Molecular Interactions in Poly(methacrylic acid)/Poly(*N*-isopropyl acrylamide) Interpenetrating Polymer Networks

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ABSTRACT: The molecular interactions between the component networks in poly(methacrylic acid)/poly(*N*-isopropyl acrylamide) (PMAA/PNIPAAm) interpenetrating polymer networks (IPNs) were investigated using attenuated total reflectance (ATR)-Fourier transform IR (FTIR) spectroscopy. Hydrogen-bond formation was noted between the carboxyl groups of PMAA and the amide groups of PNIPAAm. The ATR-FTIR results showed shifts in the carboxylic and amide groups, indicating the existence of hydrogen bonding between these two individual networks within the IPNs. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 1077–1082, 2001

Key words: interpenetrating polymer networks; hydrogels; hydrogen bonding; poly(methacrylic acid); poly(*N*-isopropyl acrylamide)

INTRODUCTION

Polymer hydrogels are water-swollen polymer networks containing physical or chemical crosslinks. Some of the hydrogels are capable of responding to external stimuli, such as pH, temperature, ionic strength, and electric field. Among them, pH-sensitive and temperature-sensitive hydrogels were extensively investigated for possible use in various biological applications and chemomechanical systems.[1–14] Interpenetrating polymer networks (IPNs) composed of pH-sensitive poly(methacrylic acid) (PMAA) and temperature-sensitive poly(*N*-isopropyl acrylamide) (PNIPAAm) were synthesized as discussed in a previous publication.[15] This PMAA/PNPAAm IPN hydrogel exhibited combined pH and temperature sensitivity. The synthesis and characterization of these materials was discussed in the previous work. In this study we concentrated on the investigation of molecular interactions with these IPN systems.

For fundamental studies of the polymer structure, it is important to elucidate molecular interactions within this IPN system. IR spectroscopy techniques are widely used in the study of such molecular interactions. Many parameters can be investigated through IR spectroscopy, including the chemical composition, chain branching, configuration, conformation of the polymer system, and steric and geometric isomerism.[16] IR spectroscopy is also used to identify and determine the concentration of solutes or additives in polymer materials.[17,18]

In this study we focused on the investigation and identification of molecular interactions in the PMAA/PNIPAAm IPNs using attenuated total reflectance (ATR)-Fourier transform IR (FTIR) spectroscopy. We were particularly interested in the intermolecular interactions between the two individual networks within the IPNs, such as hydrogen-bond formation and van de Waals and hydrophobic interactions.

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Copolymers and IPNs of two polymers that form hydrogen-bonded complexes have been extensively studied.[1,19–27] These polymer complexes involve carboxyl groups (proton donors) and ether or amide groups (proton acceptors). Figure 1 illustrates the molecular structures of the homopolymers (PMAA and PNIPAAm) and the possible hydrogen-bond formation between the two networks. In the PMAA/PNIPAAm IPNs the protons in the carboxylic groups in PMAA can interact with the amide groups in PNIPAAm, resulting in hydrogen-bond formation between these groups. The formation of hydrogen bonding can usually be determined by the peak shiftings of the hydrogen-bonded functional groups to lower wave numbers in IR spectroscopy.[17,21] The goal of this research was to identify any significant hydrogen-bond interaction within the IPNs.

For FTIR analysis, polymers may be used as solutions, solids, powders, or films. On the other hand, because IPNs are crosslinked, they cannot be handled as solutions. Clearly, it is desirable to take FTIR spectra of IPNs in their hydrogel state. However, the absorption of water interferes with the absorption of functional groups. After considering the complexity of the IPN preparation and the resolution of the spectrum, a horizontal ATR-FTIR method was used in this study.

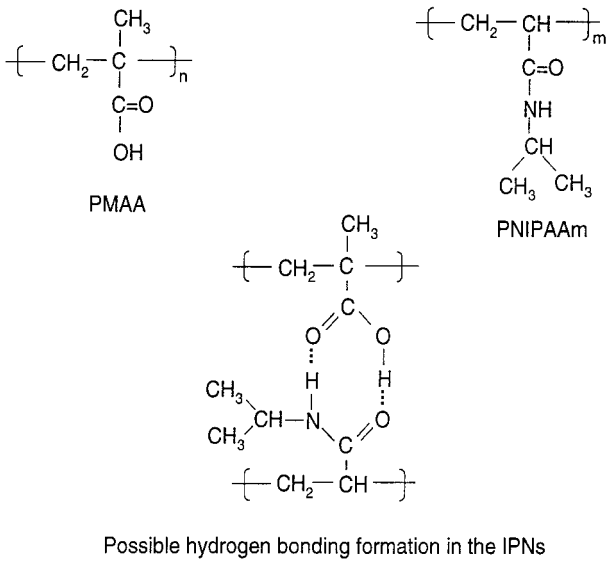

Figure 1 The molecular structures of PMAA and PNIPAAm and the hydrogen-bond formation between the two networks in the IPNs.

EXPERIMENTAL

IPN Preparation

Sequential UV solution polymerization was used to prepare IPN samples of MAA and NIPAAm. Prior to the reaction, both monomers were purified of reaction inhibitors: NIPAAm (Fisher Scientific, Pittsburgh, PA) was recrystallized in benzene/hexane, and MAA (Aldrich, Milwaukee, WI) was distilled under a vacuum to remove *p*-methoxyphenol.

The purified MAA was dissolved in methanol (40/60 v/v/) with 1 mol % the crosslinking agent tetraethylene glycol dimethacrylate (TEGDMA, Polysciences, Warrington, PA) and 1 wt % of the initiator 2,2-dimethoxy-2-phenyl acetophenone (DMPA, Aldrich). Nitrogen was bubbled through the monomer–solvent mixture for 20 min to remove oxygen dissolved in the reaction mixture. The solution was cast on glass plates equipped with spacers and reacted under an UV source with an intensity of 1 mW/cm^2 for 30 min. The polymer was then removed from the plates and immersed in deionized water to remove the unreacted monomers. The gel was taken out and placed in fresh deionized water 3 times a day for 5 days before it was dried in air and then dried in a vacuum oven. To incorporate the second network, the dried polymer network of PMAA was swollen in NIPAAm and methanol solution with the same crosslinking agent and initiator concentration till equilibrium.

The swollen gel was placed under the same UV source and polymerized for 10 min to form the IPN. The reaction time for the second polymerization was shorter than for the first one. This was due to the higher conversion of the second polymerization. The IPN was subsequently washed as mentioned previously to remove the unreacted monomers. The IPNs could also be synthesized using PNIPAAm as the first network. However, the results showed that it was easier to prepare a PNIPAAm-rich IPN system using PMAA as the first network.

IPN Characterization

The compositions of the formed IPNs were determined by elemental analysis for nitrogen (model 240C elemental analyzer, Perkin–Elmer). Equilibrium and oscillatory swelling studies were conducted on these IPN hydrogels as functions of the environmental pH, temperature, and ionic strength to examine the behavior of the IPN hydrogels upon swelling in water or pH buffer solutions. The IPN hydrogels were cut into thin

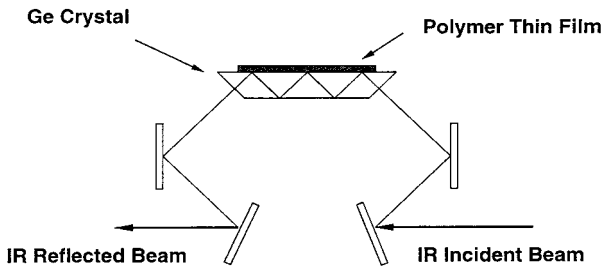

Figure 2 The sample setup on an ATR cell.

10-mm diameter disks and dried. In the equilibrium swelling experiments the dried IPN disks were placed in a pH buffer solution with a specific pH value and allowed to swell to equilibrium before being transferred to another buffer solution with a different pH value or ionic strength. The IPN samples were swollen in buffer solutions for an equal period of time before they were placed into a solution with a higher pH value or higher temperature. The swelling was evaluated in terms of the volume swelling ratio (Q), which was calculated as the ratio of hydrated volume to dry volume. The gel volume was measured by the buoyancy technique. The gels were weighed in air and heptane separately and the volume of the gel was determined by dividing the density of heptane from the weight difference.

Differential scanning calorimetry (DSC) was used to determine the low critical solubility temperature (LCST) of the IPNs. DSC (Model DSC 2910, TA Instruments, New Castle, DE) experiments were performed on swollen hydrogel specimens of 15 mg by heating from 15 to 60°C at 2°C/min. The temperature-sensitive collapse of the hydrogels was identified as an endotherm in the thermograms. The onset of the thermogram corresponded to the LCST transition.

FTIR Spectroscopic Studies

ATR-FTIR spectroscopy was used for the study of polymer thin films.[16,28,29] Figure 2 illustrates the sample setup on the ATR cell. A germanium crystal was placed in a crystal holder sitting on top of the ATR cell. The polymer thin film was cast on the surface of the crystal. The IR incident light passed through a part of the optical system and hit the germanium crystal. The angle of incidence beam at the crystal–air interface was 45°. The IR beam penetrated a small distance into the polymer thin film and was able to reflect several times before being collected by the detector. Because the depth of penetration of the IR beam into the surface layer was typically approximately equal to one-tenth of the wavelength of the radiation, intimate contact between the polymer thin film and the crystal must be guaranteed.

To increase the sensitivity of the FTIR spectrum, an MCT detector was used in this study. Liquid nitrogen was used to cool down the detector prior to the experiments. The depth of the beam penetration[16] was determined by

$$d_p = \frac{\lambda}{2\pi n_c \sqrt{\sin^2\theta - \left(\frac{n_s}{n_c}\right)^2}} \quad (1)$$

where d_p is the depth of penetration, λ is the wavelength of the IR light, θ is the incident angle of the beam, and n_s and n_c are the respective refractive indices of the sample and crystal.

In our first ATR-FTIR study we prepared IPN hydrogel samples using a sequential polymerization method.[15] The samples were cut into strips to fit the shape of the germanium crystal surface. ATR-FTIR spectra were obtained in the swollen and dry states of the IPNs. However, when swollen IPN samples were used, the absorption of the water covered the detailed structure information of the IPN and decreased the resolution. When the dried IPN samples were used, no matter how hard we tried to keep the surface of the sample flat, it was impossible to have the required intimate contact between the IPN and crystal. In order to overcome these problems, we polymerized the IPNs *in situ* on the germanium crystal.

To prepare the IPNs on the germanium crystal, a MAA methanolic solution with 60 vol % of MAA monomer, 1 mol % of TEGDMA crosslinking agent, and 1 wt % of DMPA initiator was used as the polymerization solution for the PMAA primary network. Four drops of this solution (approximately 0.1 mL) were applied on the germanium crystal. A coating of solution was formed that was approximately 0.2 μm in thickness. The holder of the crystal was then immediately put into a glove box filled with nitrogen and polymerized under UV light (1 mW/cm^2) for 2 min. The polymerization time was decreased due to the small amount of monomer. A thin film of PMAA was formed on top of the germanium crystal after the polymerization. The surface was gently washed with deionized water to remove the MAA monomer residuals and the methanol. After washing, dried air was blown over the thin PMAA film to make sure that the methanol and water had evaporated and the film was totally dried.

The second polymerization was then conducted by diffusing the second monomer solution into the thin film. Four drops of NIPAAm methanolic solution (0.4 g/*M*, approximately 0.1 mL) with 1 mol % of TEGDMA and 1 wt % of DMPA was spread on top of the thin PMAA film. Because of the thin PMAA film, the second monomer solution easily diffused through the film without destroying the intimate contact between the thin film and the crystal.

After the solution penetrated through the thin film, the second polymerization was conducted again on the ATR holder under UV light for 2 min. The final surface was washed with deionized water and dried. In doing so, we mimicked the polymerization conditions of the IPNs on the germanium crystal. On the interface between the crystal and the IPN film, PMAA and PNIPAA chains coexisted and the contact between the polymer and the crystal was very close.

RESULTS AND DISCUSSION

Possible Interactions within IPNs

Before discussing the results of the FTIR spectra, it is important to examine the molecular structures of the individual networks in the IPNs. As shown in Figure 1, the carboxylic group is the characteristic group of PMAA. When the environmental pH is lower than the pK_a (pH 5.5) of PMAA, the carboxyl groups are able to form hydrogen bonds with other proton accepting groups. In the second network of PNIPAAm the amide group is the characteristic group and it is also a proton accepting group, which can form hydrogen bonds with the carboxylic acid group in PMAA. On the other hand, the carboxyl and amide groups can also interact with water to form hydrogen bonding. Because we investigated the IPNs in their dry state, the interference with water could be neglected. A possible hydrogen-bond structure for this system is indicated in Figure 1. The intermolecular interactions between the two individual polymer networks were of great interest to this study.

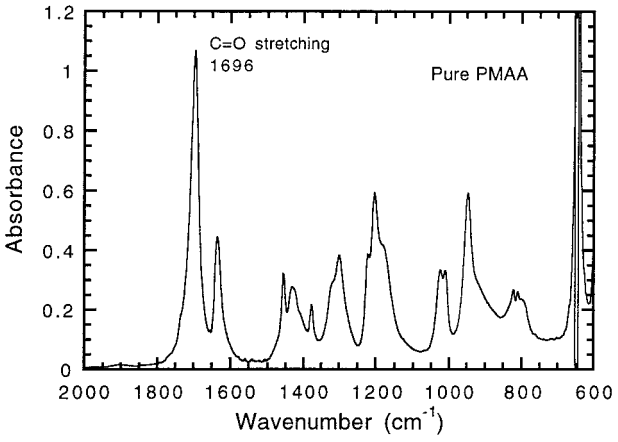

Figure 3 An ATR-FTIR spectrum of PMAA thin film prepared from a 60 vol % methanolic solution of MAA.

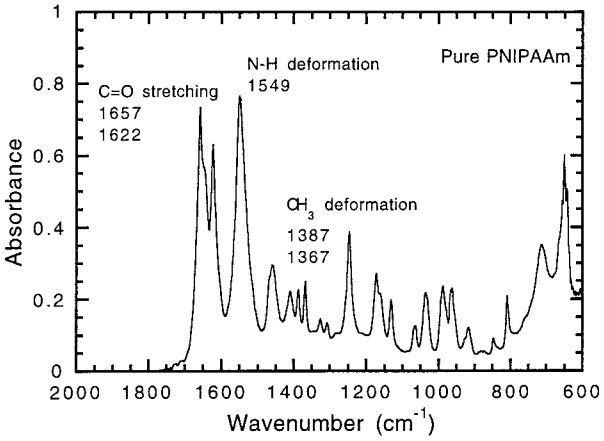

Figure 4 An ATR-FTIR spectrum of PNIPAAm thin film prepared from a 0.4 g/mL methanolic solution of NIPAAm.

Results of ATR-FTIR Analysis

The ATR-FTIR studies were carried out to increase the resolution and investigate the possible molecular interactions within the IPN thin film. The above-mentioned sampling method on the ATR crystal greatly improved the resolution of the spectra and also gave us a way to mimic the behavior of a complicated IPN system on the surface of the germanium crystal.

The ATR-FTIR spectra of the pure component polymers are shown in Figures 3 and 4. A summary of the FTIR peaks of PMAA and PNIPAAm is presented in Table I. From the FTIR spectrum of PMAA, the peak at 1696 cm^{-1} represents the C═O double-bond stretching vibration in the carboxylic acid groups of PMAA, as shown in Figure 3. The double peaks at 1657 and 1622 cm^{-1} in Figure 4 indicate the C═O double-bond stretching vibration in the amide groups of PNIPAAm. The peak at 1549 cm^{-1} indicates the N—H deformation vibration in the amide groups. In addition, the stretching vibration of the methyl groups

Table I Main FTIR Peaks of Poly(methacrylic acid) (PMMA), Poly(*N*-isopropyl acrylamide) (PNIPAAm), and Their IPNs

Functional Vibrations	Absorption Wave Numbers of Polymers (cm^{-1})
C═O Stretching in carboxylic group of PMAA	1696
C═O Stretching in amide group of PNIPAAm	1657, 1622 doublet
N—H Deformation in amide group of PNIPAAm	1549
CH_3— Stretching in isopropyl group of PNIPAAm	1387, 1367

in PNIPAAm was also unique in this study, because they were connected to a tertiary carbon atom, which made them different from the methyl groups in PMAA.

The three small peaks at 1387 and 1367 cm^{-1} indicated the stretching vibration of these methyl groups in PNIPAAm. The purpose of this investigation was to find out if the characteristic peaks of the pure component networks can hold in the spectrum of the IPNs. The wave number of each vibration was determined by eq. (2). As mentioned before, the formation of hydrogen bonding and other molecular interactions affects the position of the involved peaks by shifting to a lower wave number. This is due to the decrease in the force constant of the vibration caused by the formation of hydrogen bonds.

$$\bar{\nu} = \frac{1}{2\pi C}\sqrt{\frac{k}{\mu}} \tag{2}$$

where $\bar{\nu}$ is the wave number of the vibration, C is the speed of light, k is the force constant, and μ is the reduced mass of the vibration elements.

The ATR-FTIR spectrum of a PMAA/PNIPAAm IPN thin film prepared by the UV sequential polymerization method is shown in Figure 5. If no molecular interaction took place in the IPN, the peaks in the spectrum of the IPN should be a simple summation of the peaks in pure PMAA and PNIPAAm without shifts in the peak wave numbers. In the Figure 5 comparison of the pure PNIPAAm, there was no shift in the wave numbers for the methyl groups in the IPN thin film. The three small peaks indicating the stretching vibration of the methyl groups had the exact wave numbers as those obtained from the pure PNIPAAm. This was what we expected, because the methyl groups cannot interact with other groups in the system.

However, in the spectrum of the IPN, we observed shifts in the N—H deformation peak of the PNIPA network and the C═O stretching peak in the PMAA network of the IPN. The wave number of the N—H peak decreased from 1549 to 1545 cm^{-1}, and the wave number of the C═O peak decreased from 1696 to 1693 cm^{-1}. The shifts for both peaks were about four units to the lower wave number. The equipment error was within one unit. This result indicated that there was an interaction between the carboxylic groups of PMAA and the amide groups of PNIPAAm. Also, the width of the peaks in the IPNs increased compared with the pure polymers. This was an additional indication of potential hydrogen-bond formation in the IPNs as indicated in Figure 1.

CONCLUSIONS

ATR-FTIR spectroscopy was used in this study to elucidate the intermolecular interactions within a PMAA/PNIPAAm IPN system. A hydrogen-bond structure between the carboxylic acid group in PMAA and the amide group in PNIPAAm was proposed. The ATR-FTIR results showed small shifts in the wave numbers of the above characteristic groups, which was an indication of hydrogen-bond interactions between the PMAA and PNIPAAm networks.

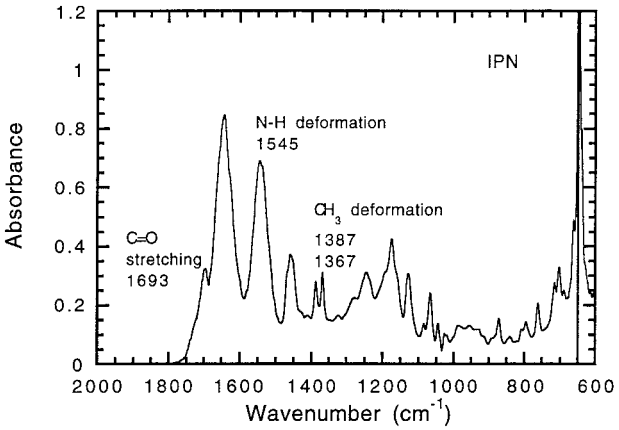

Figure 5 An ATR-FTIR spectrum of a PMAA/PNIPAAm IPN thin film prepared by UV sequential polymerization.

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