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INTERMACROMOLECULAR COMPLEXATION BETWEEN POLY(METHACRYLIC ACID) HYDROGELS AND POLY(ETHYLENE GLYCOL)

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ABSTRACT

The interaction of poly(methacrylic acid) (PMAA) hydrogels with poly(ethylene glycol) (PEG) has been investigated by means of FT-IR spectroscopy and refractometry. It has been shown that PEG molecules penetrate a swollen PMAA network and form intermacromolecular complexes (IMCs) with PMAA. The kinetics data indicate that the decrease of the chain length of PEG macromolecules results in the lowering of the rate of PEG diffusion in the gel. The dissociation constants K and the composition θ of PMAA gel-PEG complexes have been determined. It was found that the stability of IMCs as well as the equilibrium fraction of PEG in the IMC lower sharply with a decrease of molecular weight of PEG. The complexation causes a contraction of the PMAA gel in neutral medium and the collapse of the gel in acid medium. It was found that at an excess of PMAA with respect to PEG, the complex forms essentially in the outer layer of the gel.

INTRODUCTION

The formation of nonionic intermacromolecular complexes (IMCs) between linear poly(methacrylic acid) (PMAA) and poly(ethylene glycol) (PEG), their structure, and their properties were studied thoroughly [1]. It was shown that the IMCs are formed through intermacromolecular hydrogen bonds between the oxygen atoms of PEG and the carboxy groups of PMAA. These IMCs are also stabilized by hydrophobic interactions.

In recent years, investigations of the IMCs formed by PMAA networks and PEG were begun [2-7]. Osada and coworkers studied [2-6] the contraction of PMAA membranes caused by their interaction with PEG of different molecular weights, but the composition of the IMC and the constants of IMC formation have not been determined.

In Ref. 7 one of us studied the conformational transitions in IMC formed by a PMAA network with various charge density and PEG. It has been noted that the charge density of the network and the concentration and molecular weight of PEG significantly influence the properties of the IMC. However, Ref. 7 did not present any quantitative results on the composition of IMC. The kinetics of IMC formation has also not been studied.

The aim of the present work is to study the kinetics of the formation and the equilibrium properties of the IMC formed between PMAA hydrogels and PEG of different molecular weights.

EXPERIMENTAL

PMAA gels were prepared by free radical copolymerization of methacrylic acid (99.5 mol%) and *N,N'*-methylenebisacrylamide (0.5 mol%) in aqueous solution. Ammonium persulfate (4.4×10^{-3} mol/L) and *N,N,N',N'*-tetramethylethylenediamine (TEMED) (4.4×10^{-3} mol/L) were, respectively, the initiator and accelerator. Gelation was carried out in cylindrical tubes at room temperature for 24 hours. The prepared gel was washed in a large amount of distilled water for 3 weeks. The weight fraction of the polymer in the swollen network was determined by the formula $\beta = m_{\text{dry}}/m_{\text{sw}}$, where m_{dry} is the mass of the dry gel and m_{sw} is the mass of the swollen gel. The value of β for the prepared PMAA gel was 0.0069.

PEG with molecular weights of 1500, 3000, and 6000 (Loba Chemie, Fischamend, Austria) were used without preliminary purification.

To prepare the PMAA gel-PEG complexes, the PMAA gel samples (approximately 0.7 g) were put in solutions of PEG in distilled water (2 mL water per 1 mg dried PMAA network). The samples remain in the solutions at 25°C for the time required to attain equilibrium. When equilibrium was established, the gel samples were weighed and the PEG concentration in the solution was measured. The relative equilibrium weight of the gel samples was characterized by the m/m_0 ratio, where m is the mass of the sample at the equilibrium state and m_0 is the mass of the sample after synthesis. The absorption of PEG by PMAA gels results in a decrease of PEG concentration in the external solution. The concentration of PEG in solution was measured with laser differential refractometer KMX-16 (Chromatix, USA). The PEG content in the IMC was calculated by subtraction of the equilibrium concentra-

tion of PEG in the surrounding solution from the initial concentration of PEG. The IMC composition was characterized by the ratio of PEG/PMAA repeating units in the gel, θ . The initial ratio of PEG/PMAA repeating units in the system was designated by q .

The PMAA gel-PEG complexation was studied by FT-IR spectroscopy. The infrared spectra were recorded with a Bruker IFS-45 Fourier transform infrared spectrometer (Germany) at a resolution of 2 cm^{-1} . A minimum 32 scans were signal averaged. The samples of dried gels were examined as pressed KBr disks.

RESULTS AND DISCUSSION

When the PMAA hydrogel is immersed in an aqueous solution of PEG, the linear polymer penetrates in the network. The equilibrium concentration of PEG in the gel is higher than in water by a factor of 5–10. The last fact is the evidence for IMC formation.

The kinetics of PEG absorption by PMAA hydrogel is shown on Fig. 1. It is obvious that the PEG content in the gel increases and reaches a limiting value after a certain period of time.

Since the initial size and shape of the samples in the experiments were identical, the kinetics curves characterize the relative velocity of diffusion of linear macromolecules of various chain lengths in the gel.

The time of half completion of IMC formation, τ , can be used as the qualitative characteristics of the velocity of diffusion. From the data presented in Fig. 1 it

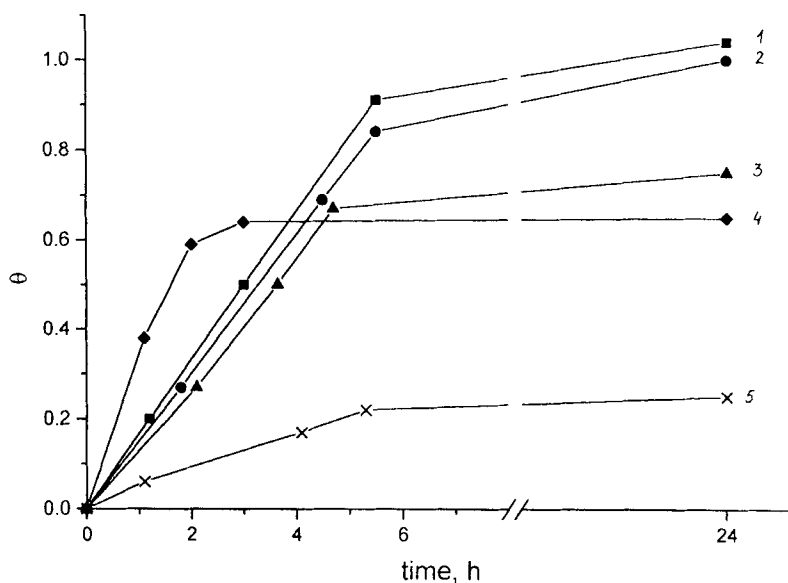


FIG. 1. The kinetics of absorption of PEG by PMAA hydrogels in water (1, 2, 4, 5) and in 10^{-4} N HCl solution (3) at different molecular weights of PEG and different initial ratios q of PEG and PMAA repeating units: (1, 3) PEG 6000, $q = 10$; (2) PEG 6000, $q = 7$; (4) PEG 1500, $q = 10$; (5) PEG 6000, $q = 0.5$.

can be seen that the value of τ for PEG 6000 is three times higher than for PEG 1500.

Figure 1 also illustrates the kinetics of PEG absorption for different initial polymer concentrations in solution. The data obtained indicate that when the PEG 6000 initial concentration decreases by a factor of 20, the initial rate of absorption of PEG decreases also, but by a much smaller factor (Curves 1 and 5, Fig. 1).

The equilibrium fractions of PEG in the IMC's Θ as a function of the initial concentration of PEG with different molecular weights in water are presented in Fig. 2 (Curves 1, 2, and 4). From this figure we notice that the equilibrium magnitudes of Θ increase and reach limiting values with increasing initial concentrations of PEG. The limiting values of Θ_{\max} depend strongly on the molecular weight of PEG: they increase from 0.6 for PEG 1500 to 1.3 for PEG 6000. Analogous results were obtained for linear PMAA-PEG complexes in the Ref. 8. The authors showed that complexes prepared from PEG with molecular weight lower than 1000 have a Θ less than 0.1. The complexes with PEG 2000 and 3000 have Θ equal to 0.11 and 0.38, respectively, at 25°C. The complexes prepared from PEG of higher molecular weight (7500 and 20,000) have Θ values nearly equal to 1.0.

Figure 2 shows that the equilibrium value of Θ_{\max} for the IMC with PEG 6000 is higher than 1.0 ($\Theta_{\max} = 1.3$). Thus the IMC contains 1.3 PEG repeating units per 1 unit of PMAA instead of 1 per 1, which is the condition for the maximum number of hydrogen bonds between two polymer components.

The IR spectra of the IMC with $\Theta_{\max} = 1.3$ are presented in Fig. 3(a). As may be seen from these spectra, there are three bands of stretching vibrations of PMAA

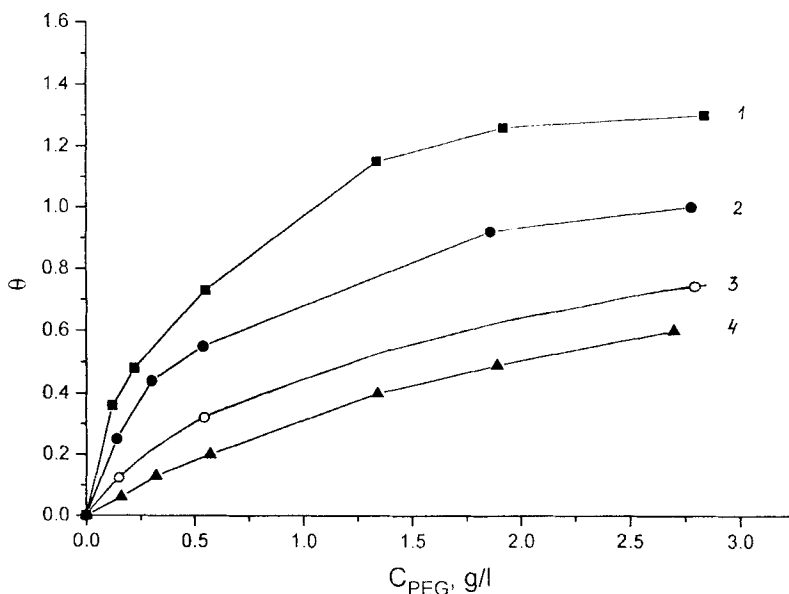


FIG. 2. The dependences of the ratios of PEG and PMAA repeating units in the complex Θ on initial concentration of PEG solutions in water (1, 2, 4) and in 10^{-4} N HCl (3). (1, 3) PEG 6000, (2) PEG 3000, (4) PEG 1500.

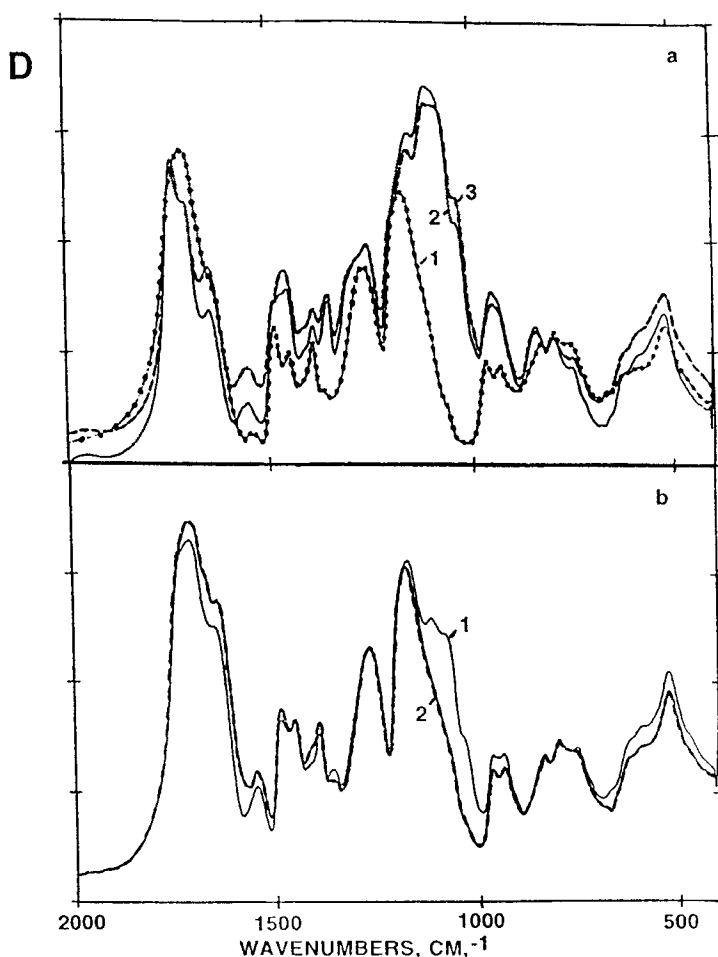


FIG. 3. (a) IR spectra of the PMAA gel (1) and of PMAA gel-PEG complexes in the outer (2) and inner (3) layers of the gel at a PEG/PMAA ratio in the network $\Theta = 1.3$. (b) IR spectra of PMAA-PEG complexes in the outer (1) and inner (2) layers of the PMAA gel at a PEG/PMAA ratio in the network $\Theta = 0.32$.

carboxy groups: 1) at 1733 cm^{-1} , corresponding to COOH groups, which form hydrogen bonds with PEG; 2) at 1700 cm^{-1} , corresponding to COOH dimers, which form intramolecular hydrogen bonds in PMAA; and 3) at 1642 cm^{-1} , corresponding to COO^- ions. The assignment of these bands was made on the basis of the position of the corresponding bands in the spectra of the IMCs of linear PMAA and PEG [9, 10]. According to Refs. 9 and 10, in the IR spectra of IMCs of linear PMAA-linear PEG, the carbonyl absorption at 1730 cm^{-1} is due to the formation of H-bonds with PEG, while the band at 1708 [9] or 1700 cm^{-1} [10] corresponds to the dimeric carboxyl form of PMAA.

Thus for complexes of crosslinked PMAA with PEG as well as for complexes of linear PMAA with PEG, the carboxy groups of PMAA do not all participate in the formation of hydrogen bonds with PEG even with an excess of PEG in the IMC.

This result can be explained by the fact that the end groups of PEG do not take part in the complexation. In addition, macromolecules of PEG can form loops in the complex [9]. Polymer units in loop segments may not participate in the formation of hydrogen bonds.

Let us consider the interaction of a PMAA network with PEG as a function of the degree of complex formation between the network and linear polymer, Θ . For the IMC of a given composition, the effective dissociation constant $K(\Theta)$ of the complex may be written as follows:

$$K(\Theta) = \alpha C / (1 - \alpha) \quad (1)$$

where α is the degree of dissociation of the complex and C is the equilibrium concentration of PEG in solution. Values of α can be obtained from the experimental values of Θ and Θ_{\max} : $\alpha = \Theta / \Theta_{\max}$, where Θ_{\max} is the maximum PEG/PMAA ratio in the IMC.

The obtained values of K and also the corresponding changes of free energy ΔF are listed in Table 1. It can be seen that the stability of complexes lowers sharply with a decrease in the length of PEG macromolecules. This effect is analogous to that observed for the complexes of linear PMAA with PEG [8]. The other feature of the data obtained is that IMC stability decreases with an increase of Θ . As may be seen from Table 1, values of K rise with an increase of Θ .

Of special interest is the study of the distribution of PEG in the gel phase, particularly at low fractions of PEG in the gel.

Investigation of the interaction of polyelectrolyte networks with oppositely charged linear polymers [11–13] has shown that linear polymer sorption proceeds similarly to frontal heterogeneous reactions in solids. The process of transport of linear polyions into the gel occurs through a repetitive interpolyelectrolyte exchange reaction, that is, by layer-by-layer displacement of linear polyelectrolyte from the periphery to the center of the gel specimen with no mixing of polyions in a radial direction. As a result, when the amount of linear polymer is small, the complex is formed mainly in the outer layer of the gel.

One can also expect the nonuniform distribution of PEG in PMAA gel-PEG complexes. This assumption rests on the results of the study of the structure of

TABLE 1. The Dissociation Constants $K(\Theta)$ of the Complex PMAA Network-PEG and the Free Energy Changes ΔF of Complex Formation for Different Compositions (Θ) of the Complex and Molecular Weights of PEG

Θ^a	$10^5 K / (\text{mol} \cdot \text{L}^{-1})$			$\Delta F / (\text{kJ} \cdot \text{mol}^{-1})$		
	PEG 6000	PEG 3000	PEG 1500	PEG 6000	PEG 3000	PEG 1500
0.32	3.25	8.1	56	25.6	23.3	4.4
0.47	5.7	10.0	58	24.2	22.0	4.4
0.70	7.4	13.2	82	23.5	22.1	4.2
1.1	6.25	—	—	24.0	—	—
1.27	5.70	—	—	24.3	—	—

^a $\theta = [\text{PEG}] / [\text{PMAA}]$ in the complex.

complexes between linear PMAA with high molecular weight and PEG in aqueous medium [14, 15]. It has been shown that with an excess of PMAA, the distribution of PEG is uneven; some PMAA macromolecules form complexes with PEG while others do not participate in complex formation at all.

The distribution of PEG in the PMAA gel volume was studied by IR spectroscopy. PEG has an intense absorption band at 1100 cm^{-1} . Figures 3(a) and 3(b) show the spectra of the outer and inner layers of the gel which forms the IMC with $\Theta = 1.3$ and 0.32 , respectively. It can be seen that with a small amount of PEG (Fig. 3b) the PEG band (at 1100 cm^{-1}) is greater in the outer layer of the gel than in the inner layer. Thus, the content of PEG in the outer layer is higher than in the inner layer of the gel. For the gel which forms the IMC with $\Theta = 1.3$, the IR spectra for the outer and inner layers of the PMAA gel-PEG complexes are nearly identical (Fig. 3a). So, with an excess of PEG, its distribution in the gel volume is even.

Complexation of PMAA gels with PEG results in gel shrinkage. Figure 4 illustrates the contraction of PMAA gels caused by interaction with PEG 3000. From this figure we can see that an increase of the equilibrium fraction of PEG in the IMC results in a decrease of the relative mass of the gel. In comparison with the results obtained in Ref. 7, where a 30-fold decrease of gel volume in the presence of PEG was observed, the changes of the mass of the gel in our case are relatively small; the weight of the gel decreases by a factor of 2-3.

A study of the collapse of charged polymer networks has shown that gels in a bad solvent can be in a metastable state, in which they contain a great excess of a solvent. The volume of such gels is not restored to its original value after drying [16].

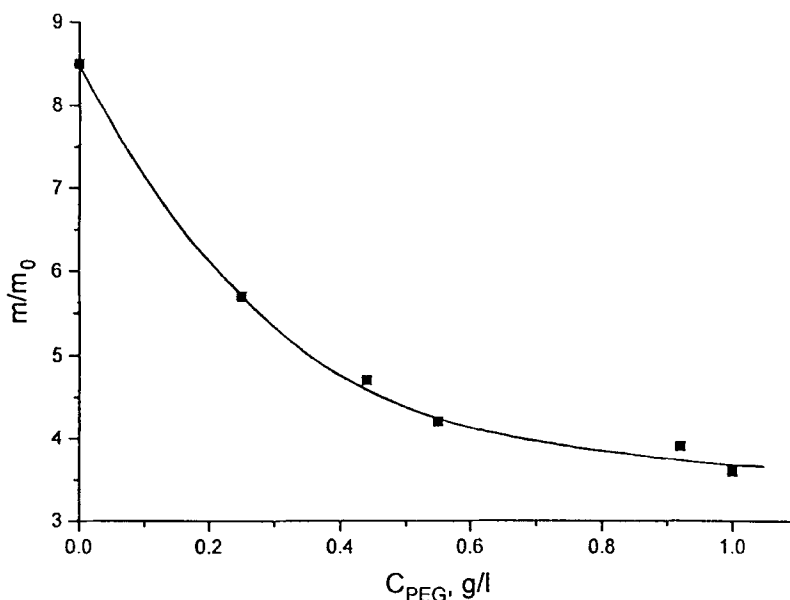


FIG. 4. The contraction of PMAA gels in PEG 3000 solutions in water at different PEG/PMAA ratios in the network Θ .

In order to prove that the high swollen state of the IMC obtained in this work is the equilibrium state, we dried the IMC in air to 10% of its original mass and then we put it into the initial solution. The gel regained its original mass. Hence, at equilibrium the IMC gels contain about 99% water.

One reason for the high degree of swelling of the IMC is the presence of a small amount of charges on the network chains. These charges arise from both PMAA dissociation and the presence of the base TEMED in the initial polymerization mixture. Small amounts of ions can produce excessive osmotic pressure in the swollen network, which prevents the total collapse of the IMC. The presence of charged carboxylate ions in the gel was confirmed by IR spectroscopy data (Fig. 3a). The IR spectrum of the dried PMAA network shows two small bands at 1640 and 1400 cm^{-1} , which can be assigned to asymmetric and symmetric COO^- stretching vibrations, respectively. The dissociation of PMAA is suppressed in a solution of a strong acid. In the IR spectrum of a PMAA network which had been placed in a solution of a strong acid (HCl), these bands were absent. Thus one can assume that the addition of a small amount of acid will lead to contraction of the network.

It was shown that the addition of 0.16 mol HCl per 1 repeating unit of PMAA in the absence of PEG results in a decrease of the volume of the gel by a factor of 30. In the presence of PEG the gel volume in HCl in these conditions decreases by a factor of 100. The ionization of PMAA by the addition of NaOH breaks hydrogen bonds in the gel, and the gel regains its original mass.

Hence, the state of a PMAA gel in the presence of PEG can be illustrated by a number of equilibria, schematically represented in Fig. 5.

The influence of the addition of low molecular weight acid on Equilibrium II remains unknown. It is obvious that a decrease of the degree of ionization of carboxy groups in the network promotes hydrogen bond formation between PMAA units as well as IMC formation. For this reason, direct measurements of the IMC composition Θ in water and in HCl solution (0.16 mol per 1 PMAA repeating unit) were made.

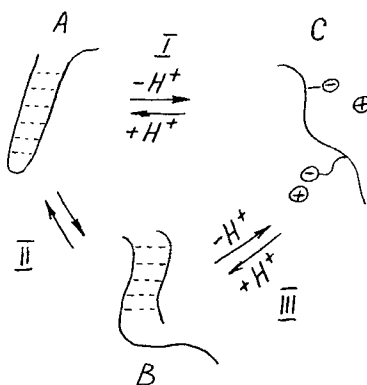


FIG. 5. Schematic representation of possible equilibria in the PMAA gel in a solution of PEG in water. (A) Segments of PMAA chains which form intramolecular hydrogen bonds, (B) segments of PMAA chains which form complexes with PEG, and (C) ionized segments of PMAA chains.

Figure 2 illustrates the dependencies of Θ on the initial concentration of PEG 6000 in water (Curve 1) and in a solution of HCl (Curve 3). It can be seen that the addition of a small amount of acid results in a decrease of the values of Θ . Thus, Equilibrium II must be displaced in the direction of the formation of additional intramolecular hydrogen bonds of PMAA and the release of PEG in the solution.

Another factor which contributes to the decrease of PMAA gel-PEG complexation in an acid medium could be the simple shrinkage which accompanies complete protonation of PMAA in a strong acid. As a result of shrinkage, the free volume available to the inwardly diffusing PEG is reduced, which leads to a decrease of PMAA gel-PEG complex formation.

CONCLUSION

The molecular weight of PEG was shown to have an impact on PMAA hydrogel-PEG interactions. The rate of PEG diffusion in the gel decreases with an increase of PEG chain length. The increase of molecular weight of PEG also results in an increase of the equilibrium fraction of PEG in the IMC and in the increase of IMC stability.

It was shown by FT-IR spectroscopy that for a deficiency of PEG with respect to PMAA the complex is formed mainly in the outer layer of the gel. The distribution of linear polymer in the gel volume becomes even with an excess of PEG. Hence, PEG seems to penetrate into the gel by frontal diffusion.

Linear polymer PEG capable of forming complexes with network chains can induce conformational changes in the gel. Complexation causes contraction of the PMAA gel in neutral medium and the collapse of the gel in acid medium.

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