

Interpenetrating polymer networks with controllable intermolecular hydrogen bonding: Swelling behavior

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Summary

The swelling behavior in different solvents of IPNs based on poly(butyl acrylate) and modified polystyrene containing strong proton-donor hydroxyl groups is studied. The experimental data of the volume fractions of the networks in the swollen state V_{expt} at equilibrium are compared with those expected from the Thiele-Cohen equation (V_{TC}), which assumes that the two networks are independent and no additional crosslinks form during the formation of the IPNs. For the IPNs without inter-component hydrogen bonding, V_{expt} in toluene are in good agreement with V_{TC} . As the hydroxyl content increases, the deviation of V_{expt} from V_{TC} increases indicating more crosslinks form in the process of IPN formation. This deviation in the solvents of proton-acceptor type becomes smaller but still apparent. This result implies that hydrogen bonding between the components is destroyed by the solvents but the physical entanglements formed during the formation of the IPNs remain.

Introduction

A systematical study on IPN (interpenetrating polymer networks) with introduced hydrogen bonding has been carried out in this laboratory (1,2). This communication aims at exploring the nature of the crosslinks in the IPNs, particularly those formed during the process of IPN formation, by swelling study. The IPN system studied in this communication is the same as that reported previously (1,2), i.e. the interpenetrating networks of poly(butyl acrylate) (PBA) and PS(OH), a random copolymer of styrene and hydroxyl-containing comonomer HFMS ($\text{CH}_2=(\text{CH}_3)\text{C}-\text{C}_6\text{H}_4-\text{C}(\text{CF}_3)_2(\text{OH})$). In the IPNs, both the densities of inter-component hydrogen bonds and intra-component crosslinks of PBA and PS(OH) networks are independently adjustable. Therefore, it makes possible to study the effect of hydrogen bonding on the miscibility at different levels of crosslinking and the effect of the crosslinking at different levels of hydrogen bonding.

For a single polymer network, the Flory-Rehner (3) equilibrium swelling equation has been widely used to study the swelling behavior and to determine the crosslink density, i.e., the number of moles of network chains per cm^3 , N , from the volume fraction of polymer in the swollen mass, v :

$$\ln(1 - v) + v + \chi v^2 = -V_s N (v^{1/3} - v/2)$$

where V_s is the molar volume of the solvent and χ is the polymer-

solvent interaction parameter. For homo-IPNs, i.e., where two networks are chemically identical except for crosslink level, assuming the two networks elastically and chemically independent, Thiele and Cohen (4) derived the corresponding equation (T-C equation)

$$\ln(1 - v_1 - v_2) + v_1 + v_2 + \chi (v_1 + v_2)^2 = -v_s N_1 (v_1^{1/3} - v_1/2) - v_s N_2 ((v_2^0)^{2/3} v_2^{1/3} - v_2/2)$$

where subscripts 1 and 2 refer to polymer networks 1 and 2 respectively, so, v_1 and v_2 represent the volume fractions of the two polymers in the equilibrium swollen state while v_2^0 represents that of network 2 in the dry state, and N_1 and N_2 denote the crosslink densities of the corresponding single networks in mol/cm³, which are determined by swelling the single networks based on the Flory-Rehner equation. Therefore, The T-C equation can be used to predict the swelling behavior of an IPN expressed by the total volume fraction, $v = v_1 + v_2$, provided the solvent-polymer interaction parameter χ is known and N_1 and N_2 are obtained experimentally. Afterwards, Hargest et al.(5) have extended the T-C equation to IPN systems composed of two different polymer networks by simply replacing the interaction parameter χ in the T-C equation by an average interaction parameter

$$\chi_s = w_1 \chi_1 + w_2 \chi_2$$

where w_1 and w_2 are the weight fractions of polymers 1 and 2, respectively, and χ_1 and χ_2 are the interaction parameters for polymers 1 and 2, respectively.

It is noticed that the T-C equation is derived based on the assumptions that both networks are continuous in space, but chemically and elastically independent. Therefore, by comparing the values of the total polymer volume fraction, $v_1 + v_2$ expected by the T-C equation, v_{TC} , with those determined from the swelling of IPNs, v_{expt} , instructive information related to the possible addition of new physical crosslinks during the formation of IPN systems can be obtained. In fact, in a plot of v_{TC} vs. v_{expt} , if the data lie on the right side of the line $v_{TC} = v_{\text{expt}}$, it implies that new physical or chemical crosslinks are added during IPN formation, which leads to low swelling and consequent high v_{expt} values.

Based on this argument, Siegfried et al.(6) studied swelling of polystyrene homo-IPNs in toluene and found the experimental data are quite close to the line of $v_{TC} = v_{\text{expt}}$, which indicates no substantial additional crosslinks form accompanying the IPN formation. The data reported by Millar et al.(7), Shibayama et al.(8) and Thiele et al.(4) and summarized by Siegfried et al.(6) confirmed this conclusion. Moreover, instead of homo-IPNs, Hargest et al.(5) studied swelling of anionic/cationic IPNs based on crosslinked polystyrene and poly(4-vinyl pyridine). The data also demonstrate that no new physical or chemical crosslinks appeared substantially during the IPN information. The data for the IPNs of polyurethane/polystyrene reported by Lipatov et al.(9) were analyzed by Hargest et al.(5) using the T-C equation. It was found that all the data lie above the theoretical line showing a greater degree of swelling than predicted. In short, so far there have been no swelling data of IPNs in literature indicating the formation of

additional crosslinks in the process of IPN preparation. But what is the situation for the IPNs with strong inter-component hydrogen bonding?

Experimental

A series of sequential IPNs comprising PBA and PS(OH) (w/w 50/50) were prepared by free radical polymerization. Acrylic anhydride and divinylbenzene were used as crosslinking agents for PBA and PS(OH), respectively. PBA networks a,b,c and d with respective M_c values (average molecular weight between crosslinks in kg/mol) of 9.7, 5.1, 4.2 and 3.2 were prepared as the first network and PS, PS(OH)-5 and PS(OH)-30, where the numbers refer to HFMS contents (mol%), were used as the second networks. All the IPNs have the same crosslink density of the second network PS(OH), i.e., 1% crosslinking agent was used for the polymerization. The details of the IPN preparation is described elsewhere (1).

Swelling experiments of the IPNs were performed with the solvents of toluene, methyl ethyl ketone (MEK) and tetrahydrofuran (THF). The interaction parameters of PBA and PS with the solvents are cited from reference (10). The interaction parameters between PS(OH) with different hydroxyl content and the solvents were calculated from the corresponding solubility parameters in the solvents according to the well-known Scott equation

$\chi = B + V_s (\delta - \delta_s)^2 / RT$. The solubility parameters of PS(OH)-5 and PS(OH)-30 are found to be 19.4 and 20.5 $J^{1/2}/cm^{3/2}$, respectively, by equilibrium swelling measurements of the corresponding PS(OH) networks in thirteen solvents covering a broad range of solubility parameters from 16.4 to 25.0 $J^{1/2}/cm^{3/2}$.

Results and Discussion

We discuss the results of the IPNs of PBA/PS without the hydroxyl groups first. As shown in Fig.1, without exceptions, all the swelling data of the IPNs with different crosslink degrees of PBA networks (a, b, c and d) in the three solvents lie on or quite close to the line $v_{TC} = v_{expt}$. This accordance obviously indicates that under the condition of no inter-component hydrogen bonding, during the formation of the IPNs, i.e., the formation of the second network in the matrix of the first one, two networks keep independent and no new crosslinking structure appears. This is just the same as the behavior of the IPNs discussed above (4-9).

Introducing the hydroxyl groups in IPNs results in a deviation of the swelling data of the IPNs in toluene from the T-C equation. As shown in Fig.2, for the case of IPNs containing PS(OH) with 5 mol% HFMS units, independently on the crosslink density of PBA networks, apparent shifts of the data to the right side of the line, $v_{TC} = v_{expt}$, are observed. The deviation becomes more pronounced when the hydroxyl content in PS(OH) increases to 30 mol%. This progressive decrease of swelling of the IPNs in toluene with increasing the introduced hydroxyl groups in PS(OH) is undoubtedly associated with the formation of the inter-component hydrogen bonds. In our previous work (1,11) it was reported that almost all hydroxyl groups in both PS(OH)/Poly(alkyl acrylate) IPNs and the blends of the corresponding linear polymers are involved in forming hydrogen bonding with carbonyl groups as evidenced by the disappearance of the infrared stretching bands of the free and

self-associated hydroxyl groups. Therefore, it is in expectation that the crosslinks due to hydrogen bonding formed in the process of IPN formation will affect the swelling behavior of the IPNs. A simple calculation may provide a intuitive estimation of the effect of the introduced hydrogen bonding on the crosslinking structure, i.e. For the IPNs of PBA/PS(OH)-30 in toluene, from the data shown in Fig.2, the polymer fractions V predicted by the T-C equation and measured experimentally are about 0.25 and 0.45, respectively. By substituting these values to the T-C equation and assuming the two networks having the same crosslink density, the V values correspond to crosslink densities of 1.8×10^{-4} and 9.3×10^{-4} mol/cm³, respectively. This result shows that the crosslinking density increases about five times in the process of IPN formation. Of course, this substantial change of the crosslink structure in the IPNs is a very important factor, which has to be fully considered in studying the structure and properties of the IPNs.

The contribution of hydrogen bonding to the decrease of the swelling of the IPNs may, intuitively be classified into two parts - the first, hydrogen bonds themselves constitute physical crosslinking structure; and the second, hydrogen bonding between the network chains promotes interpenetration between the chains, which leads to more chain entanglements. Now we may ask whether it is possible to distinguish the two kinds of the crosslink increments experimentally?

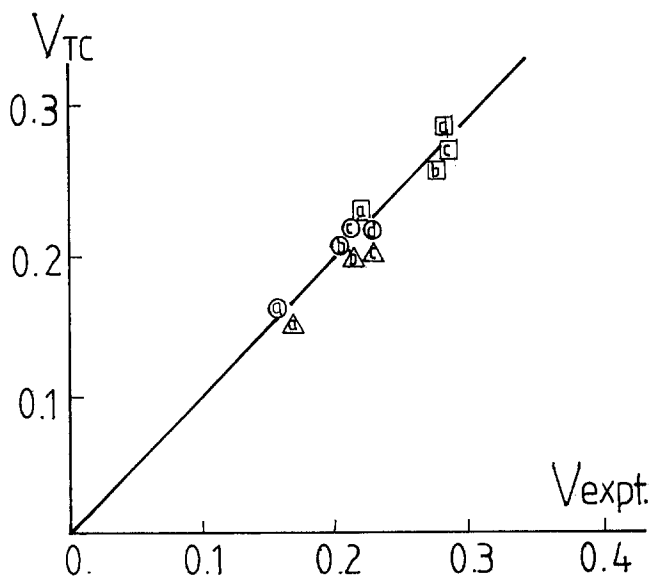


Fig.1 V_{TC} vs. V_{expt} for the IPNs without hydrogen bonding in different solvents, \circ - toluene, \triangle - THF, \square - MEK, a, b, c and d refer to the average molecular weights between the crosslinks of PBA networks being 9.7, 5.1, 4.2 and 3.2 kg/mol, respectively

In our previous study on solution properties of PS(OH) and poly(ethyl methacrylate) (PEMA) by fluorescence spectroscopy (11), it was found that in a non-polar medium, PS(OH) can form macromolecular complex with PEMA due to the inter-component hydrogen bonding. Of much interest is that decomplexation occurs when a solvent of proton-acceptor type such as MEK and THF is added, even in a small amount, into the solution. This indicates that the proton-acceptor solvent molecules are able to supersede the carbonyl groups in PEMA in forming hydrogen bond with PS(OH). Considering this conclusion, comparison of the swelling of the IPNs with high hydroxyl content in non-polar solvent with that in proton-acceptor type solvents would be of interest.

Fig.3 presents the results of PS(OH)-30/PBA IPNs in toluene, THF and MEK. It is apparent that the data obtained for in THF and MEK are close to each other but show substantial difference with the T-C equation. If the inter-component hydrogen bonds are really destroyed in THF and MEK, then this difference can be attributed to the contribution of the additional chain entanglements formed in the process of IPN formation since they are not apparently affected by changing the solvents. Nevertheless, the swelling in MEK and THF is still much larger than that in toluene, obviously, this difference stems from the contribution of hydrogen bond itself.

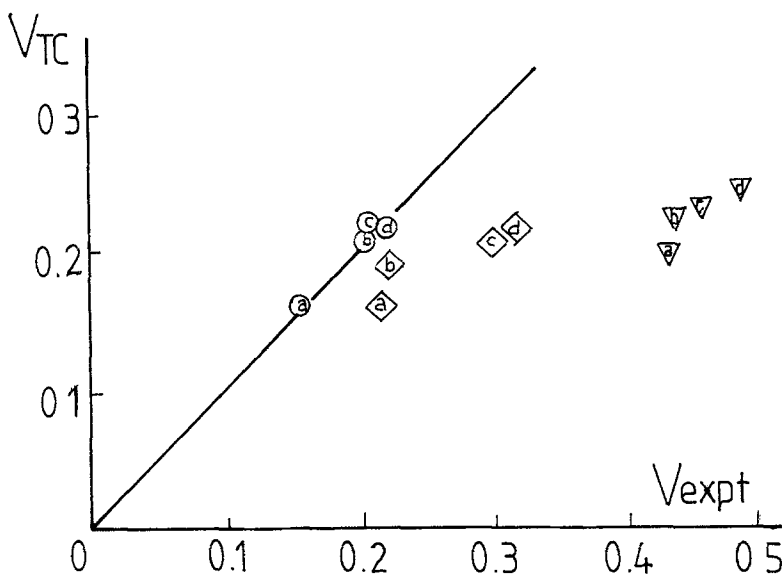


Fig.2 V_{TC} vs. V_{expt} in toluene for the IPNs with different hydroxyl contents in PS(OH):

○ - 0 mol%, ◇ - 5 mol%, ▽ - 30 mol% a, b, c and d refer to the average molecular weights between the crosslinks of PBA networks being 9.7, 5.1, 4.2 and 3.2 kg/mol, respectively

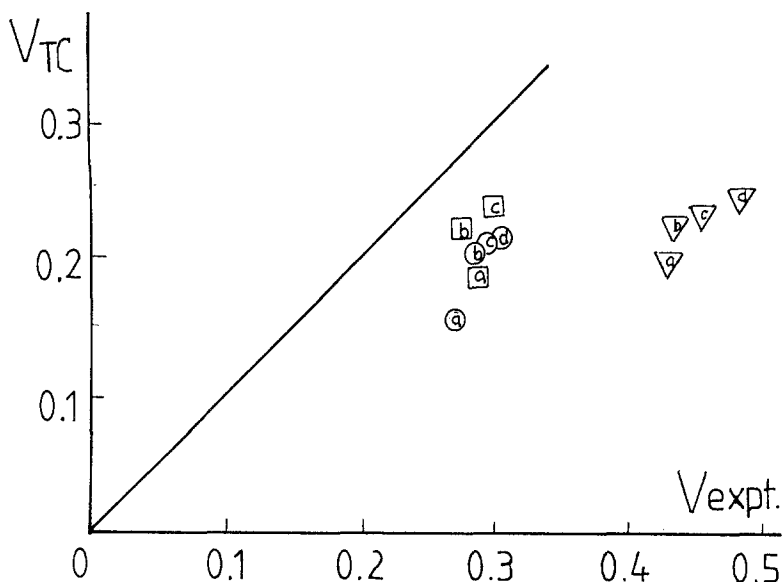


Fig.3 V_{TC} vs. V_{expt} for the IPNs with 30 mol% OH in PS(OH) in different solvents: \circ - toluene, ∇ - THF, \square - MEK, a, b, c and d refer to the average molecular weights between the crosslinks of PBA networks being 9.7, 5.1, 4.2 and 3.2 kg/mol, respectively

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