# Blends Composed of Poly(*N*-isopropylacrylamide) and an Ethylene/Vinyl Alcohol Copolymer: Thermal and Morphological Studies

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**ABSTRACT:** Blends of poly(*N*-isopropylacrylamide) (PNIPAM) and an ethylene/vinyl alcohol copolymer (EVAL) were obtained through casting from dimethyl sulfoxide (DMSO) solutions and phase inversion in 50/50 DMSO/$H_2O$ solutions. The miscibility and morphology of the PNIPAM/EVAL blends were investigated with thermal and morphological analysis. Differential scanning calorimetry indicated that the crystallinity of EVAL decreased with increasing PNIPAM content and that the blends cast from DMSO/$H_2O$ solutions were miscible in the melt state. Measurements of the melting point depression allowed the determination of the interaction energy density (*B*) and Flory–Huggins interaction parameter ($\chi_{12}$) with the Nishi–Wang equation. The negative *B* and $\chi_{12}$ values obtained were examined in terms of the specific intermolecular interactions between the polymers. Scanning electron micrographs revealed that blends obtained by the casting method led to dense membranes, whereas the phase-inversion method rendered typical macroporous membranes. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 501–505, 2004

**Key words:** stimuli-sensitive polymers; melting point; thermal properties; blends; membranes

## INTRODUCTION

Environmental stimuli-response hydrogels are materials that can modulate the swelling ratio in response to external stimuli such as temperature,[1–3] pH,[4] chemicals,[5] photoirradiation,[6] and electric fields.[7] Stimuli-sensitive polymer systems can reversibly change their volume and shape according to some physicochemical factors.[8] These chemical (pH, metabolite, and ionic-factor) and physical (temperature and electrical-potential) signals alter the interactions between the polymer chains or between the polymer chain and solutes present in the system, thereby changing some polymer properties such as solubility and swelling.[4]

Among these stimuli-sensitive polymers, thermosensitive and pH-sensitive materials have been intensively studied for drug delivery systems and enzyme activity control because temperature and pH are important quantities in the human body.[9,10] Thermosensitive hydrogels with an upper critical solution temperature (UCST) shrink by cooling below the UCST in a positive temperature-sensitive system, whereas in a negative temperature-sensitive system, hydrogels with a lower critical solution temperature (LCST) contract by heating above the LCST.

Chemically crosslinked poly(*N*-isopropylacrylamide) (PNIPAM) is an important example of a negative temperature-sensitive system. A thermosensitive PNIPAM hydrogel exhibits a reversible volume-phase transition from a swollen state to a shrunken state around the LCST of the linear PNIPAM segments.[9–11] The linear PNIPAM chain is soluble in cold water but separates from solution upon heating through the LCST (at 31°C).[12,13]

Linear and crosslinked PNIPAMs have received increasingly attention for their representative thermosensitivity and easy preparation. Many studies of PNIPAM have focused on pharmaceutical applications[9,14] (drug-release-regulating devices) and mass-separation applications[15–17] (thermosensitive membranes). However, PNIPAM has weak mechanical strength because of its high water content, which limits its practical applications. To solve this problem and improve its mechanical properties, researchers have tried copolymerizing, blending, and forming interpenetrating polymer networks. Following this principle, we have already reported miscibility studies of blends involving PNIPAM and poly(vinyl alcohol) (PVA), poly(vi-

nyl pyrrolidone) (PVP), poly(acrylic acid) (PAA),[18] and poly(ethylene glycol). The latter were used for methane and carbon dioxide separation from biogas.[19]

Presently, we are studying blends composed of PNIPAM and an ethylene/vinyl alcohol copolymer (EVAL), which is a thermoplastic resin with a semicrystalline structure with potential applications for contact lenses[20] and vascular grafts.[21]

This work was aimed at the preparation of PNIPAM/EVAL blends, through casting and phase-inversion methods, and the evaluation of the intermolecular interactions between the polymers. This was achieved by an analysis of the miscibility and morphology, mainly with differential scanning calorimetry (DSC) and scanning electron microscopy (SEM).

## EXPERIMENTAL

### Materials

PNIPAM was synthesized via a free-radical mechanism, under a nitrogen atmosphere, according to a method described by Freitas.[22] The monomer (*N*-isopropylacrylamide; Aldrich, Milwaukee, WI) and initiators (ammonium persulfate and sodium metabisulfite; Reagen, Rio de Janeiro, Brazil), which were analytical-grade, were used as received. EVAL (Clarene® R20), with an ethylene molar content of 40%, was supplied by Solvay & Cie (Rosignano, Italy). Other chemicals were reagent-grade.

### Casting blends

Two polymer solutions in dimethyl sulfoxide (DMSO; 2 wt %) were separately prepared by the dissolution of PNIPAM and EVAL samples at room temperature
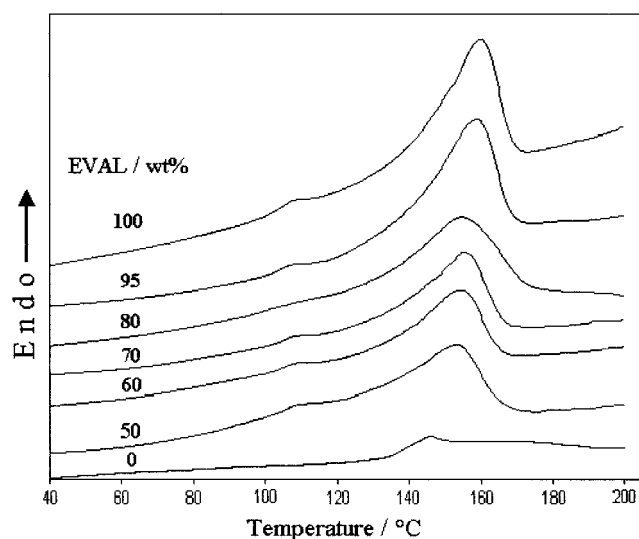


**Figure 1** DSC curves for PNIPAM/EVAL casting blends (heating rate = 10°C min$^{-1}$).
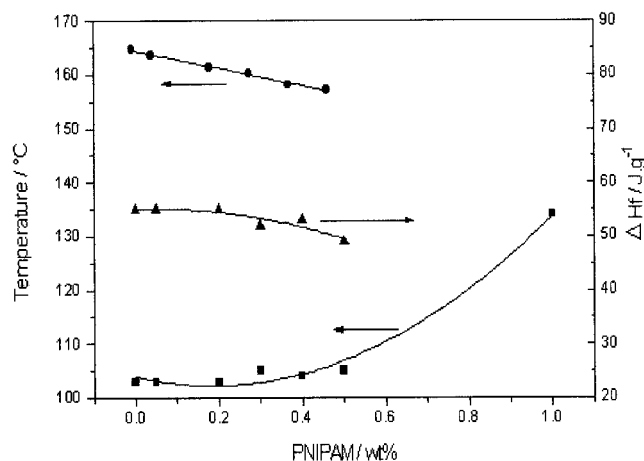


**Figure 2** Phase diagram for PNIPAM/EVAL casting blends: (●) $T_m$, (▲) enthalpy of fusion, and (■) $T_g$.

with continuous stirring. These solutions were mixed in desired proportions and then stirred for 30 min. The relative compositions of the two polymers in the mixed solutions ranged from 5/95 to 50/50 (w/w) PNIPAM/EVAL. The polymers and blends were cast on Petri plates through DMSO evaporation in a drying oven at 40°C. The films were stored in a desiccator.

### Phase-inversion blends

PNIPAM (20 wt %) and EVAL (15 wt %) solutions were prepared in DMSO, mixed to obtain the desired proportions, and stirred for 30 min at room temperature. PNIPAM/EVAL solutions (1.5 mL) were dropped onto glass slices (2 cm × 10 cm) and immersed in a 50/50 DMSO/H$_2$O solution. After 30 min of phase inversion, the blends were removed, dried by the freeze-drying method, and stored in a desiccator.

### DSC

DSC curves were obtained with a PerkinElmer (USA) DSC 7. Samples of about 5 mg, under a nitrogen flow in aluminum pans, were used at a scanning rate of 10°C min$^{-1}$.

### SEM

SEM micrographs were obtained with a JEOL (Japan) JSM-T300 (at 15 kV) with samples that were ripped at the ambient temperature and sputter-coated with gold.

## RESULTS AND DISCUSSION

### Miscibility studies

The miscibility of PNIPAM/EVAL casting blends was studied with DSC. Figure 1 displays the PNIPAM,

EVAL, and PNIPAM/EVAL DSC curves. The results obtained from DSC are summarized in Figure 2. Pure EVAL exhibited a glass-transition temperature ($T_g$) at 103°C and a relatively broad melting endotherm [i.e., melting temperature ($T_m$)] with a peak at 160°C. The PNIPAM homopolymer presented $T_g$ at 134°C. The blends, in all the compositions studied, showed a single endothermic peak corresponding to the melting of the crystalline phase of EVAL and only one $T_g$ that did not change appreciably with the composition. The $T_g$ observed in Figure 1 was very near $T_g$ of pure EVAL, and this suggested that the amorphous phase was rich in a semicrystalline copolymer. It was not possible to detect $T_g$ of PNIPAM in these systems because of its proximity to the intense EVAL melting peak. As the PNIPAM content increased, this endothermic melting peak became broader, with an associated systematic depression in $T_m$ values (from 160°C for pure EVAL to 153°C for a 50/50 system; see Fig. 2). This indicated that some kind of interaction between the two polymers became more prominent at elevated temperatures near $T_m$ of the semicrystalline polymer. A simultaneous fusion heat reduction (see $\Delta H_f$ in Fig. 2) indicated that the EVAL crystallinity degree decreased because of blending with PNIPAM, and the lowering in the crystallinity was more evident for the higher PNIPAM concentrations.

In recent years, many studies have been reported of polymer blends exhibiting miscibility with a concomitant melting point depression ($\Delta T_m$): poly(3-hydroxybutyrate) (PHB) and poly(3-hydroxybutyrate-co-hydroxyvalerato) with poly(epichlorohydrin-co-ethylene oxide) (PECH-EO),[23] poly(ethylene oxide) (PEO) with poly(epichlorohydrin) and PECH-EO,[24] PHB with cellulose acetate butyrate,[25] PVA with PAA,[26] PVA with PVP,[27] and PVA and EVAL with hyaluronic acid (a naturally occurring mucopolysaccharide).[28] This phenomenon was explained by Nishi and Wang[29] in
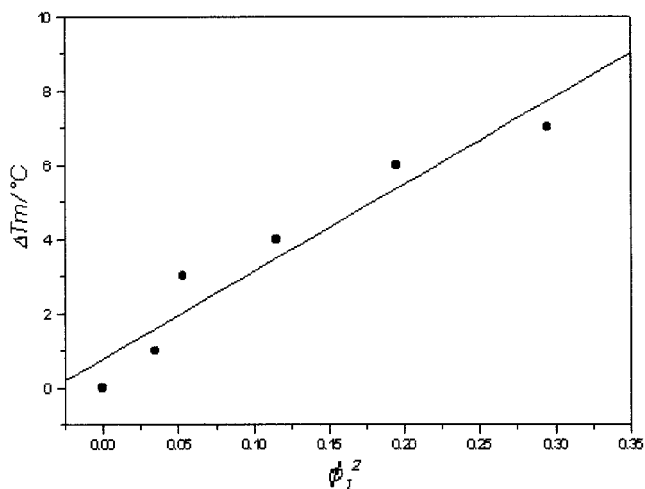
terms of thermodynamic mixing accompanied by exothermic interactions between a crystalline polymer and an amorphous one. According to these authors, $\Delta T_m$ can be determined as follows:

$$\Delta T_m = T_m^0 - T_m = - T_m^0 (V_{2u}/\Delta H_{2u}) B \phi_1^2 \quad (1)$$

where subscripts 1 and 2 designate the amorphous and crystalline polymers, respectively; $T_m{}^0$ is the pure crystalline polymer melting temperature; $T_m$ is the blend melting temperature; $V_u$ is the molar volume of the repeating unit; $\Delta H_u$ is the enthalpy of fusion per mole of the repeating unit; $B$ refers to the interaction energy density of the two polymers; and $\phi$ is the volume fraction. In practice, $B$ is related to the Flory–Huggins polymer–polymer interaction parameter ($\chi_{12}$) by the following relationship:

$$B = R T_m^0 (\chi_{12}/V_{1u}) \quad (2)$$

where $R$ is the universal gas constant.

According to eq. (1), $\Delta T_m$ of the crystalline component is proportional to the square of the amorphous polymer volume fraction ($\phi_1^2$). Assuming a linear relationship between $\Delta T_m$ and $\phi_1^2$ we constructed the plot displayed in Figure 3; the solid line was obtained by the least-square method. As shown in this figure, $\Delta T_m$ of PNIPAM/EVAL linearly increases with $\phi_1^2$ according to the following equation:

$$\Delta T_m = 23.503 \phi_1^2 + 0.78 \quad (3)$$

The observed small intercept (0.78°C) can be assigned to residual entropic effects.[30]

From the slope (25.503°C) of the curve shown in Figure 3, we could calculate $B$ and $\chi_{12}$ with eqs. (1) and (2), respectively, with the following values: 1.16 g cm$^{-3}$ and 32.41 cm$^3$ mol$^{-1}$ for the specific density and molar volume, respectively, of EVAL,[31] and 117.0 cm$^3$ mol$^{-1}$ for the molar volume of PNIPAM.[32] Unfortunately, the latent heat of fusion of 100% crystalline EVAL ($\Delta H_{2u}$) was not available, and this made it impossible to specify $B$. However, because the EVAL crystallinity was estimated within a range of 25–40% and $\Delta H_f$ of these copolymers was obtained experimentally, ranges of $B$ and $\chi_{12}$ values could be estimated. These results are reported in Table I, and the values

**TABLE I**
**B and $\chi_{12}$ for PNIPAM/EVAL Blends as a Function of the Crystallinity of EVAL**

| Crystallinity (%) | $B$ (cal cm$^{-3}$) | $\chi_{12}$ |
|---|---|---|
| 25 | −3.53 | −0.48 |
| 40 | −2.20 | −0.30 |



**Figure 3** Variation of $\Delta T_m$ with $\phi_1^2$.

**TABLE II**
**$B$ and $\chi_{12}$ Values for Some Binary Blends with Components Compatible in the Melt**

| Blend | $B$ (cal cm$^{-3}$) | $\chi_{12}$ | Reference |
|---|---|---|---|
| PVA/PVP | −7.1 | −0.65 | 27 |
| HA/Clarene R20 | −6.6 to −5.9 | −1.9 to −1.6 | 28 |
| PEO ($M_w = 3.65 \times 10^5$)/PMMA | −1.07 | −0.139 | 33 |
| PEO ($M_w = 4.0 \times 10^6$)/PMMA | −1.01 | −0.131 | 33 |

HA = hyaluronic acid; $M_w$ = weight-average molecular weight; PMMA = poly(methyl methacrylate).

are very close to those reported for other compatible polymer blends shown in Table II.

The negative $\chi_{12}$ values obtained for the PNIPAM/EVAL systems supported the idea that these blends were compatible in the melt and suggested very strong intermolecular interactions, such as hydrogen bonding, between molten EVAL and amorphous PNIPAM. The small $\Delta T_m$ value (0.78°C) for $\phi_1^2 = 0$ in eq. (3) reflects the reduced contribution of the entropic effects to $\chi_{12}$.

The previous discussion was based only on the thermodynamic behavior. However, $\Delta T_m$ may also be caused by morphological effects such as lowering of the crystal perfection or geometry due to the presence of the amorphous polymer.[29] These morphological effects can be removed by the estimation of the thermodynamic polymer–polymer interaction parameter ($\chi_{12}$) through the Hoffman–Weeks method[34,35] with data for samples crystallized isothermally at various temperatures.

## Morphological investigations

The morphological studies were carried out with ripped-surface samples. SEM was performed for blends obtained by casting and phase-inversion methods. Such blend preparation methods rendered typical dense and macroporous membranes, respectively. Figure 4 shows SEM micrographs for two representative 30/70 PNIPAM/EVAL membranes. Figure 4(a) suggests that the casting method was able to rend a dense membrane composed of two distinct zones: a very compact region and a porous one. However, the phase-inversion method allowed the preparation of macroporous and heterogeneous membranes [Fig. 4(b)]. This micrograph presents a 30/70 PNIPAM/EVAL membrane cross section obtained by phase inversion in a 50/50 DMSO/H$_2$O solution. Two macroporous groups were observed with dimensions varying from 20 to 200 $\mu$m; this indicated potential applications in suspensions separation.

## CONCLUSIONS

By casting from DMSO solutions and by phase inversion from 50/50 DMSO/H$_2$O solutions, we prepared blends composed of PNIPAM and EVAL. The miscibility and morphology of the components were studied with DSC and SEM, respectively. DSC results revealed that the EVAL crystallinity decreased with the incorporation of PNIPAM. The systematic depression in $T_m$ of EVAL allowed us to conclude that the polymer pair was thermodynamically miscible. This miscibility may have been due to easily occurring interactions such as hydrogen bonding. The SEM studies revealed that dense and macroporous membranes
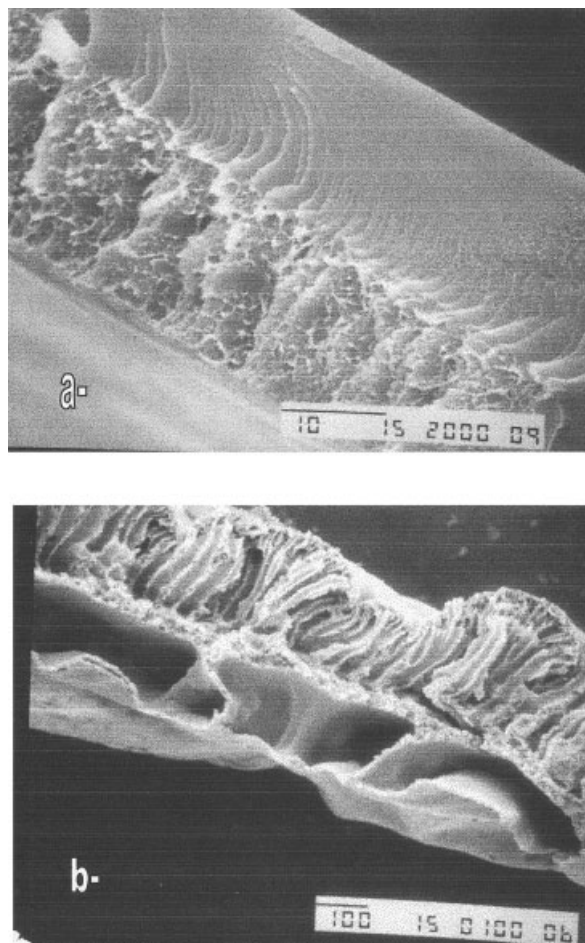


**Figure 4** Surface SEM micrographs of 30/70 PNIPAM/EVAL (a) casting and (b) phase-inversion membranes.

were obtained by the casting and phase-inversion methods, respectively.

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