

# Gradient Interpenetrating Polymer Networks. I. Poly(ether Urethane) and Polyacrylamide IPN

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## Synopsis

The swelling properties of poly(ether urethane)s and the preparation of interpenetrating polymer networks (IPNs) from a poly(ether urethane) thermoplastic elastomer and hydrogel forming polyacrylamide have been studied. The acrylamide monomer was polymerized with simultaneous crosslink formation, in the presence of the swollen thermoplastic elastomer. Upon removal of the swelling solvent, an IPN was obtained which absorbed water in the manner of a hydrogel but had mechanical properties superior to a hydrogel.

## INTRODUCTION

Although some reports can be found in the literature,<sup>1,2</sup> polymeric systems possessing spatial gradients of structure and properties have received relatively little attention. Gradients in properties may be confined to layers close to the surface, thereby modifying surface properties without impairing the properties of the bulk. The use of such systems for biomedical applications, which was contemplated in the past<sup>1,3</sup> is adapted here for the surface modification of poly(ether urethane)s.

Flexible blood-compatible materials have been the focus of considerable effort in the past few years.<sup>4</sup> One promising approach has been the preparation of composite materials from polymers having desirable physical characteristics by modifying their surfaces with hydrogels.<sup>5</sup> The binding of hydrogels to the surface of poly(ether urethane)<sup>6</sup> has been carried out mainly by different grafting techniques.<sup>7-9</sup> Here, we report the binding of hydrogels through preparation of interpenetrating polymer networks (IPNs) of hydrogels and poly(ether urethane)s. A somewhat similar method was used by Predecki<sup>10</sup> to bond poly(hydroxyethyl methacrylate) to silicon rubber.

Interpenetrating polymer networks are a special type of polymer mixture consisting of two polymer networks synthesized within each other.<sup>11</sup> On a molecular level, they can be viewed as interlocked macrocycles of two species which are chemically not bonded to each other, yet are physically inseparable.<sup>12</sup> Polymer mixtures are often thermodynamically unstable and, therefore will phase separate, which in IPNs will depend on the intimacy of the interlocking.<sup>13</sup> Different synthetic routes for obtaining IPNs have been described, the three main ones being: (1) synthesis of one network, imbibing it with the monomer of a second type, followed by polymerization and crosslinking—the product is referred to as a sequential IPN; (2) mixing of two prepolymers of different kinds

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followed by crosslinking each through an independent mechanism so as to avoid chemical bonding between the two systems; the product is referred to as a simultaneous IPN; (3) synthesis of one network, imbuing it with a monomer of a second type without a crosslinking agent so that upon polymerization a linear polymer is obtained which is not interlocked yet is intimately entangled with the first system; the product is referred to as a pseudo IPN or a "snake cage."<sup>14</sup>

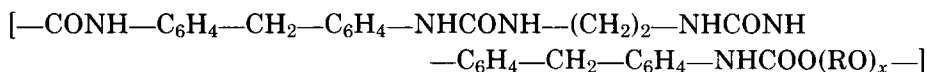
Poly(ether urethane)s belong to the family of thermoplastic elastomers with the general structure  $(AB)_n$ , consisting of "hard" and "soft" segments.<sup>15,16</sup> The hard segments are composed of relatively immobile and short polyurethane sequences, and at room temperature are below their second-order transition temperature. The hard segments are connected by soft flexible polyether chains, which at room temperature are above their second-order transition temperature. Unfavorable interaction between dissimilar segments and hydrogen bonding between polyurethane sequences lead to phase separation and the formation of hard domains which are aggregates of several polyurethane sequences, in a soft polyether matrix. The hard domains act as physical crosslinking points, forming a network which gives the material its high elasticity. The poly(ether urethane)s can be dissolved in solvents which disrupt the physical crosslinks. It ought to be possible to select solvents that would swell the soft matrix without significantly disrupting the physical crosslinking points of the network. By appropriate polymerization of a chemically crosslinked polymer within the "soft" matrix, this polymer would be interlocked with the poly(ether urethane), thus obtaining a system which is a hybrid between a sequential and a pseudo IPN.

In this article, we report the results of swelling studies with poly(ether urethane)s, the preparation of IPNs from polyacrylamide hydrogels<sup>17</sup> and poly(ether urethane), and the effect of several parameters on the composition and properties of the IPNs.

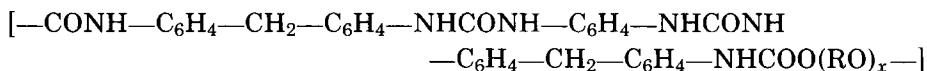
## EXPERIMENTAL

### Materials

Two types of poly(ether urethane)s obtained from SRI International, Menlo Park, CA, were used: (1) designated 3-2000-1-E by SRI International<sup>18</sup> (abbreviated 3-2000 in this article) with a repeat unit:



(2) designated 3-1000/425(7/3)-1-X by SRI International (abbreviated 3-1000 in this article), with a repeat unit:



The former is prepared in a two-step process from diphenylmethane 4,4'-diisocyanate and polypropylene glycol with  $(\text{RO})_x$  of average molecular weight 2000, using 1,2-diamino ethane as the extender (density: 1.071). The latter is prepared in the same way, with  $(\text{RO})_x$  standing for a blend of two poly(propylene oxides), 70% of molecular weight 1000, 30% of molecular weight 425 using 1,4-diamino benzene as the extender (density: 1.136).

Polymerization reagents included: acrylamide (Polysciences, Inc.), ultrapure grade, recrystallized three times from acetone; methylenebisacrylamide (MBA) (Polysciences, Inc.), recrystallized twice from methanol; azobisisobutyronitrile (AIBN) (Polysciences, Inc.), recrystallized twice from methanol; *N*-allyl acrylamide (Polysciences, Inc.), used as received and tetraethyleneglycol dimethacrylate (TEGDMA) (Polysciences, Inc.) used as received. Dioxane and tetrahydrofuran (Fisher Scientific Co.) were of reagent grade and distilled over sodium before use. *n*-hexane and ethanol (Fisher Scientific Co.) were of analytical grade and used as received. All other solvents were of analytical or reagent grade, and used as received.

### Swelling Studies

Measurements on the uptake of solvent and monomer by poly(ether urethane) were carried out on films prepared by casting 15% (w/w) solutions in dimethyl formamide on glass, drying in a draft oven at 70°C, extraction with ethanol and water, consecutively. Duplicate samples of 20 × 20 × 0.25 mm were swollen in designated solvents at 30°C for 16–20 h in equilibrium swelling studies, or for a shorter period in swelling kinetics studies. Changes in weight were recorded by weighing swollen samples in preweighed, capped vials. Changes in area were determined by measurement on swollen film sample between two plate-glass squares.

### Preparation of IPNs

Triplicate samples of 20 × 20 mm and uniform thickness 0.25–0.63 mm ( $\pm 0.03$ ) were immersed for 16 to 20 h at 30°C in a swelling solution containing the acrylamide, crosslinker, and initiator. The swollen samples were hung on Nichrome hooks suspended from a glass stand in a 3-L glass reactor equipped with a condenser. Polymerization was initiated by refluxing *n*-hexane inside the reactor; refluxing was stopped after 20 min. The specimens were then immersed in ethanol at 30°C for 6 h, and in water at 30°C for 24 h followed by vacuum (1 torr) drying to constant weight.

The amount of polyacrylamide formed was calculated from pre- and postpolymerization dry weights, correcting for weight loss of poly(ether urethane) during swelling. This correction was based on a series of experiments measuring weight loss as a function of film thickness in a given swelling solution (inhibited with hydroquinone). Water uptake capability of the IPN was defined as the weight uptake in water at 30°C, during 24 h divided by the weight of the dry extracted IPN.

### Electron Microscopy and Mechanical Measurements

Transmission electron micrographs were obtained with a Phillips 200 electron microscope. Samples were stained with 2% aqueous osmium tetroxide<sup>19</sup> followed by drying under high vacuum. Stained specimens were embedded in epoxy resin, following a procedure for soft specimens.<sup>20</sup> Sections 10  $\mu$ m thick were cut using a MT-2 Sorvall microtome.

Tensile properties were measured on an Instron universal testing instrument,

using specimens of  $80 \times 3 \times 0.50$  mm. Swollen specimens were immersed in 0.85% saline at  $30^\circ\text{C}$  for 100 h prior to the test. Initial gauge length was 2.56 cm and ram speed was 50 cm/min.

Modulus determinations were performed on a tensile creep apparatus as described elsewhere<sup>21</sup> with specimen as described previously and loads in the range of 4–50 g.

## RESULTS

### Swelling Properties of Poly(ether urethane)s

The swelling properties of poly(ether urethane)s (PEUs) were studied with a series of solvents (Table I). The volume swelling  $S$  given by the ratio

$$S = V_s/V_o \quad (1)$$

of the initial and final volumes  $V_o$  and  $V_s$  of the specimen, respectively, was determined from the measured weight uptake of sheet specimens as described in the Experimental section. Additivity of polymer and solvent volumes was assumed in the calculation of  $V_s$  so that

$$V_s = W_o/\rho + (W_\infty - W_o)/\rho_s \quad (2)$$

where  $W_o$  and  $W_\infty$  are the weights of polymer before and after swelling, respectively, and  $\rho$  and  $\rho_s$  are the densities of polymer and solvent, respectively. The swelling was close to equilibrium [swelling times equal to at least ten time constants, see eq. (4)]. The plot of  $S$  versus the solubility parameter  $\delta$  of the swelling solvents,<sup>22</sup> given in Figure 1 for PEU 3-2000, shows that swelling is maximized for  $\delta \sim 9.2$  and  $\delta \sim 11.4$ . The data in Table I shows that PEU 3-2000 swells considerably more than PEU 3-1000.

The areas  $A_s$  and  $A_o$  of the swollen and unswollen sheet samples were also determined and used to define another swelling index  $g$  given by

$$g = A_s/A_o \quad (3)$$

If the sample swells isotropically, and additivity of volumes is obeyed, then  $g^{3/2}$  should equal  $S$ . By contrast, the data in Table I show that  $g^{3/2}$  can be larger than  $S$  for PEU 3-2000 and that the degree of this anisotropy depends on solvent properties. The anisotropy is dominant for solvents with large  $S$  as tetrahydrofuran but is minimal or does not exist for solvents with small  $S$  as cyclohexane.

In order to obtain a quantitative parameter to describe the swelling data of PEU 3-2000 (Fig. 2), the data was fitted by the equation:

$$W_t - W_o = (W_\infty - W_o)(1 - e^{-kt}) \quad (4)$$

where  $W_o$ ,  $W_t$ , and  $W_\infty$  are the weights of a polymer specimen before swelling, swollen for a time  $t$ , and swollen to equilibrium, respectively. It was found that eq. (4) gave a good fit, provided that the initial solvent uptake rate  $k(W_\infty - W_o)/W_o$  (see Table I) was less than  $0.06 \text{ min}^{-1}$ . For larger solvent uptake rates, only the initial swelling was fitted. The discrepancy between the data and eq. (4) at longer times, can be seen in Figure 2. Values of the time constant  $\tau = k^{-1}$  determined for several solvents from plots of  $\ln(W_\infty - W_t)$  vs.  $t$  are listed in Table I along with the equilibrium solvent uptake  $(W_\infty - W_o)/W_o$ .

TABLE I  
 Swelling Parameters for PEU<sup>a</sup> in Different Solvents

Solvent	Solvent		3-2000				
	$\delta^b$ cal/cm <sup>3</sup>	$\eta^c$ cp	$S^d$	$S/g^{3/2} t$	$\frac{(W_\infty - W_0) \epsilon}{W_0}$	$k^{-1} h$ min	$k(W_\infty - W_0) i$ min <sup>-1</sup>
Cyclohexane	8.2	0.90	1.23	0.98	0.37	—	—
<i>n</i> -butylacetate	8.5	0.69	1.82	1.06	1.57	—	—
Carbon tetrachloride	8.6	0.89	1.62	1.03	2.32	—	—
Toluene	8.9	0.55	1.87	1.14	1.38	—	—
Ethyl acetate	9.1	0.43	1.81	1.06	1.43	—	—
Benzene	9.2	0.60	1.80	1.06	1.56	—	—
Chloroform	9.3	0.54	2.97	1.15	6.55	—	—
Tetrahydrofuran	9.5	0.49	4.94	1.25	4.89	(35)	0.140
Acetone	9.9	0.30	1.87	1.16	1.23	—	—
Dioxane	10.0	1.17	2.70	1.13	2.83	(35)	0.081
<i>n</i> -octanol	10.3	8.08	—	—	1.20	105	0.011
<i>n</i> -heptanol	10.6	5.85	—	—	0.90	76	0.012
<i>n</i> -butanol	11.4	2.59	2.20	1.22	2.69	88	0.031
Benzyl alcohol	11.6	5.20	—	—	11.2	182	0.062
Ethylene glycol	12.1	1.55	—	—	2.89	90	0.032
monomethyl ether	12.7	—	1.38	1.07	0.70	—	—
Nitromethane	12.7	1.06	1.50	1.23	0.83	33	0.025
Ethanol	14.5	0.55	1.53	1.25	0.86	—	—
Methanol	14.6	16.6	1.03	0.85	0.038	—	—

<sup>a</sup> Polyurethane films 0.51–0.59 mm thick, swollen at 30°C for 16 hr.

<sup>b</sup> Solubility parameters (ref. 23).

<sup>c</sup> Viscosity (ref. 23).

<sup>d</sup> Degree of volume swelling [see eq. (1)].

<sup>e</sup> Degree of area swelling [see eq. (3)].

<sup>f</sup> Swelling anisotropy.

<sup>g</sup> Equilibrium solvent uptake ratio [see eq. (4)].

<sup>h</sup> Swelling time constants [see eq. (4)], values in parentheses are approximate.

<sup>i</sup> Initial solvent uptake rate.

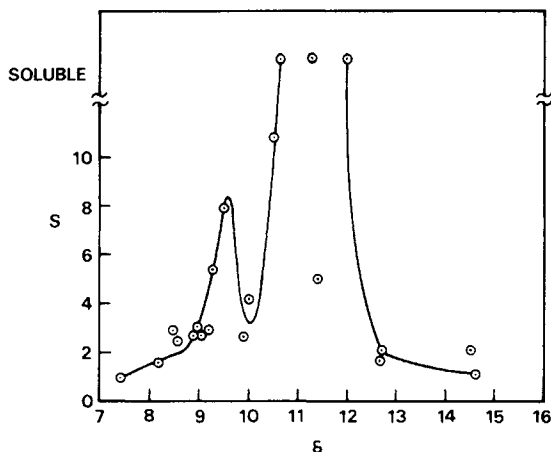


Fig. 1. Dependence of degree of swelling ( $S$ ) on solubility parameter ( $\delta$ ) of solvent for PEU 3-2000.

Swelling experiments were also carried out in binary systems, primarily of acrylamide and a solvent. These binary solutions usually gave larger  $S$  and extracted more of the PEU than the solvent alone (Table II), sometimes giving a synergistic effect. Thus, a 3*M* solution of acrylamide in dioxane extracted more PEU than either molten acrylamide or dioxane separately. The effect of increasing acrylamide concentration on the extraction capacity is seen in Figure 3. Time constants for swelling in acrylamide binary solutions (Table III), were determined by swelling separate PEU specimens for different times. Following measurement of the weight increase due to solvent and monomer, the volatile solvent was evaporated to permit determination of the acrylamide uptake by weight. The time constants of the solutions, as well as of each of the components, were distinctly larger than those observed for the pure solvent. Moreover, as the acrylamide concentration in the solution was increased, both the swelling time constants and the equilibrium uptake of acrylamide and solvent by the PEU specimen, also increased. When comparing the swelling characteristic of 1.4*M* acrylamide in dioxane and 3*M* acrylamide in ethanol, it was noted that the acrylamide initial rate of penetration from both solutions was identical. Yet, in the former, the dioxane penetrated ten times faster than the acrylamide, whereas in the latter the ethanol penetrated only three times as fast as the acrylamide.

### IPN Composition and Properties

The effects of several parameters on the composition and properties of the IPN were investigated. Those included the concentration of monomer, initiator, and crosslinker, the solvent used, and the duration and method of heating the sample to effect polymerization.

Increasing the concentration of the monomer in the swelling solution invariably caused an increase of the vinyl polymer fraction in the resulting IPN. The results for acrylamide are shown in Figure 4; the correlation is not linear, and high concentrations of acrylamide were relatively less effective than low concentrations. The water uptake capability of the IPN was proportional to

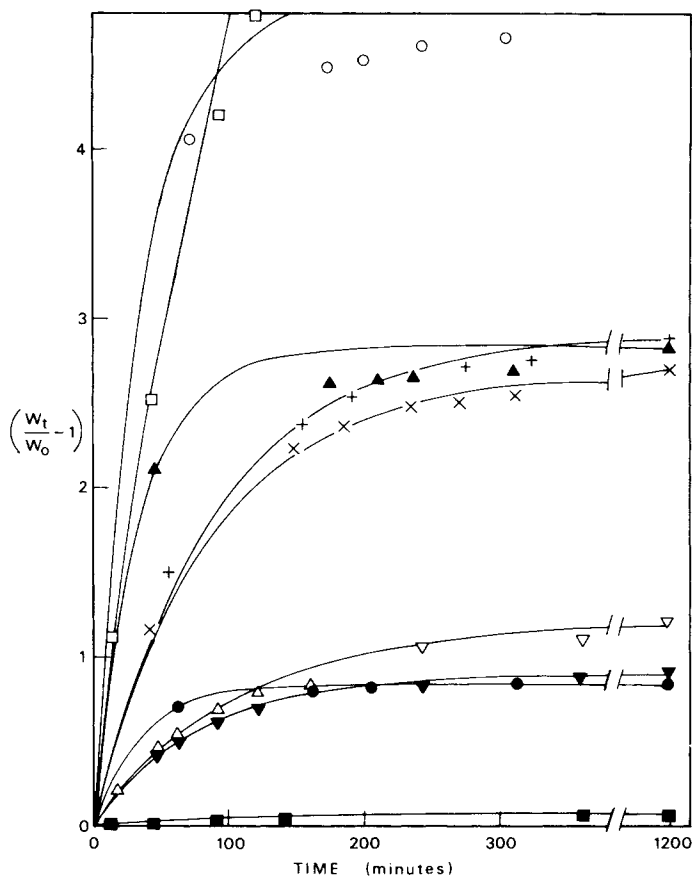


Fig. 2. Solvent uptake as function of time for PEU 3-2000 swollen in different solvents [lines based on eq. (4), using constants from Table I]. O, tetrahydrofuran; □, benzyl alcohol; ▲, dioxane; +, ethylene glycol monomethyl ether; X, *n*-butanol; ▽, *n*-octanol; ▼, *n*-heptanol; ●, ethanol; ■, ethylene glycol.

the fraction of the hydrogel former in the IPN, provided this fraction was larger than a certain critical minimum. The data in Figure 5 show that this minimum was around 10% for polyacrylamide (PAM), and that the water uptake was 2 g water/g PAM, for PAM fractions above this value.

Increasing the initiator concentration had a marked effect on the composition of the IPN. As can be seen in Figure 6, there was some autopolymerization of acrylamide; but increasing the initiator concentration up to 0.03M resulted in an almost linear increase in the weight fraction of PAM in the IPN. In the case of 1.4M acrylamide in dioxane as the swelling system, there was a marked leveling off of the initiator effect at  $[AIBN] = 0.03M$ . With 3M acrylamide in ethanol swelling solutions, no significant leveling off was observed up to initiator concentrations of 0.09M.

As seen in Figure 7, reactions carried out in the absence of crosslinker gave products in which the fraction of PAM was above 10%. Addition of crosslinker increased the fraction of PAM in the IPN (when all other variables were kept constant) and decreased the water uptake capability of PAM. In the ethanolic system, there appeared to be less scatter of experimental points than in the di-

TABLE II  
Effect of Acrylamide on PEU<sup>a</sup> Swelling and Weight Loss<sup>b</sup> during Swelling

Solvent	$\delta$ , cal/cm <sup>3</sup>	$a = \frac{W_{\infty} - W_0}{W_0}$ solvent only	$b = \frac{W_{\infty} - W_0}{W_0}$ AM <sup>c</sup>	$b/a$	% wt. loss in solvent only	% wt. loss in AM solution <sup>c</sup>
Bis(2-methoxyethyl) ether	8.1 <sup>d</sup>	3.52	4.60	1.31	6.6	14.4
Bis(2-ethoxyethyl) ether	8.2 <sup>d</sup>	2.40	3.43	1.43	2.2	6.6
Tetrahydrofuran	9.5	4.90	—	—	11.5	—
Acetone	9.9	1.19	1.85	1.55	3.8	5.9
Dioxane	10.0	2.83	7.80	2.76	8.4	12.0
<i>n</i> -butanol	11.4	2.69	3.69	1.37	6.2	6.6
Acetonitrile	11.9	0.56	0.93	1.66	1.7	2.7
Ethylene glycol monomethyl ether	12.1	2.89	—	—	14.7	9.6
Nitromethane	12.7	0.68	1.28	1.88	1.8	3.5
Ethanol	12.7	0.83	1.21	1.46	2.6	1.4
Acrylamide	14.0 <sup>d,e</sup>	—	—	—	12.0 <sup>e</sup>	—
Methanol	14.5	0.83	1.12	1.35	2.9	1.7

<sup>a</sup> Poly(ether urethane) 3-2000.

<sup>b</sup> Swelling 16 hr at 30°C; 0.55 mm film thickness.

<sup>c</sup> 1.4M solution of acrylamide.

<sup>d</sup> Calc. (see ref. 24).

<sup>e</sup> Swelling 1 hr at 95°C with hydroquinone inhibitor.



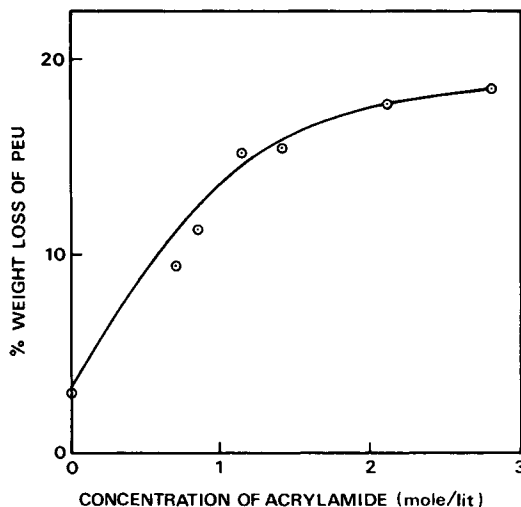


Fig. 3. Weight loss of PEU 3-2000 during swelling in solutions of acrylamide in dioxane.

oxane system. Both systems demonstrated a critical concentration of crosslinker above which there was either no effect on the PAM fraction in the IPN, or probably even a negative effect. It was of interest to note that thicker films tended to give increased  $W_{\text{PAM}}/W_{\text{IPN}}$ , when all other variables were equal.

The most obvious effect of the solvent was on the degree of swelling of the PEU. Thus, in experiments where tetrahydrofuran (THF) was used, the specimens were frequently disfigured and cracked due to excessive swelling. The ethanolic and dioxane swelling systems showed considerably less deformation than THF and had a similar capability of introducing acrylamide into the matrix (Table III). The dioxane system caused more extraction from the PEU specimen, as well as distortion, than did the ethanolic system. The data, in Figures 6 and 7,

TABLE III  
Effect of Acrylamide (AM) on Swelling Kinetics of PEU 3-2000

Swelling medium	$W_{\infty} - W_o$ <sup>a</sup>		$k^{-1}$ , <sup>b</sup> min	$\frac{k(W_{\infty} - W_o)}{W_o}$ , <sup>c</sup> min <sup>-1</sup>
	$W_o$			
<i>Dioxane</i>	2.83		35	0.081
1.4M AM/dioxane	7.78		107	0.073
Acrylamide component	0.77		107	0.007
Dioxane component	7.01		107	0.066
<i>Ethanol</i>	0.83		33	0.025
1.4M AM/ethanol	1.24		43	0.029
3M AM/ethanol	2.15		76	0.028
Acrylamide component	0.58		83	0.007
Ethanol component	1.57		79	0.021
H <sub>2</sub> O	Very low		—	—
3M AM/H <sub>2</sub> O	0.075		47	0.0016
5M AM/H <sub>2</sub> O	0.12		75	0.0016
7M AM/H <sub>2</sub> O	0.24		100	0.0024

<sup>a</sup> Equilibrium weight uptake ratio [see eq. (4)].

<sup>b</sup> Swelling time constant.

<sup>c</sup> Initial weight uptake rate [see eq. (4)].

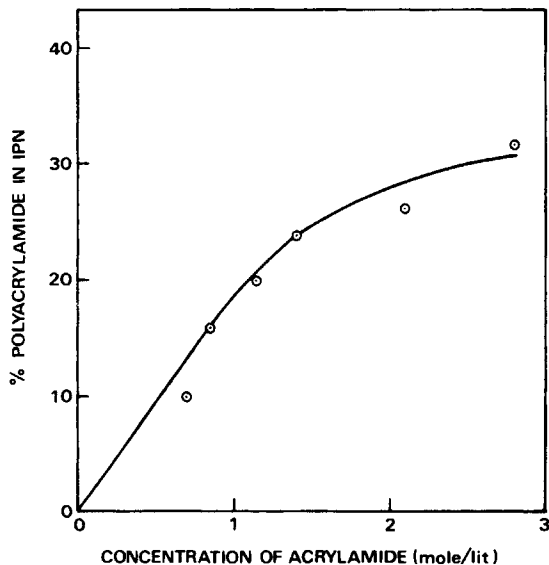


Fig. 4. Effect of acrylamide concentration in swelling solution on polyacrylamide fraction in IPN ( $W_{\text{PAM}}/W_{\text{IPN}}$ ). (Solvent: dioxane, concentration of AIBN and MBA in swelling solution was 1.0 mole % of acrylamide concentration).

show a marked difference in the fraction of polyacrylamide in the IPN between the ethanolic and dioxane systems.

Of the different heating methods tested, the best results were obtained when the vapors of refluxing *n*-hexane were used as the heat transfer agent. Heating in an oven resulted in rapid evaporation of the solvent and only slight polymerization; heating with steam resulted in a surface covered with polyacrylamide gel "pimples." No experiments were carried out with spring loaded molds. The surface of specimen heated with hexane vapors was smooth. As the hexane vapor

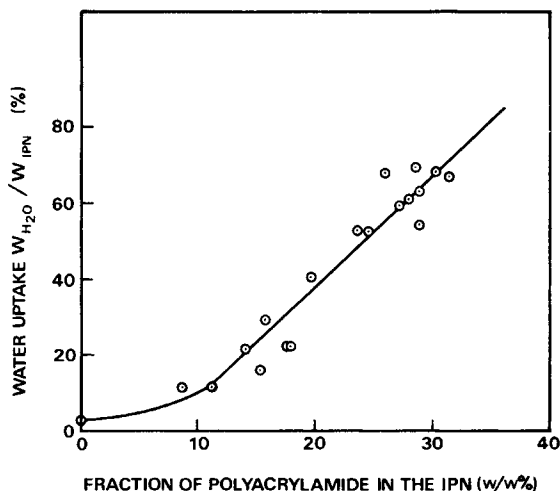


Fig. 5. Dependence of water uptake capability of IPN (prepared from PEU 3-2000, using swelling solutions with molar ratio acrylamide: MBA = 100:1) on polyacrylamide fraction ( $W_{\text{PAM}}/W_{\text{IPN}}$ ).

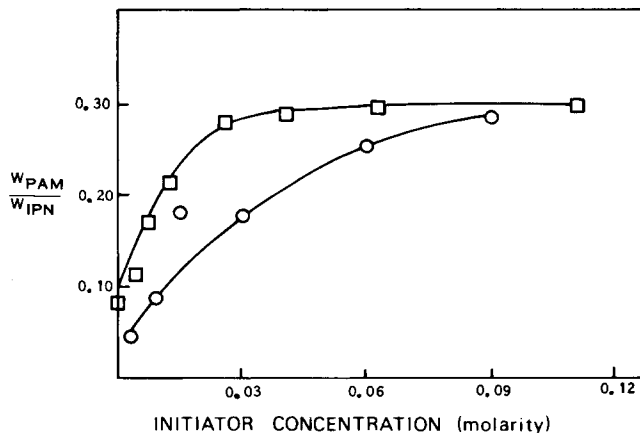


Fig. 6. Effect of initiator (AIBN) concentration on polyacrylamide fraction in IPN prepared from PEU 3-2000 films (thickness = 0.25 mm).  $\circ$ , 0.03M MBA, 3M acrylamide/ethanol;  $\square$ , 0.014M MBA, 1.4M acrylamide/dioxane.

contacted the swollen specimen, it caused contraction, accompanied by exudation of swelling solution. The exudation was decreased in several experiments by partial evaporation of the swelling solvent, short of crystallization of monomer, prior to heating. The effect of heating duration can be seen in Figure 8, which suggests that there was a certain induction period after which polymerization started. Heating beyond 20 min did not appear to increase the fraction of PAM in the tested system.

Some limited experiments were carried out to characterize the morphology and mechanical properties of the hydrogel IPN materials. The transmission electron micrograph (TEM) of an osmium tetroxide stained IPN of PAM and PEU 3-2000 (Fig. 9) shows a domain structure in these IPNs, with a typical domain diameter of 30–50 nm. Similar TEMs were obtained with samples in which 1 mol % *N*-allyl acrylamide was incorporated as a label for the PAM domains. Homogeneity of a sort on a larger scale is demonstrated by experiments in which a series of IPNs of PEU 3-2000 and PAM were extracted with DMF at 60°C to constant weight. The amount of PEU extracted was 90–95% of that originally present in the IPN. In all cases, a continuous PAM matrix was obtained, which upon swelling in water, took up approximately 600% of its own weight in water. Tensile properties were measured for PEU 3-2000 and its IPN with PAM in the dry- and water-swollen state. It was found that for the dry IPNs, the modulus and tensile strength increase with increasing PAM content, whereas the reverse trend was obtained with the swollen IPNs.

## DISCUSSION

The correlation between the degree of swelling and the solubility parameter (Fig. 1) shows that the swelling is maximized for two values of  $\delta$ . The individual points scatter from the curve shown, indicating that the correlation is somewhat crude, probably because of differences among the contributions of dispersion, polar and hydrogen forces to the solubility parameter of the different swelling media.<sup>22</sup> It seems clear, nevertheless, that the swelling is maximized for  $\delta \sim 9.2$

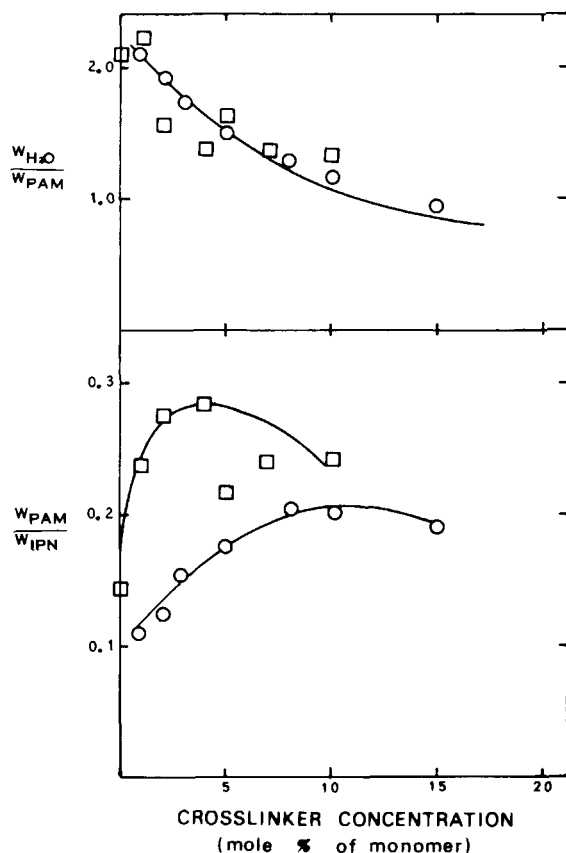


Fig. 7. Effect of crosslinker concentration on polyacrylamide fraction and water uptake capability in IPN prepared from PEU 3-2000 (thickness = 0.25 mm). O, TEGDMA in 3M acrylamide/ethanol, 0.006M AIBN; □, MBA in 1.4 acrylamide/dioxane, 0.014M AIBN.

and  $\delta \sim 11.4$ , the first evidently corresponding to preferential swelling of the polyether soft matrix and the second corresponding to partial or complete desegregation of the hard domains.<sup>25</sup> Thus, the unique domain structure of the PEU<sup>26</sup> allows swelling of the polyether component of the block copolymer, while the hard domains preserve the dimensional integrity of the material. This also explains the difference between the swelling properties of the two PEU polymers investigated in this article (see Table I). In PEU 3-2000 the hard domains constitute 22 wt % of the polymer, whereas in PEU 3-1000 the hard domains constitute 43 wt %. Moreover, in PEU 3-1000 the polyether chains between the hard domains are much shorter than in 3-2000. Hence, not only is there less soft matrix in 3-1000, but the constraints to swelling are much stronger.

The anisotropy of the swelling measured by the ratio  $S/g^{3/2}$  appears to increase with increasing  $S$ . The rate of increase differs for the solvents with  $\delta \geq 10$  and those with  $\delta \geq 12$ , with  $S/g^{3/2}$  increasing much more rapidly with increasing  $S$  for the latter. Values of  $S/g^{3/2}$  greater than unity, indicate that the thickness increased more than the dimension in the plane of the sheet as the sheet was swollen. A nonuniform composition of the PEU or a variation in its morphology across the thickness of the sheet might explain this result. The published

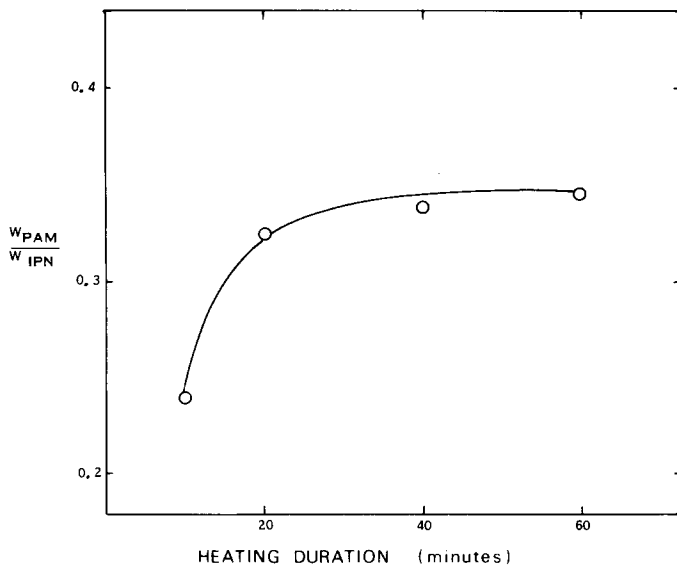


Fig. 8. Effect of heating duration on polyacrylamide fraction in IPN prepared for PEU 3-2000 films (thickness = 0.25 mm; swelling solution: 3M acrylamide/ethanol, 0.03M MBA, 0.09M AIBN).

ESCA<sup>27</sup> and ATR<sup>28</sup> data of thermoplastic polyurethanes, which suggest a surface rich in polyether, support this explanation.

The swelling kinetics reveal that the swelling rate depends more on solvent viscosity than on equilibrium solvent uptake, suggesting that the rate-controlling step in solvent uptake is the diffusion of the solvent. The kinetics of swelling with binary solutions was also viscosity dependent. Thus, swelling was slower

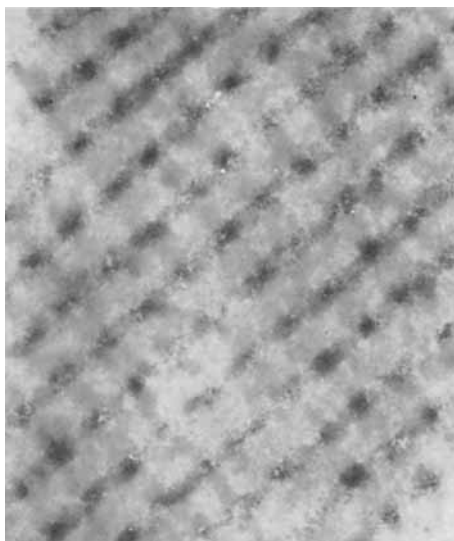


Fig. 9. Transmission electron micrograph of IPN of PEU 3-2000 and polyacrylamide stained with osmium tetroxide. Magnification 72800 $\times$  (IPN prepared by swelling PEU 3-2000 in 1.4M acrylamide/dioxane,  $W_{PAM}/W_{IPN} = 0.20$ ).

with solutions of acrylamide in ethanol and dioxane than with the pure solvents, in spite of the increased swelling capability of these systems (Table III). The fact that the ethanol component penetrates much slower than did the dioxane component from their respective acrylamide solutions could be highly significant in cases where controlled diffusion to a limited depth of a material is desired.

The synergistic effect of acrylamide and the solvent on the extraction of PEU (Table II and Fig. 3) may be a result of the domain structure of the PEU. Thus, the acrylamide, which has a solubility parameter close to that of the hard domains, may cause disassociation of some sections of the urethane blocks, thereby permitting greater swelling of the polyether soft matrix.

The swelling model suggested previously can be the basis of a working hypothesis for the events during the polymerization step. Thus, the binary system of acrylamide and solvent swells the soft polyether matrix of the PEU and causes a certain loosening of the hard domains, without causing their complete disruption—the latter would have resulted in full dissolution of the PEU. The acrylamide monomer is thus fairly evenly dispersed in the swollen PEU polymer. Upon initiation effected by heating, there is rapid polymerization, the kinetics of which is determined primarily by monomer and initiator concentration. The monomer kinetics has the advantage of the gel effect or Trommsdorf effect,<sup>29</sup> i.e., the high viscosity of the swollen polyether matrix impedes diffusion and, therefore, slows termination involving combination of free macroradicals. The polymerization kinetics compete with the contraction of the swollen film resulting from the penetration of the hexane heat transfer agent, which is a “non-sweller” of PEU. This contraction tends to exude unreacted monomer as well as short chains. The exudation from films swollen in concentrated acrylamide solutions causes more acrylamide loss than that from films swollen in dilute acrylamide solutions. This explains why the former are less effective in increasing the polyacrylamide fraction in the IPN (Fig. 4). The effect of the initiator concentration on the amount of acrylamide conversion (Fig. 5) may also be related to the competing kinetics of polymerization and contraction. Thus, high initiator concentration results in faster polymerization and smaller loss of monomer by exudation. The expected effect of lowering the molecular weight due to a higher number of growing chains was compensated—at least up to a certain concentration—by the crosslinking of the growing chains. The autopolymerization of acrylamide observed in Figure 6 has been documented in the literature.<sup>30</sup> The fact that increasing the crosslinker concentration resulted in increased conversion (Fig. 7) may be due to the interlocking of the PAM network with the physically crosslinked PEU system. Crosslinking of polyacrylamide in the absence of the crosslinker, probably occurred through spontaneous branching<sup>31</sup> and imidation reactions.<sup>32</sup> The exudation is slower in thicker films, as it depends upon diffusion of hexane molecules into the matrix, explaining the observation of improved monomer conversion in thicker films. The difference between dioxane and ethanol systems as far as conversion was concerned (Figs. 6 and 7) is probably due to the good chain-transfer properties of ethanol.<sup>33</sup>

The induction time suggested by Figure 8 is a result of dissolved oxygen (air) in the swelling solution. It has a beneficial function, in preventing spontaneous polymerization during the swelling period. The fact that an optimal heating period was observed is also associated with the exudation phenomenon.

Owing to the incompatibility of the soft polyether matrix and the growing

polyacrylamide, phase separation must occur during some stage of the polymerization. The domain size depends on the structure of the PEU, its elastic strain acting as a restraint against growth. The polyurethane structure could also have an effect on the nucleation density of the PAM domains. Since the PAM is a highly crosslinked system, most of its domains are expected to be linked. This surmise is supported by the extraction experiments cited previously which showed that a continuous PAM matrix could be recovered by dissolution of the PEU. Some of the PAM was probably grafted on the PEU through a chain-transfer mechanism, thus preventing the full extraction of all PEU.

The morphology observed in Figure 9, was that of the PAM domains (dark) dispersed in the soft matrix. The hard domains of the PEU are much smaller,<sup>34</sup> typically of 5 nm diam, and are not expected to be stained by  $\text{OsO}_4$ . The fact that the PAM was stained was probably due to some terminal vinyl groups. This is supported by the results with *N*-allyl acrylamide, where it was found that the allyl groups, known<sup>35</sup> to be less reactive in polymerization, did not change the staining pattern. The model which is proposed for the IPNs prepared here is illustrated in Figure 10.

In the terminology of Sperling,<sup>11</sup> the system could be categorized as a pseudo IPN, similar to the interstitial polymers of Allen.<sup>36</sup> From the evidence presented previously, the system is physically probably closer to a sequential IPN. Based on this model, it is postulated that in order to achieve a reasonable level of entanglement of the hydrogel network and the heterophase elastomer, it is essential that (1) the hydrogel be crosslinked to the extent necessary to reduce the concentration of unattached hydrogel molecules to a very low level; and (2) polymerization and crosslinking occur rapidly compared with the molecular diffusion processes so as to minimize monomer exudation and gross phase separation of the growing polymer from the PEU matrix.

The water uptake properties of hydrogel IPNs depend on the hydrophilicity of the hydrogel forming monomer, its fraction in the IPN, and its degree of crosslinking. The water uptake capability increases linearly with polyacrylamide fractions above 8% (Fig. 5). Among the reasons for decreased water uptake by polyacrylamide below a fraction of 8% could be that polyacrylamide at this level is isolated in domains to which water cannot diffuse, or that a progressive disruption of the organized domains of the PEU rubbery matrix starts with poly-

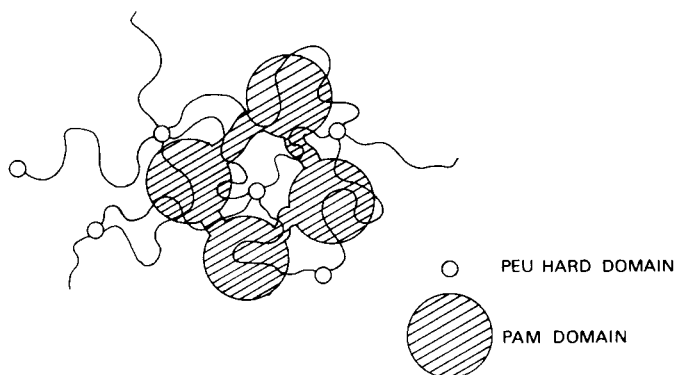


Fig. 10. Morphological model of IPN of poly(ether urethane) and polyacrylamide. ○, PEU hard domain; ◐, PAM domain.

acrylamide concentrations above 8%. The drop in water uptake with increased crosslinking density (Fig. 7) is expected<sup>37</sup> as crosslinks resist the swelling of a network. The rate of water uptake, though not measured in this work, can be predicted from the studies of Weiss, Van Vliet, and Silberberg,<sup>38</sup> to be faster in systems with higher crosslinking densities.

## CONCLUSIONS

It has been demonstrated that poly(ether urethane) thermoplastic elastomers have swelling properties which reflect the heterophase block copolymer nature of the material. These swelling properties were utilized in the preparation of a unique family of interpenetrating polymer networks with a hydrogel-forming polymer. The properties of the resulting IPNs were a hybrid between those of the thermoplastic elastomer and the hydrogel.

The authors wish to thank Ms. B. Schick for technical assistance and Dr. M. Morgan for helpful comments. This work was supported by contract NO1-HB-3-2949, Biomaterials Program, National Heart Blood and Lung Institute, NIH.

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Received July 16, 1980

Accepted November 4, 1980