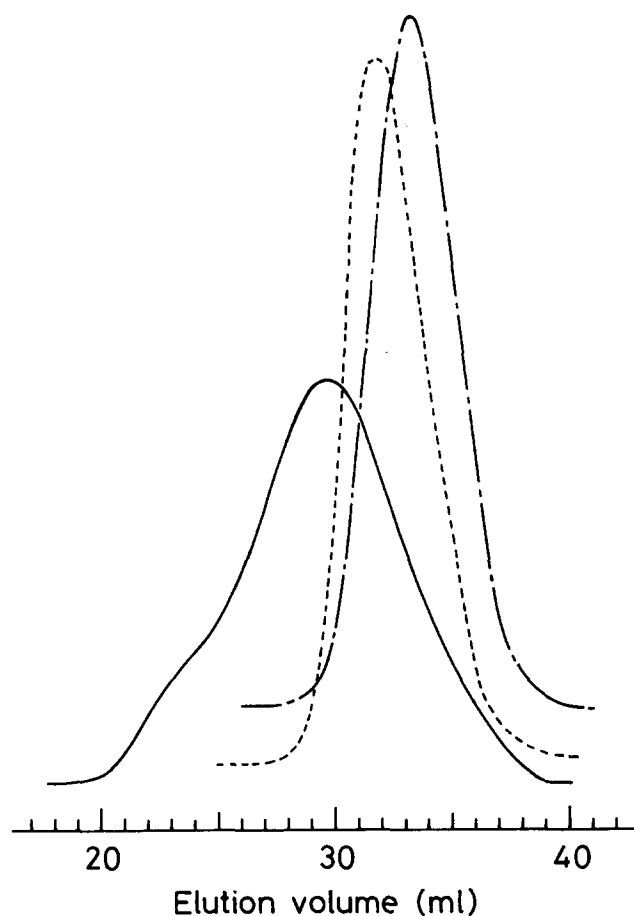


Figure 2 Change of g.p.c. curve for PEO[2] caused by complexation with PAA[2]: —, before complexation; ---, after complexation at  $20^\circ\text{C}$ ; ···, after complexation at  $50^\circ\text{C}$ . The complexation was made by mixing PEO and PAA solutions ( $0.005 \text{ mol l}^{-1}$ ; pH 2) in a volume ratio of 2:1

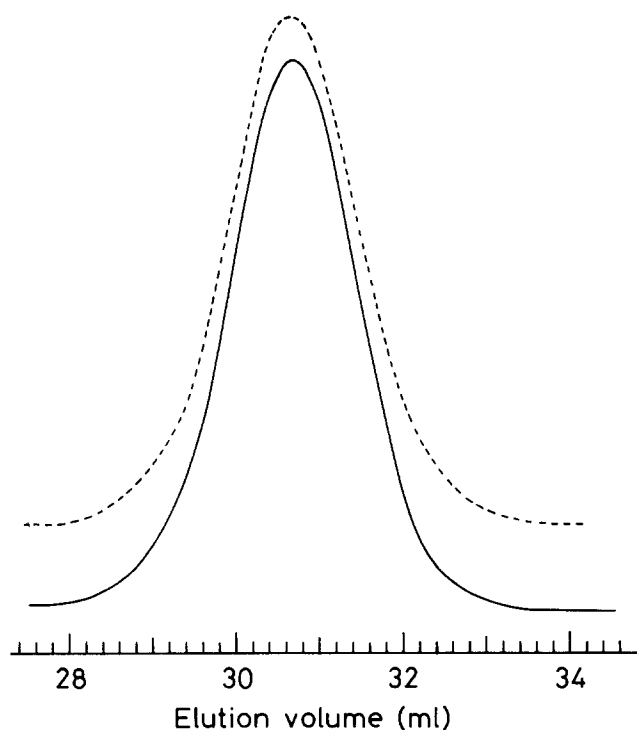


Figure 3 Change of g.p.c. curve for PEO[1] caused by complexation with PAA[2]: —, before complexation; ---, after complexation at 50°C. The complexation conditions are the same as described in Figure 2

could mean that, during the course of the complexation, the high molecular weight fraction of PEO preferentially forms the complex with PAA, and the molecular weight range of the complexed PEO fraction is broadened out to the low molecular weight side by increasing temperature.

The investigation was further extended to the system composed of PEO[1] and PAA[2]. The complexation was done under the same conditions as described above. It was confirmed that no uncomplexed PAA remains in the system. The composition of the complex was PAA:PEO = 1:1.2 at 20°C and 1:1.3 at 50°C. Figure 3 shows the g.p.c. data of PEO[1] before and after the complexation. In contrast to the high molecular weight PEO, no distinguishable difference is observed in both elution patterns even when the complexation was made at 50°C. Consequently, it is apparent that, in the case of the low molecular weight PEO, the *MWD* is unchanged by complexing with the high molecular weight PAA.

In order to confirm this result, the complexation between PEO[1] and PAA[1] was carried out under the same conditions as mentioned above. In this case, however, the g.p.c. curve shows a broad elution pattern because part of the uncomplexed PAA remains in the system after the complexation (see Figure 4). Thus, it is necessary to remove the uncomplexed PAA to obtain accurate g.p.c. data of PEO after the complexation. For this purpose, trimethylammonium glycol chitosan iodide (TGCI), or 6-O-(2-hydroxyethyl)-2-(trimethylammonium)-chitosan iodide<sup>6,9</sup>, was used as a precipitant for the uncomplexed PAA, since it has been found<sup>10</sup> that TGCI forms stoichiometrically a water-insoluble polyion complex with PAA in the pH range above 10. As shown in Figure 4, the elution pattern after which both precipitated complex and uncomplexed PAA were removed is in agreement with that of PEO[1] before the complexation,

although a small peak which could be due to the residual PAA appears in the elution volume range around 34 ml. It is therefore found that the *MWD* for the low molecular weight PEO is also unchanged by the complexation with the low molecular weight PAA.

The  $M_w/M_n$  ratios of PEO before and after the complexation with PAA, estimated from g.p.c. data, are summarized in Table 1. The following important features are recognized: (a) The *MWD* for the high molecular weight PEO becomes shortened and shifts to the low molecular weight side after the complexation with the high and low molecular weight PAA. (b) These are accelerated with the increase in the complexation temperature. (c) No remarkable change in the *MWD* arises from complexing the low molecular weight PEO with the high and low molecular weight PAA. On the other hand, the data on the composition of PEO-PAA complex showed that the content of PEO in the complex prepared at 50°C is larger than that at 20°C (see above). The

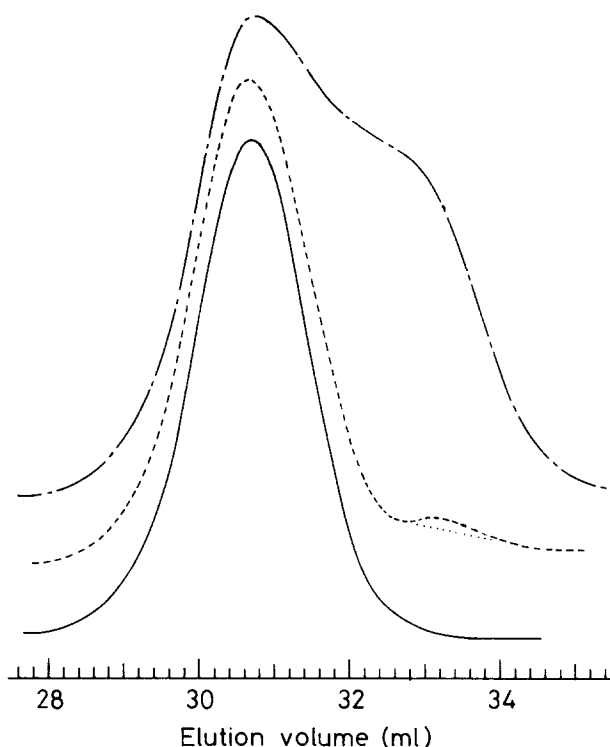


Figure 4 Change of g.p.c. curve for PEO[1] caused by complexation with PAA[1] at 50°C: —, before complexation; ---, after complexation (these g.p.c. data were obtained for the supernatant containing uncomplexed PAA); - · -, after complexation (this was obtained for the sample from which the uncomplexed polymer has been removed by treating with TGCI). The complexation was carried out under the same conditions as shown in Figure 2

Table 1 Change in  $M_w/M_n$  ratio of PEO caused by complexation with PAA at different temperature\*

Sample	Before complexation	After complexation with PAA[1]		After complexation with PAA[2]	
		20°C	50°C	20°C	50°C
PEO[1]	1.23	1.20	1.22	1.24	1.23
PEO[2]	20.2	4.84	—	3.43	2.46

\* The complexation was carried out under the same conditions as mentioned in Figure 2

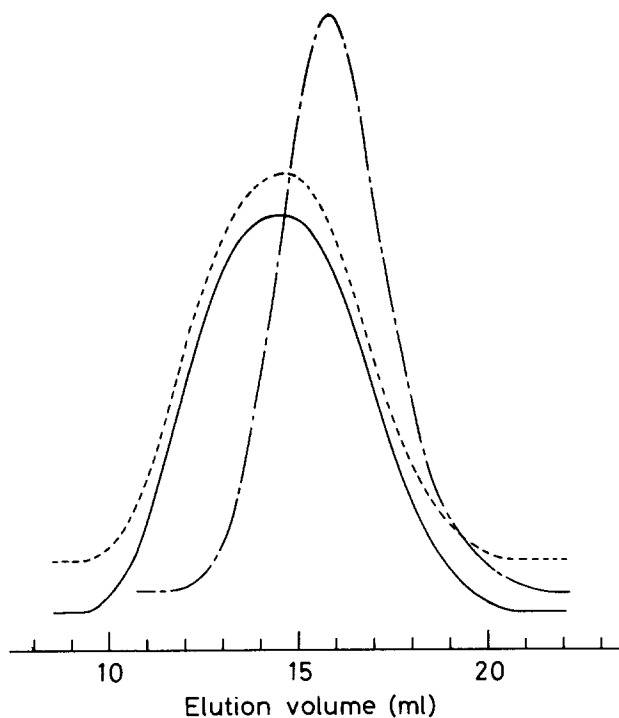


Figure 5 Change of g.p.c. curve for PAA[2] caused by complexation with PEO[2] and TGCI: —, before complexation; ---, after complexation with PEO[2] at 20°C; - · -, after complexation with TGCI at room temperature. TGCI was complexed with double the molar quantity of PAA at pH 10. The complexation between PAA and PEO was carried out under the same conditions as described in Figure 2, except that the mixing ratio of PEO to PAA is reversed

sequence of these events suggests that the polymer-polymer complexation between PEO and PAA deals with an equilibrium reaction and the equilibrium constant is dependent on the chain length of PEO and also the complexation temperature. These are in fair agreement with the fact that the stability constant of PEO-PAA complex increases with increasing temperature and molecular weight of PEO<sup>5</sup>.

Taking into account the results described above, it is possible to assume that the change in the *MWD* for PAA could take place during the course of the complexation. In order to confirm this assumption, PEO[2] was complexed

with double the molar quantity of PAA[2] at 20°C. According to the method of Attia and Rubio<sup>11</sup>, it was confirmed that no uncomplexed PEO remains in the supernatant from which the precipitated complex was removed. The composition of the resulting complex was PAA:PEO=1:1.1. The g.p.c. curves of PAA[2] before and after the complexation are shown in Figure 5. In this Figure, the result after the complexation with TGCI is further included to examine the *MWD* change caused by the complexation between oppositely charged polyions. It is found that no pronounced change appears in the g.p.c. curve of PAA after the complexation with TGCI, whereas there is a remarkable difference in the elution patterns for PAA before and after the complexation with PEO. These mean that the equilibrium constant for the complexation between PEO and PAA is dependent not only on the chain length of PEO but also on that of PAA.

## CONCLUSION

The present study indicates that the molecular association between PEO and PAA deals with an equilibrium reaction. Hydrogen bonding<sup>1</sup> between the ether oxygens in PEO and the carboxyl groups in PAA and hydrophobic interaction<sup>5</sup> between the methine and/or methylene groups in both polymers, which could be influenced by chain length and temperature, can be considered to play an important role in the molecular association process.

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