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Semi-IPNs based on Polyacrylamide and Poly(itaconic acid)

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Summary

Semi-IPNs based on polyacrylamide (PAAm) and poly(itaconic acid) (PIA) were prepared by two different techniques, polymerizing itaconic acid in the presence of polyacrylamide gel (Samples I) and by making the polyacrylamide gel in the presence of poly(itaconic acid) (Samples II), with different PAAm/PIA ratios. The swelling behavior of the semi- IPNs reveals that gels with low PIA content swell more, while those with high PIA content swell less than a pure PAAm gel, probably due to the formation of intermacromolecular gel-polymer complexes on the basis of hydrogen bonds.
The results of thermal analysis indicate an improved thermal stability of the hydrogels and complexes compared with PIA and PAAm.

Introduction

Hydrogels are slightly crosslinked three-dimensional hydrophilic polymer which retain large quantities of water without dissolution. Networks can be built from homo- or copolymers and crosslinking points can be chemical or physical bonds.

Stimuli capable hydrogels demonstrate a large volume transition and associated phase transition as a function of physical and chemical variables, such as: temperature, pH and ionic strength as well as electrical and magnetic fields, is used to create new intelligent materials for applications in pharmacy, medicine, biology and industry[1]. Homopolymers alone cannot meet divergent demand in terms of both good mechanical properties and performance. In order to improve the mechanical properties of these materials, the semi-interpenetrating polymer network (semi IPN) technique can be used, i.e. the combination of two polymers, one of them in a network form, where one of the polymers has been synthesized in the presence of the other.

In this work, two series of semi-IPNs on the basis of polyacrylamide and poly(itaconic acid) were synthesized using different techniques. All samples were characterized by their IR spectra and thermal behavior and the results are compared with PAAm/PIA complexes, examined in our previous study. All complexes were synthetized by template polymerization – once of AAm on PIA[2] (Complexes I), and in the other case by polymerizing IA using PAAm as a template (Complexes II) [3]. Template polymerization was chosen because it is known that the composition of such complexes is 1:1 in terms of interacting groups of the monomer units and their structure is more ordered than in the case of complexes obtained by simple mixing two polymer solutions. The polymers in such complexes have a compact distribution of hydrogen bonds, the so-called cooperative effect[4].

Experimental

Materials: Acrylamide (AAm) and itaconic acid (IA) were obtained from Fluka AG and used without further purification. 2,2'-Azobisisobutyronitrile (AIBN) (Merck) was recrystallized from methanol before use. N,N'-Methylenebisacrylamide (MBA) (Fluka) was used without purification. Ammonium persulfate (APS) (Fluka) and potassium pyrosulfate (KPS) (Fluka) were used as the initiator and the accelerator, respectively, without purification. Distilled water was used for the swelling measurements.

Preparation of the hydrogels: Polyacrylamide (PAAm) gel was synthesized in the presence of ammonium persulfate initiator and potassium pyrosulfate accelerator with the crosslinker N,N'-Methylenebisacrylamide at 40^0 C for one hour. For the synthesis of the first series of PAAm/PIA semi-IPNs (Samples-I), itaconic acid (IA) was polymerized with ammonium persulfate initiator and potassium pyrosulfate accelerator in the presence of a previously synthesized polyacrylamide (PAAm) gel. The second series of PAAm/PIA semi-IPNs (Samples-II) was prepared by synthesizing the PAAm gel, with the same initiator, accelerator and crosslinker as mentioned before, at 40 °C in the presence of previously made linear PIA. Distilled water was used in all polymerizations. The mass ratio of IA/ PAAm in the initial mixture was: 10/90, 20/80, 35/65, 45/55, 60/40 and 70/30 for semi-IPNs-I, and in the case of Samples-II the ratio of PIA/ AAm was: 5/95, 10/90, 20/80, 40/60, 50/50 and 60/40. The dried gels were immersed in distilled water for two weeks to eliminate extractable components. The gels were collapsed first in an acetone/water (1:1) mixture, then in acetone and finally dried under vacuum at room temperature to constant mass. The synthesis of PIA and PAAm has been described elsewhere[2,3].

Characterization: Elemental analysis. In Table 1 is shown the chemical composition of semi-IPNs estimated by organic elemental analysis. *Swelling Studies.* Dried gel disc was immersed in distilled water at 25^0C and it was weighed at a proper time intervals. The equilibrium mass swelling ratios (SR_{eq}) for the PAAm gel and semi-IPNs were determined as the ratio of the equilibrium swollen gel mass to the dry gel mass. *IR spectra.* The IR spectra were registered with a Perkin-Elmer 283B spectrophotometer using the KBr technique. *Thermal analysis.* The thermogravimetric analysis was performed using a Perkin-Elmer TGS-2 system, under a N_2 atmosphere at a heating rate of $10^0 min^{-1}$, in the temperature range of 50-650^{0}C. The DSC thermograms were recorded using a Perkin-Elmer DSC-4 instrument at a heating rate of 10^{0}min^{-1}, under nitrogen atmosphere. All spectra were recorded in the temperature range from 50-350^{0}C.

Discussion

Hydrogel composition. The PIA/PAAm ratio in some hydrogels varied from the ones in the initial mixture.

Swelling behavior. One of the main characteristic that influence swelling of hydrogels is the slightly crosslinked network structure with long linear parts between the network centers, which exhibit properties of a single polymer chain. As a measure of swelling the molecular weight of the polymer chain between two neighboring crosslinking points (M_c) can be calculated. Highly crosslinked polymers have a more dense structure and will swell less than the same hydrogel with a lower crosslinking ratio, but the chemical structure of a hydrogel also affects its swelling.

M_c can be calculated from the following equation[5]:

$$M_c = -V_1 \cdot d_P \frac{\left(v_S^{1/3} - v_S/2\right)}{\ln\left(1 - v_S\right) + \chi v_S^2 + v_S} \qquad (1)$$

where : V_1- is the molar volume of water at 25^{0}C (18.0 cm^3/mol), d_p- the polymer density, v_S-the volume fraction of PAAm network in the swollen gel at equilibrium , χ_{12}-the Flory-Huggins interaction parameter between solvent and polymer (0.48 [6]).

The dry PAAm gel density was determined by gravimetric method at 25^{0}C to be d_p^{25}= 1.1926 gcm^{-3}. The volume fraction of PAAm network in the equilibrium swollen gel was calculated from equation (2) [5]:

$$v_S^{-1} = d_p(SR_{eq} - 1)d_w^{-1} + 1 \qquad (2)$$

where d_w is the density of water at 25^{0}C (0.99707 gcm^{-3}).

According to equations (1) and (2), the calculated values of v_s and M_c are:

v_S = 0,042 and M_c= 115 400.

The calculated M_c value indicates that PAAm gel is not highly crosslinked.

The results for SR_{eq} of the semi-IPNs are presented in Fig.1 and Fig.2. It is obvious that both types of gels with low PIA content swell more than the PAAm gel, due to the enhanced gel hydrophility in the presence of a polyelectrolyte, while the gels with higher PIA content have lower values of SR_{eq} than the PAAm gel. As the percent of PIA increases the possibility of complexation due to H-bonds increases and for that reason the SR_{eq} in both series decrease.

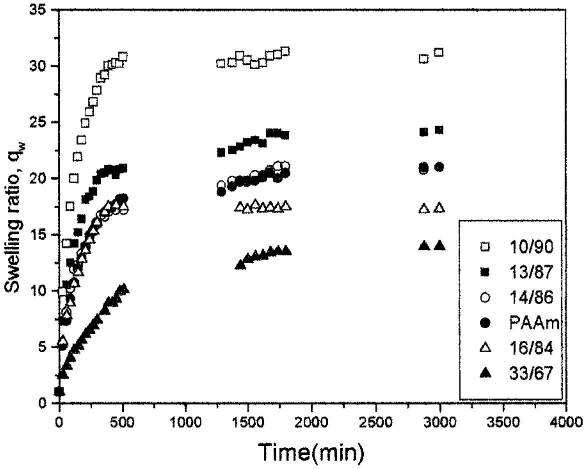

Fig.1: The swelling behavior of Samples I (PIA/PAAm)

It is evident that Samples-II swell approximately two times more than Samples-I of the same composition. The formation of PAAm gel in Samples-II is highly affected by the presence of linear poly(itaconic acid) which leads to a lower chemical crosslinking degree and better swelling compared to Samples-I. This applies for samples with the PIA content up to 40 wt.%. For higher PIA contents (over 50 wt.%) the SR_{eq} in Samples-II are drastically reduced. This can be explained by the enhanced formation of hydrogen bonds - between the carboxyl groups of PIA and the carbonyl or amide groups of PAAm[2]. These bonds act as physical crosslinks and reduce the swelling of the gel.

IR analysis

Infrared spectroscopy was used to verify that the reduced swelling of hydrogels with high a PIA content was the result of hydrogen bonding. The IR spectra of hydrogels showed absorption bands at frequencies which represent the characteristic absorption bands of the individual components: PAAm (3400, 3205, 2930, 1660, 1620, 1445, 1330 and 1120 cm^{-1}) and PIA (3430, 3006, 1725, 1635, 1399, 1204 and 1023 cm^{-1}). Thus the PIA/PAAm-II (59/41) hydrogel shows similar spectral features: 3400, 3006, 2920, 1720, 1660, 1640, 1430, 1420, 1190 and 1125 cm^{-1} resulting from the individual components.

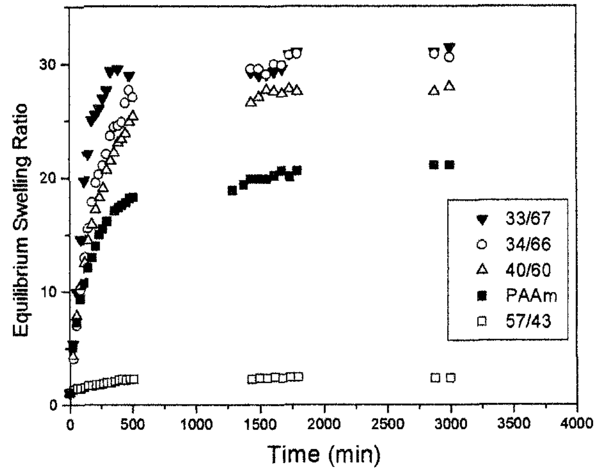

Fig.2: Swelling behavior of samples II (PIA/PAAm)

A band at 1590 cm^{-1}, not present in the spectra for individual components, but characteristic for hydrogels and complexes, was also found[2]. This is in agreement with data from the literature, where FTIR studies on polymonoitaconate/polyacrylamide complexes showed the development of a new band at around 1610 cm^{-1} which is about 30 cm^{-1} lower than those of the amide I modes [7].

DSC analysis of IPNs xerogels

It is clearly visible that the temperature of the first endothermic peak ($T_{DSC\ max\ I}$) in DSC scans (Table 1), which is ascribed to PIA degradation, is located at a higher temperature in the case of the semi-IPNs and complexes than for pure PIA. Higher $T_{DSC\ max\ I}$ for Samples-I than for Samples-II and the complexes is probably the consequence of the higher MBA incorporation in Samples-I. Because complexes are formed by hydrogen bonding only, the similar values for Samples-II, with high PIA wt.%, and complexes indicate that in Samples-

II H-bonds are present to a higher degree than chemical bonds. According to the DSC thermogram the glass transition for the PAAm gel is at 169^{0}C. A higher T_g value than quoted in literature [8] is to be expected due to its crosslinked structure. The glass transition of poly(itaconic acid) is not detectable by DSC measurements because its thermal degradation starts at a low temperature (~ 120^0 C) masking the glass transition.

From the glass transition temperature measurements the interactions in a multicomponent system can be studied. The existence of T_g in semi-IPNs with higher PIA content confirms that complexation between PIA and PAAm gel exists. The glass transiton in the DSC thermograms of the hydrogels and complexes, is detected at lower temperature than it could be expected, which is explained by the plasticizing effect of bound water[9]. High degree of complexation in semi-IPN with high PIA content is confirmed by T_g values which are close to those for complexes.

Table 1. The first endothermic peak maxima in the DSC thermograms

	Sample		$T_{DSC\ max\ I}$, °C	T_g, °C
Hydrogels	PAAm	-	-	169
Hydrogels	Samples-I	16/84	182	-
Hydrogels	Samples-I	40/60	187	125
Hydrogels	Samples-II	57/43	160	123
Hydrogels	Samples-II	59/41	161	122
Complexes	PIA/AAm	(1:1)	160	122
Complexes	IA/PAAm	(1:1)	155	121
Polymer	PIA	-	147	-

TG analysis of IPNs xerogels

Semi IPNs have better thermal stability than the PAAm gel, which in turn is more stable than the poly(itaconic acid). Figure 3 shows DTG maxima for homopolymers and the hydrogels. As it can be seen, the DTG curve of PIA has three maxima, at 185°C, 315°C and 388°C, which have been assigned to the elimination of water and the formation of polyanhydride, followed by decarboxylation of previously formed anhydride groups and the breaking of the main polymer backbone[10]. The thermal degradation of PAAm occurs via two degradation steps. It is stable up to 285°C and decomposes above this temperature with liberation of ammonia and formation of imide groups. DTG maxima are at 326°C and 410°C [11].

In the derivative TGA curves for hydrogels, three characteristic weight loss peaks are observed. The thermal stability of hydrogels and complexes is influenced, among other parameters, by the presence of hydrogen bonds. The first degradation process in all samples is practically the anhydride formation from two available carboxyl groups in PIA, which in hydrogels and complexes are involved in hydrogen bonding with polyacrylamide side groups. The first step before anhydride formation must be breaking of hydrogen bonds, which cann't be detected because it occurs without weight loss. The anhydride formation (DTG 1) is thus delayed in accordance with the proportion of such intermolecular interactions.

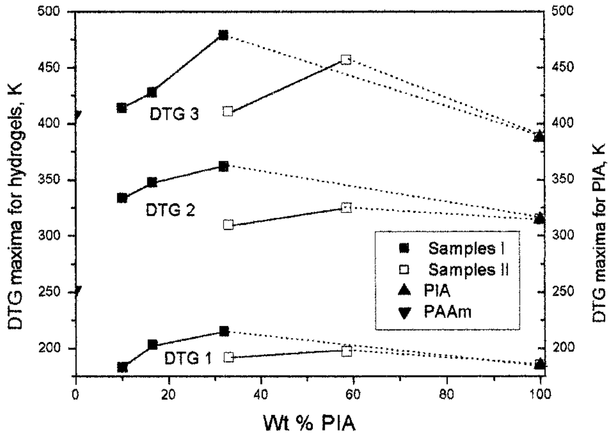

Fig.3: DTG maxima versus wt.% PIA

According to Figure 3 the position of DTG maxima shows better thermal stability of Samples I compared to Samples II. DTG 1 maxima is dislocated towards higher temperatures as the content of PIA in semi-IPNs increases due to the hydrogen bonding which is present to a higher degree. The same trend is observed in DTG 2 and DTG 3 maxima for the samples with the higher PIA wt.%. So it can be concluded that structures formed at temperatures above 300^0C lead to a better thermal stability of gels with higher PIA content. The better thermal stability of Samples I is probably due to the synthesis technique. They were obtained by polymerization of itaconic acid in the presence of previously made PAAm gel having as a consequence higher MBA incorporation leading to chemical bonds. On the other hand, in the case of Samples II the formation of PAAm gel is highly affected by the presence of linear PIA so H-bond formation is more pronounced.

Conclusion

Different types of the hydrogels based on PIA and PAAm were prepared and compared with PIA/PAAm complexes investigated earlier. The results confirm that PIA interacts with PAAm gel, resulting in an interpolymer complex formation - hydrogen bonding being the primary mechanism of that interaction. A new band at 1590 cm $^{-1}$, present in the FTIR spectra of complexes and semi-IPNs, confirms the existence of hydrogen bonds. The main difference in the degree of swelling and thermal behaviour between the two series of hydrogels is due to the difference in their synthesis technique.

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