

Swelling Behavior of Interpenetrating Polymer Networks Containing Ionic Groups

Interpenetrating polymer networks (IPN's) are prepared by swelling a polymer network I with monomer II, plus crosslinker and activator, and polymerizing II in situ.¹⁻⁹ While the concept of molecular interpenetration may be reached only in the limit of true compatibility between networks I and II, the products of such syntheses have been shown to exhibit a complex phase morphology usually involving both a cellular structure of about 1000 Å and a fine structure of about 100 Å.^{3,6,8} Depending on whether polymers I and II are similar or different in chemical nature, dynamic mechanical spectroscopy studies indicate greater or lesser amounts of molecular mixing between the two components, but never true molecular mutual solution. However, more molecular mixing occurs with IPN's than with the corresponding mechanical blends,^{9,10} probably because of the mechanical entrapment of visiting chain portions by the crosslinked structure of the host phase.

All of the IPN's prepared to date in this laboratory have been composed of simple organic materials: acrylics, methacrylics, styrenes, and butadiene have seen extensive use. At this time, we wish to report on the synthesis and swelling behavior of IPN's containing ionic groups along one of the networks. These materials are, of course, related to the ionomers.¹¹⁻¹⁵ The ionomers are known to phase separate into domains rich in ionic groups and a continuous phase nearly devoid of ions. In the present case, then, one may expect the presence of three phases: ionic domains, network I chains, and network II chains. In fact, however, the ionic domains would be expected to permeate only its associated network phase, leaving the other relatively unperturbed.

Since the entire material is, in fact, thermoset, the IPN will not truly dissolve in any solvent. Yet the great differences between the phases suggest that swellents containing a wide range of solubility parameters might effectively swell the material. Since one phase would be expected to remain relatively unswollen under many conditions, interesting physical properties for such materials are expected.

This note will report on the synthesis of poly(ammonium acrylate-co-ethyl acrylate)/polystyrene, P(NH₄A-co-EA)/PS IPN's, their inverses, and homopolymers. Swelling was carried out using either water or toluene.

EXPERIMENTAL

Styrene and solutions of varying ratios of acrylic acid (AA) and ethyl acrylate (EA) were the monomers used for the synthesis. To 100 ml of each monomer was added 0.3 g benzoin as a photoinitiator and 0.5 ml tetraethylene glycol dimethacrylate as a crosslinker. Two series of IPN's were prepared, based on 20/80 and 25/75 AA/EA monomer ratios, with styrene serving as the complementary monomer. In addition, several materials containing a wide range of compositions were prepared. After formation of P(AA-co-EA) or PS as network I, the complimentary monomer was swollen in and allowed to come to equilibrium before being polymerized in situ, forming the IPN. Crosslinkers and activators were used as above. As previously described,¹ the materials were synthesized in the form of sheets with the use of ultraviolet radiation. The compositions of the IPN's and their parent networks are shown in Table I. The first-listed polymer forms network I.

All the finished IPN's and their parent networks were soaked in aqueous ammonium hydroxide solutions of increasing concentration up to 1 molar, to convert the acrylic acid portion to ammonium acrylate. (Direct soaking in 1 molar ammonium hydroxide solutions sometimes caused stress cracking.) Each sample was then dried under vacuum at 60°C for at least 3 hr. The resulting poly(ammonium acrylate-co-ethyl acrylate)/polystyrene, P(NH₄A-co-EA)/PS, IPN's, inverses, and parent materials were submitted to Dr. George Robertson, Florham Park, N.J., for carbon, hydrogen, and nitrogen

TABLE I
Composition and Equilibrium Swelling of Ionic IPN's and Parent Networks*

Sample no.	Composition		Swell-ent	Per cent swelling	
	Per cent	Polymers		Experi-mental	Theo-retical ^b
1	100	PS*	w	1.09	—
			t	1030	—
2	20-co-80	P(AA-co-EA)	w	1620	—
			t	45.1	—
3	25-co-75	P(AA-co-EA)	w	3860	—
			t	34.2	—
4	(14-co-55)/31	P(AA-co-EA)/PS	w	385	1110
			t	116	352
5	(23-co-68)/9	(PAA-co-EA)/PS	w	600	3520
			t	53.9	112
6	62/(8-co-30)	PS/P(AA-co-EA)	w	42.7	618
			t	463	653
7	35/(16-co-49)	PS/P(AA-co-EA)	w	77.4	2520
			t	263	385

* PS = Polystyrene; AA = acrylic acid; EA = ethyl acrylate; w = water; t = toluene.

^b Assuming no interpenetration or restriction.

analyses. Although complicated by traces of water stubbornly remaining in these hygroscopic materials, the analyses indicated: (1) that the ratio of AA to EA entering the sample to form network II was close to the steeping monomer mix ratio; and (2) that the quantity of nitrogen in the samples corresponded roughly to the quantity of original acrylic acid on a molar basis, suggesting complete conversion.

The swelling experiments were carried out as follows: Each sample was weighed and soaked in deionized water until swelling equilibrium appeared to be achieved (usually overnight), followed by damping dry with towels and reweighing in the swollen state. Samples were then redried and reweighed. This procedure was repeated using toluene as the swellant. The three separate dry weights obtained indicated little variance, and were averaged for the subsequent calculations. For the first general series, however, the sample length before and after swelling was noted. Volume changes as the cube of the length (isotropy) were assumed.

RESULTS

General Behavior in Water

A number of P(NH₄A-co-EA)/PS materials of varying composition were swelled in water. A pseudoternary phase diagram was constructed showing the composition of each sample and its swelling behavior. Four general classes were reported: (1) the IPN stress cracked during swelling, (2) the ionic IPN swelled less than twice its length, (3) the ionic IPN swelled approximately twice its length (volume increased about eight times), and (4) the ionic IPN swelled significantly more than twice its length.

The results are shown in Figure 1. Only PNH₄A contents below 30% appeared useful in this regard. A PS content greater than about 65% caused relatively little swelling to occur. In the intermediate regions, relatively small changes in composition led to great swelling changes, thus suggesting the more exacting experiment below.

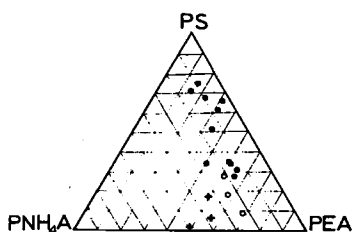


Fig. 1. General behavior of P(NH₄A-co-PA)/PS IPN's to swelling by water: + IPN breaks on ionization; ● ionic IPN swells less than twice its length; ○ ionic IPN swells twice its length; ○ ionic IPN swells more than twice its length.

Swelling Restriction Studies

It was of interest to examine whether these complex phase materials exhibited any swelling restriction. The basis for the swelling restrictions experiment is the method of Zapp,¹⁶ who employed differential solvents to examine interfacial bonding between different elastomer phases. A differential solvent is defined, according to Zapp, as one which is a good swellant for one phase and a poor swellant for the other phase. In the present context, the theory suggests that if two macroscopically continuous interpenetrating networks (or phases) exist, the presence of the less swollen phase will restrict the swelling of the more swollen phase, and vice versa. If one phase is continuous and the other discontinuous, the swelling will be restricted only when the swellant is preferential to the discontinuous phase.

The per cent swelling was calculated for each case according to the well-known formula

$$\% \text{ swelling} = \frac{(\text{weight of swollen polymer} - \text{weight of dry polymer})}{\text{weight of dry polymer}} \times 100. \quad (1)$$

From the % swelling of the parent networks and the known mass fraction of each component in the IPN's, the theoretically expected swelling of the ionic IPN's was calculated, assuming no restriction. The experimental equilibrium swelling values are compared to the values calculated assuming no swelling restriction in Table I. Also included in Table I are the experimental swelling values for the parent networks. For simplicity, the starting monomer ratios were used in all calculations, and 100% conversion of the acrylic acid portion to ammonium acrylate was assumed.

As expected, only very slight swelling of sample 1, PS, occurred in water, but great swelling took place in toluene. The ionic parent networks, samples 2 and 3, exhibited nearly the reverse swelling characteristics. The greater swelling of sample 3 in water over sample 2 may be ascribed to the higher ammonium acrylate content.

The ionic IPN's, samples 3, 4, 6, and 7, each swelled significantly in both toluene and water. Important, however, is the observation that in each case the experimentally observed swelling is less than the theoretically predicted value. Thus, while all of the ionic IPN's swelled considerably in each solvent, the swelling apparently is restricted, as indicated by Table I. The swelling restriction is significant in most cases.

DISCUSSION

Perhaps the most troublesome portion of the experimental work resulted from the enormous hygroscopicity of the ionic IPN's. Estimating from the elemental analysis of the parent P(NH₄A-co-EA) networks of known composition, the moisture level was never reduced below about 1.5%. The ratio of AA to EA is known in samples 4 and 5, since the copolymer formed network I. While the actual ratios of AA to EA are slightly in question in samples 6 and 7, the probable error was thought to be small compared to the magnitude of the swelling restriction. It should be pointed out that the drying con-

ditions of necessity were limited because of the potential release of ammonia under more stringent conditions.

The results in Table I, however, show significant swelling restriction for samples 6 and 7 as well as 4 and 3. In most cases except the toluene swelling in samples 6 and 7, the swelling restriction is of the order of several hundred per cent. According to electron microscopy results obtained earlier,^{4,8} the PS components in networks 6 and 7 should be more continuous than the ionic network, and less swelling restriction might be expected for that case.

The incorporation of ionic groups into the PEA portion enormously complicates the morphology of this material. The probability of three phases appearing has already been discussed. The differential swelling technique was originally developed for non-specific van der Waals-type polymer-solvent interactions, and it is obvious that the interpretation is more complicated in the present case.

Nonetheless, from an experimental point of view the materials do behave as if two continuous phases existed. Hence, these experiments provide supporting evidence towards the concept of interpenetration of the phases involved. Further experiments will be required to verify the extent and level of interpenetration. Together with electron microscopy and mechanical behavior studies, swelling experiments can effectively provide more detailed information about the structure of the IPN's.

The authors wish to thank the National Science Foundation for support of this work through Grants GK-13355, Amendment No. 1, and GY-9891.

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Received April 3, 1973