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Preparation and Swelling Characteristics of Semi-interpenetrating Polymer Networks Composed of Poly(acrylamide-*co*-acrylic acid)/ Linear Poly(ethyleneimine) or Poly(ethyleneimine)-metal Complexes

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Abstract

Semi-interpenetrating polymeric networks (SIPNs) consisting of poly(acrylamide-*co*-acrylic acid) p(AAm-AAc) hydrogel matrix and linear polyethyleneimine (LPEI), polymer-metal complexes of LPEI with nickel (LPEI-Ni^{2+}), cobalt (LPEI-Co^{2+}) and zinc ions (LPEI-Zn^{2+}) were prepared by template polymerization: crosslinked AAm-AAc chains were formed in aqueous solution by crosslinking copolymerization of equimolar mixture of AAm and AAc in the presence of N,N-methylenebisacrylamide and LPEI, LPEI-Ni^{2+}, LPEI-Co^{2+}, and LPEI-Zn^{2+} respectively. The swelling degree of SIPNs in water and swelling kinetics in 0.1N NaOH and 5% NH_4OH were determined. The exponential relation $M_t/M_\infty = kt^n$ (where M_t is the mass of water absorbed at time t and M_∞ is the mass of water absorbed at equilibrium) was used for calculation of the exponent (n) describing the mechanism of water transport through these SIPN. The dynamic swelling behavior of SIPNs in alkaline media corresponds to anomalous swelling mechanism.

Introduction

Synthesis and characterization of interpenetrating and semi-interpenetrating networks are of great interest [1-3] due to improvement in the flexibility and mechanical properties of hydrogel materials [4-6], biomaterials [2] and design of stimuli-sensitive compositions [7-9]. Interpenetrating polymeric networks (IPNs) are three-dimensional structures which represent double network gel (Fig. 1a). While semi-interpenetrating polymeric networks (SIPNs) are systems consisting of three-dimensional network within the volume of which linear macromolecules are embedded. The structural model of SIPNs can be represented as a spatial network with physically entrapped linear macromolecules (Fig. 1b).

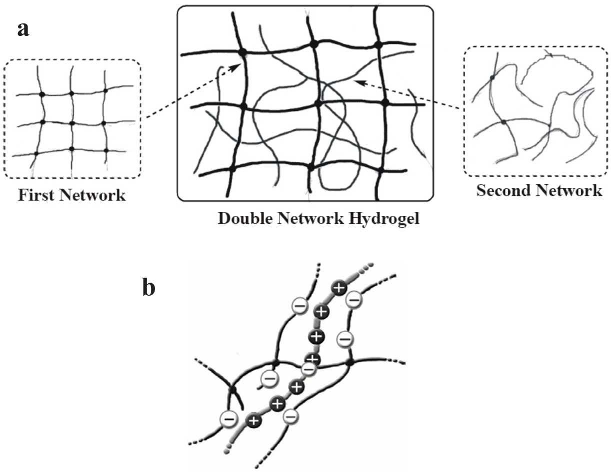

Fig. 1. Schematic representation of IPN (a) and SIPN (b).

Commonly accepted preparation methods of IPNs are sequential and simultaneous network formation [7-9]. In the former case the first polymer network

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is formed then the second monomer, crosslinker and initiator are polymerized *in situ*. In the latter case the mixture of at least two monomers, crosslinking agent and initiator are mixed followed by simultaneous polymerization. The application of freeze-thaw cycles also leads to IPNs formation of poly(vinyl alcohol) physical gel within the formed network [10]. Authors [11] reported the preparation of IPNs based on poly(vinyl alcohol)-poly(N-vinylpyrrolidone) hydrogels without any additives and crosslinkers, only in the presence of initiator. Swelling and mechanical properties were investigated for superporous hydrogels of poly(acrylamide-co-acrylic acid)/polyethylenimine interpenetrating polymer networks [12].

pH switching "on-off" SIPN hydrogels of crosslinked poly(acrylamide-*co*-acrylic acid) and linear polyallylammonium chloride were synthesized by template copolymerization [13]. The drug loading and release of the SIPN hydrogels were studied using theophylline as a model drug. Temperature- and pH-responsive SIPN hydrogels, constructed with chitosan (CS) and poly(diallyldimethylammonium chloride) (PDADMAC), were studied by FTIR, DSC, and swelling tests, under various conditions [14]. CS/PDADMAC SIPN hydrogels exhibited a relatively high swelling ratio and DSC was used for the quantitative determination of the amounts of freezing and nonfreezing water. The amount of free water increased with increasing PDADMAC content in the SIPN hydrogels.

Some examples of amphoteric SIPNs preparation were reported by authors [15,16]. These SIPNs synthesized by template polymerization contained both covalent and ionic bonds. The covalent bonds retained the three-dimensional structure of hydrogel while the ionic bonds improved the mechanical properties of SIPNs and provided temperature, pH and ionic strength sensitivity.

The SIPNs can also be obtained by interpolymer reactions, *e.g.* by interaction of ionic or nonionic polymer gels with linear macromolecules at the gel-solution interface [17-19]. The specific peculiarity of interpolymer reactions reviewed in [18] is cooperative character of interaction proceeding via "relay-race" mechanism resulting in gel contraction.

The present communication deals with the synthesis and swelling behavior of SIPNs composed of acrylamide-acrylic acid hydrogels and linear poly(ethylenemine) or linear poly(ethyleneimine)-metal complexes.

Experimental Part

Materials

Acrylic acid (AAc), acrylamide (AAm), N,N-methylenebisacrylamide (MBAA), ammonium persulfate (APS) and N,N,N',N'-tetramethylethylenediamine (TMED), linear poly(ethyleneimine) (LPEI) with M_n = 1000 were purchased from Aldrich. AAc was purified by distillation under the low pressure and kept in refrigerator. Reagent-grade metal salts $NiCl_2 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$ and $Zn(NO_3)_2 \cdot 6H_2O$ were used. Aqueous solutions of 0.1N NaOH and 5% NH_4OH were used as kinetics measurements media.

Synthesis of AAm-AAc/LPEI Networks

Reaction mixture consisting of AAm (0.5 g), AAc (0.5 mL), aqueous solution of LPEI (4 mL, 0.1 mol/L), MBAA (10 mg), APS (5 mg) and TMED (1 mg) was thoroughly stirred to obtain homogeneous solution, bubbled with nitrogen gas for 10 min to remove the dissolved oxygen. The reaction mixture was placed into plastic syringe with closed outlet at the bottom and thermostated at 60°C during 30 min. After polymerization, the hydrogels were washed with water for 7 days during which water was refreshed daily.

Synthesis of AAm-AAc/LPEI-metal Ions Networks

In other series of experiments instead of LPEI the polymer-metal complexes LPEI-Ni^{2+}, LPEI-Co^{2+} and LPEI-Zn^{2+} prepared preliminary at molar ratio of LPEI:metal = 5:1 was used. All prepared samples were washed out periodically with distilled water during 1 week and dried in vacuum to constant mass at room temperature.

Swelling and Dynamic Swelling Experiments

The swelling degree of SIPNs was determined gravimetrically and calculated using the formula $\alpha = m - m_0/m_0$ (where m and m_0 are the masses of swollen and dried gels respectively). The gravimetric experiments were performed with cylindrical gel samples with diameter and length 1 cm (mass 0.60-0.65 g). The weighing process was performed three times and the average weight was taken for calculation. Gel samples were carefully taken out from the solution and the excess of liquid from the gel surface was gently removed with a filter paper. To exclude the evaporation of solvents from the surface and gel volume, samples were weighed in closed vials. The errors in all gravimetric experiments did not exceed 5%.

The dynamic swelling behavior of the SIPNs in aqueous solutions was measured according to a reported procedure [20]. The swelling rate was expressed as $kt^n = M_t/M_\infty$, where k is the swelling rate constant, n is a characteristic exponent describing the mode of the penetrant (*e.g.* water) transport mechanism, t is the absorption time, M_t is the mass of water absorbed at time t, M_∞ is the mass of water absorbed at infinite time t_∞. The constants k and n were calculated from the slopes and intercepts of the plots of $\ln(M_t/M_\infty)$ versus $\ln t$ for M_t/M_∞ less than 0.6.

Results and Discussion

It has been reported [13] that the template copolymerization of AAm and AAc with poly(allylammonium chloride) as a matrix results in multi-block structure with long AAm and AAc sequences. One can suggest that in our system composed of poly(acrylamide-*co*-acrylic acid) hydrogel and linear poly(ethyleneimine) [p(AAm-AAc)/LPEI] the formation of SIPN with the structure illustrated in Fig. 1b will also be realized. The physically entrapped LPEI within the p(AAm-AAc) hydrogels will form the cooperative salt bonds $\sim COO^- \ NH_2^+\sim$ which in turn will act as a physically crosslinker to retard the swelling rate. In its turn the spatial structure of SIPN consisting of [p(AAm-AAc)/LPEI-metal ions] can be represented as coiled macromolecular-metal complexes embedded into the gel network. When the LPEI and LPEI-metal complexes were embedded inside an original p(AAm-AAc) hydrogel, the SIPNs were opaque as shown in Fig. 2.

Figure 3a-c shows the swelling of SIPNs in water, 0.1N NaOH, and 5 wt.% NH_4OH. In water the swelling curves of SIPNs are close to linear one and change in the following order: [p(AAm-AAc)/LPEI-Ni^{2+}] > [p(AAm-AAc)/LPEI-Zn^{2+}] > [p(AAm-AAc)/LPEI-Co^{2+}] > [p(AAm-AAc)/LPEI] (Fig. 3a). A slight swelling of [p(AAm-AAc)/LPEI] in comparison with gel-immobilized LPEI-metal complexes is probably accounted for the formation of polyelectrolyte complexes between AAm-AAc gel matrix and LPEI. Rapid swelling of SIPNs in alkaline region is due to ionization of carboxylic groups of gel matrix in the media of 0.1N NaOH and 5-wt.% NH_4OH. The swelling degree of SIPNs in solution of 5-wt.% NH_4OH is higher than in 0.1N NaOH medium although in both cases the carboxylic groups are in the protonated state. This is probably related to the specific binding of counterions (Na^+, NH_4^+) by negatively charged network, *e.g.* the hydrated Na^+ ions with small radius are bound to carboxylate ions stronger than NH_4^+ ions which have the bigger radius.

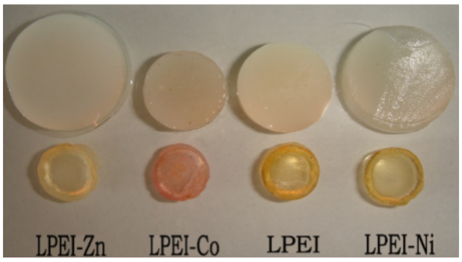

Fig. 2. SIPN samples formed from p(AAm-AAc) and LPEI, LPEI-metal complexes.

In aqueous solutions of both 0.1N NaOH and 5-wt.% NH_4OH the swelling rate of AAm-AAc gel network with immobilized polymer-metal complexes increases in the following order: [p(AAm-AAc)/LPEI] > [p(AAm-AAc)/LPEI-Co^{2+}] ≈ [p(AAm-AAc)/LPEI-Zn^{2+}] > [p(AAm-AAc)/LPEI-Ni^{2+}] (Fig. 3b,c). This can be explained by involvement of carboxylic groups of gel matrix into coordination sphere of LPEI-metal complexes and retarding the network expansion. In 5-wt.% NH_4OH the swelling degree of gel-immobilized polymer-metal complexes is in 1,5-2 times higher than that of 0.1N NaOH. One can suggest that in 5-wt.% NH_4OH medium the partial destruction of polymer-metal complexes takes place and the formed ammine complexes tend to diffuse outside the gel volume.

Table 1 presents the values of n and k describing the mode of water transport mechanism and the swelling rate constant respectively for SIPNs determined in 0.1N NaOH and 5-wt.% NH_4OH. According to Peppas *et al.* [20] the dynamic swelling behavior of hydrogels depends on the relative contribution of penetrant diffusion and relaxation of crosslinked polymer chains. A value of $n = 0.5$ corresponds to Fickian diffusion, *e.g.* the process is diffusion controlled, whereas the transport is considered to be relaxation controlled for $n \geq 1$ and as anomalous when the value of n lies between 0.5 and 1. For SIPNs the values of n in the media of 0.1N NaOH and 5 wt.% NH_4OH correspond to anomalous swelling mechanism. This type of diffusion indicates that for these gels the rate of diffusion overtakes the rate

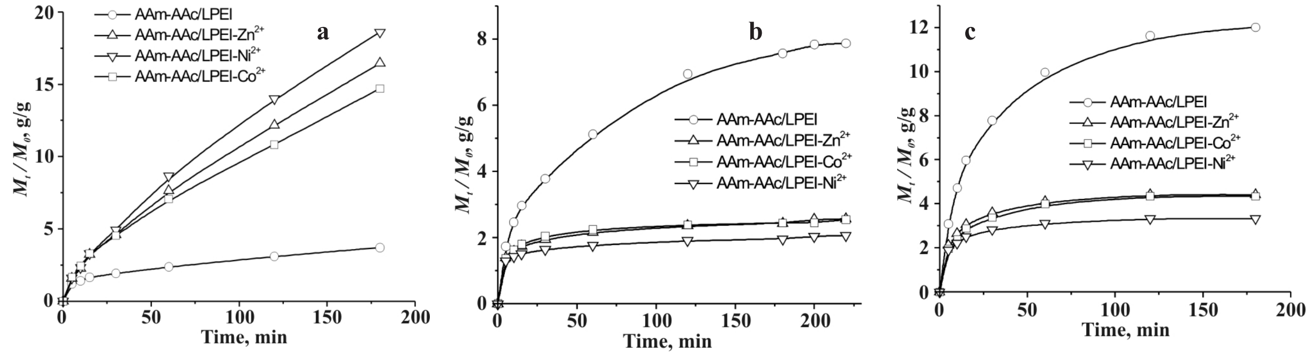

Fig. 3. Swelling of SIPNs in water (a), 0.1N NaOH (b) and 5 wt.% NH_4OH (c).

of relaxation of the polymer chains, whereas it is reverse for the Fickian type of diffusion. The values of n corresponding to $0.5 < n < 1$ may be accounted for that the immobilized within the gel matrix LPEI and LPEI-metal complexes interact with AAc groups of gel matrix and retards the swelling rate of network.

Table 1

Parameters n and k for SIPNs in 0.1N NaOH and 5 wt.% NH_4OH

System	0.1N NaOH		5 wt.% NH_4OH	
	n	$k \cdot 10^2$	n	$k \cdot 10^2$
AAm-AAc	0.95	11.8	0.99	11.9
AAm-AAc/LPEI	0.75	7.0	0.92	5.3
AAm-AAc/LPEI-Co^{2+}	0.73	11.8	0.97	9.0
AAm-AAc/LPEI-Zn^{2+}	0.90	11.6	1.03	9.0
AAm-AAc/LPEI-Ni^{2+}	0.95	11.8	0.92	11.7

Conclusions

Thus semi-interpenetrating polymeric networks consisted of p(AAm-AAc) network and LPEI or LPEI-metal complexes were synthesized by template copolymerization of acrylamide and acrylic acid in the presence of LPEI and LPEI-metal complexes. The swelling rate of SIPN in water changes as [p(AAm-AAc)/LPEI-Ni^{2+}] > [p(AAm-AAc)/LPEI-Zn^{2+}] > [p(AAm-AAc)/LPEI-Co^{2+}] > [p(AAm-Ac)/LPEI]. It is suggested that LPEI, physically entrapped within the p(AAm-AAc) hydrogels, is able to form the cooperative salt bonds with carboxylic groups of network and retard the swelling rate while the spatial structure of SIPN consisting of [p(AAm-AAc)/LPEI-metal ions] can be represented as coiled macromolecular-metal complexes embedded into the gel network. The dynamic swelling behavior of SIPN in alkaline media adjusted by 0.1N NaOH and 5 wt.% NH_4OH corresponds to anomalous swelling mechanism.

Acknowledgements

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