

## ADVANCES IN INTERPENETRATING POLYMER NETWORKS

H.L. Frisch

Department of Chemistry, State University of New York at Albany, Albany, New York  
12222

K.C. Frisch and D. Klempner

Polymer Institute, University of Detroit, Detroit, Michigan 48231

Abstract - We review briefly the synthesis, morphology and thermal and mechanical properties of interpenetrating polymer networks (IPN) as well as the related pseudo interpenetrating polymer networks, in which only one of the polymer constituents is crosslinked. Recent studies have shown that the degree of phase separation achieved in these materials is strongly dependent on the degree of compatibility of blends of the linear polymer constituents of the IPN components. We illustrate this by detailed comparisons of two classes of full and pseudo interpenetrating polymer networks. The first is formed from a polyurethane-acrylic copolymer whose components are relatively incompatible and the second series is formed from poly(2,6-dimethyl-1,4-phenylene oxide)-polystyrene which form compatible blends over essentially the whole composition range. We conclude with a brief discussion of future directions for our work.

### INTRODUCTION

Interpenetrating polymer networks (1-5) (IPN's) are a novel type of polymer alloy consisting of two (or more) crosslinked polymers. They are more or less intimate mixtures of two or more distinct crosslinked polymer networks held together by permanent entanglements with only accidental covalent bonds between the polymers, i.e. they are polymeric "catenanes" (5-7). The entanglements in IPN's must be of a permanent nature and are made so by homo-crosslinking of the two polymers. They are produced either by swelling a crosslinked polymer with monomer and crosslinking agent of another polymer, and curing the swollen polymer *in situ* (2,4,8), or by mixing the linear polymer, prepolymers or monomers in some liquid forms (Tatex (3,9,10), solution (11), or bulk (12,13)), together with crosslinking agents, evaporating the vehicle (if any), and curing the component polymers simultaneously.

IPN's possess several interesting characteristics in comparison to normal polyblends. Formation of IPN's is the only way of intimately combining crosslinked polymers; the resulting mixture exhibiting at worst only limited phase separation. Normal blending or mixing of polymers results in a multiphase morphology due to the well known thermodynamic incompatibility of polymers. However, if mixing is accomplished on a lower molecular weight level, and any subsequent polymerization is accomplished simultaneously with crosslinking, phase separation may be kinetically controlled by permanent interlocking of entangled chains.

IPN's synthesized to date exhibit varying degrees of phase separation, dependent principally on the compatibility of the polymers. With highly incompatible polymers, the thermodynamic forces leading to phase separation are so powerful that it occurs substantially before the kinetic ramifications can prevent it. In these cases only small gains in phase mixing occur. In cases where the polymers are more compatible, phase separation can be almost completely circumvented. Complete compatibility is not necessary to achieve complete phase mixing, since the permanent entanglements (catenation) can effectively prevent phase separation. With intermediate situations of compatibility, intermediate and complex phase behavior results. Thus, IPN's with dispersed phase domains ranging from a few micrometers incompatible to a few tens nanometers (intermediate) (4), finally to those with no resolvable domain structure (complete mixing) (11) have been reported.

IPN's represent a special example of topological isomerism in macromolecules, i.e. different ways of imbedding these molecules in three-dimensional space. Some permanent entanglements between the different crosslinked networks are inevitable in any sufficient intimate mixture of the crosslinked networks. These represent examples of catenation in polymer systems.

Permanent entanglements are hindering constraints on the motion of segments and ought to simulate covalently bound chemical crosslinks (15,16).

The combining of varied chemical types of polymeric networks in different compositions, often resulting in controlled different morphologies, has produced IPN's with synergistic behavior. For example, if one polymer is glassy and the other is elastomeric at room temperature, one obtains either a reinforced rubber or a high impact plastic depending on which phase is continuous (11). In the case of more complete phase mixing, enhancement in mechanical properties is due to the increased physical crosslink density achieved by this interpenetration. Synergistic properties seen in tensile strength (3,9,11,17) and impact strength (11) reflect IPN's special architecture. However, in heterogeneous IPN's which are the case encountered in most of the studies to-date, the effects of interpenetration on the morphologies and the mechanical properties of IPN's have not been clearly identified due to the many factors involved such as compatibility, intermolecular forces and grafting.

In pseudo interpenetrating polymer networks (PDIPN) composed of two chemically different polymers, one is crosslinked and the other is linear. Two different PDIPN's can be distinguished depending on which polymer is linear. PDIPN's can be synthesized without the crosslinking agents of the linear component either sequentially or simultaneously in the same way as IPN's are made. These materials as well as blends of both linear polymers should not be capable of limiting phase separation to the same extent as the full IPN (with both catenated polymers crosslinked) since no topological constraints (i.e. permanent entanglements) exist. In both PDIPN's and linear blends the linear chains can "disentangle" themselves and phase separate without breaking covalent bonds. Investigations of these materials along with the full IPN's provide valuable comparative insights on the effect of the permanent, topological entanglements on physical properties (e.g. mechanical properties) and the morphologies of IPN's; as well as in their own right providing information about potentially useful polymer composites.

We would like to illustrate these general concepts by two recent examples of IPN's investigated at the State University of New York at Albany and the Polymer Institute of the University of Detroit: The first series of IPN's, PDIPN's and linear blends involved a polyurethane and a polyacrylate component which are not strongly compatible (18). The second series of IPN's, PDIPN's and linear blends involved a polyphenylene oxide and a polystyrene component which are known to produce some of the finest examples of truly compatible linear blends (19). After comparing the morphologies and mechanical properties of these two classes of materials we will conclude by mentioning some of the open problems and new directions we are pursuing in this field.

#### POLYURETHANE-ACRYLIC COPOLYMER, IPN's, PDIPN's AND LINEAR BLENDS

The synthesis of these materials involves first the preparation of a) the polyurethane (PU) prepolymer (NCO/OH = 2:1) by reacting one equivalent of poly(1,4-oxybutylene) glycol (M.W. = 1017) with two equivalents of 4,4'-methylene bis(cyclohexyl isocyanate) and b) the acrylate copolymer (AC) prepolymer composed of eight parts n-butyl methacrylate, one part of ethyl methacrylate and one part of styrene. We refer our readers to reference (18) for experimental details.

Linear blends were prepared as follows: The PU prepolymer and 1,4-butanediol were mixed thoroughly with the acrylate copolymer syrup. 0.2% T-12, dibutyl tin dilaurate (by wt. of PU) and 1% benzoyl peroxide (by wt. of AC) were used as catalyst and initiator respectively. The mixture was cast between two glass plates provided with rubber seals around the edges and subsequently polymerized at 110°C for 24 hours. Combinations composed to 20%, 40%, 60% and 80% PU by weight were made.

Two types of pseudo-IPN's were prepared, one from a linear PU/crosslinked AC (PDIPN-2), and the other from a linear AC/crosslinked PU (PDIPN-1). The former PDIPN's were prepared from the mixture of the linear polyurethane component (PU prepolymer + 1,4-butanediol) and the acrylate copolymer syrup with ethylene glycol dimethacrylate (EGDMA). The molecular weight between crosslink sites ( $M_c$ ) was 6500. The mixture of acrylate copolymer syrup and the PU prepolymer admixed with 1,4-butanediol and trimethylolpropane (crosslinking agent) resulted in the latter PDIPN. The curing conditions and compositions were the same as in the linear blends.

Full IPN's (FIPN's) were prepared from the mixture of acrylate copolymer syrup with EGDMA and PU prepolymer with 1,4-butanediol and trimethylolpropane. The curing conditions and compositions were the same as those for the linear blends. The crosslinking densities of both polymers were the same ( $M_c = 6500$ ).

The following measurements were carried out:

**Stress-Strain Properties.** The tensile strengths and elongations at break were measured on an Instron Tensile Tester at room temperature with a crosshead speed of 2 in/min. Specimens were 0.125 inch wide dumbbells.

**Glass Transition Temperature.** The glass transition temperatures were measured on a Perkin-Elmer Differential Scanning Calorimeter, DSC-2. Measurements were carried out from -120°C to +60°C under helium at a scanning rate of 10°C per min. Specimen sizes were on the order of 20 mg.

**Hardness.** The hardness of IPN's was measured by means of Shore A and D durometers according to ASTM D 2240-75.

**Kinetic Measurements.** Three different catalyst concentrations were employed for each polymer, i.e., 0.5%, 1% and 2% of benzoyl peroxide in the acrylate copolymer; 0.02%, 0.1% and 0.5% of T-12 in the polyurethane. One gram of each sample was poured into a glass tube (12 cm long, 8 mm diameter). The tubes were subsequently sealed. These sample capsules were heated in an oil bath at 110°C. The samples were taken out at intervals and were quenched in a dry ice-acetone bath and examined for flowability. The gel time was taken as the time at which the polymerizing mass did not flow at room temperature.

**Electron Microscopy.** The sample preparation was based on Kato's osmium tetroxide staining technique and a two-step sectioning method. The specimens were exposed to OsO<sub>4</sub> vapor and cut with a LKB ultratome III to get a 0.1 μm slice. The electron micrographs were taken with an AEI 6B and a Phillips 300 transmitting electron microscope with a magnification of 95,000.

**Mechanical Spectroscopy.** Dynamic viscoelastic properties were obtained using a Rheovibron Model DDV-11 (manufactured by Toyo Measuring Instruments Co., Ltd., Tokyo, Japan). The measurements were taken over a temperature range of -90°C to 80°C using a frequency of 110 Hz, and a heating rate of 2°C/min. Sample dimensions were 0.024 x 0.6 x 3.5 cm.

**Density.** The density was measured at room temperature using a hydrostatic technique. The sample dimensions were 0.125 x 1.25 x 2.5 cm.

The morphology, as indicated by the glass transition behavior (Table 1) was heterophase. In all cases, two T<sub>g</sub>'s, corresponding to the T<sub>g</sub>'s of the component polymers, resulted. However, the T<sub>g</sub>'s were shifted inwards, indicating some phase mixing (interpenetration), most likely at the phase boundaries. The shifts were greatest with the FIPN's, indicating the greatest amount of interpenetration. In the case of the full IPN's, intermediate T<sub>g</sub>'s occurred (not shown in the Table) depending on the thermal history of the material (21). This would indicate a third phase, i.e., an interpenetrating region. The PDIPN's and linear blends showed no indication of this intermediate phase. Further studies should clarify this situation.

TABLE 1. Glass transition temperatures (°C).

	PU 100% PA 0%	80 20	60 40	40 60	20 80	0 100
FIPN	204 -	214 306	211 306	209 308	210 312	320.5
PDIPN-1	204 -	211 313	212 317	212 -	210 -	318
PDIPN-2	204 -	211 313	212 314	213 -	212 -	320.5
Linear Blend	204 -	212 320	208 319	205 -	208 -	318

The electron micrographs of the IPN's, PDIPN's and linear blends all showed heterogeneous behavior, in agreement with the T<sub>g</sub> results. This morphology was expected due to the differing solubility parameters of the two polymers. Considering the inwardly shifted glass transition temperatures obtained by DSC (Table 1), some phase mixing (interpenetration) resulted in all cases. The phase boundaries of the IPN's and PDIPN's-2 were not well defined while the PDIPN's-1 and linear blends showed well defined boundaries. In all cases the blends having a crosslinked acrylic component exhibited more interpenetration. A possible explanation would be the ease of diffusion of the growing chains. The diffusion rates of the linear and crosslinked polyurethane do not change rapidly during polymerization because the initial prepolymer viscosity is very high. However, the viscosity of the crosslinked acrylic copolymer increases faster than that of the linear acrylate copolymer. Thus the crosslinked acrylic copolymer does not have enough time to allow complete phase separation for diffusion. This is consistent with the glass transition behavior being dependent upon the polymerization

rates discussed below. Phase inversion was observed to occur around 60% polyurethane in all cases. The domain sizes in IPN's and PDIPN's-2 were about the same and ranged from 10 nm to 50 nm. However, the PDIPN-1 and linear blends showed larger domain sizes (50 - 500 nm) indicating more complete phase separation (i.e., less interpenetration). This demonstrates the importance of topology and kinetics on the morphology and degree of interpenetration of these alloys.

#### DYNAMIC MECHANICAL PROPERTIES

The dynamic storage modulus,  $E'$ , vs. temperature for the IPN's, PDIPN's and linear blends show that the general modulus response to acrylic concentration and temperature is similar for all the alloys. The modulus of the IPN's, the PDIPN's-1, the PDIPN's-2, and also the linear blends decreases systematically with increasing polyurethane concentration. This can be seen in Figs. 1 and 2, which show the modulus vs. acrylic composition for a full and pseudo-IPN. The largest jump of modulus takes place between 60% and 40% PU, indicating the phase inversion. The modulus of the alloys increased in the order of linear blends  $<$  PDIPN's-2  $<$  PDIPN's-1  $<$  FIPN's at corresponding concentrations. The high degree of phase mixing did not result in an increase of the modulus of these blends; electron micrographs showed more phase mixing in the case of PDIPN's-2 than PDIPN's-1. The damping factor,  $\tan \delta$  vs. temperature for the pseudo and full IPN's showed two peaks corresponding to the  $T_g$ 's of the polyurethane and the acrylic copolymer networks. The size of the damping peaks changed systematically with concentration of the alloys, i.e., decreased with the respective component concentration.

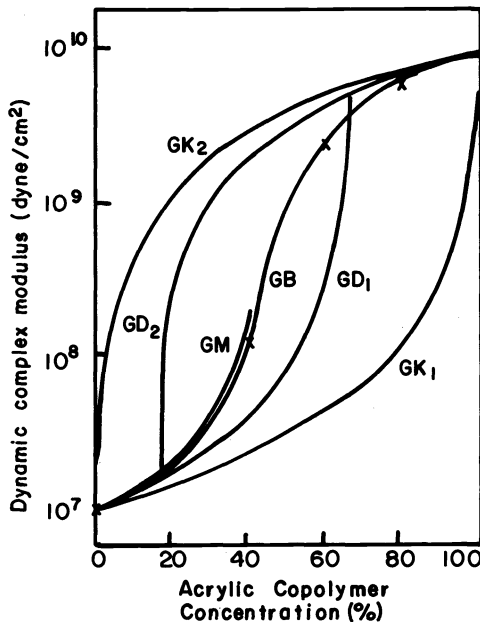


Fig. 1. Dynamic complex modulus vs. acrylic copolymer concentration for PDIPN (X) at 23°C at 110 Hz frequency (solid lines are based on theoretical models).

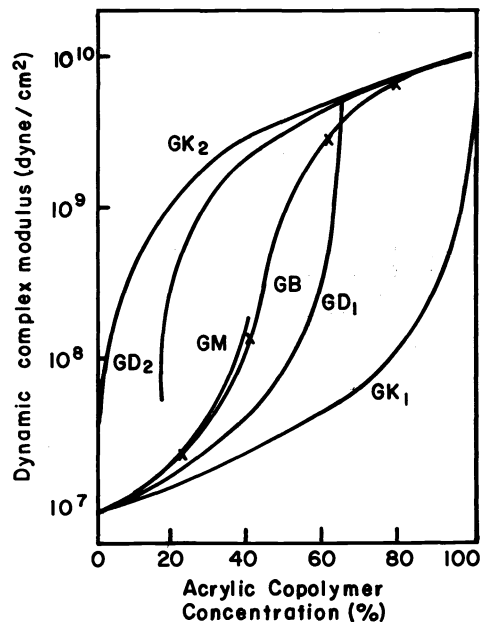


Fig. 2. Dynamic complex modulus vs. acrylic copolymer concentration for FIPN (X) at 23°C at 110 Hz frequency (solid lines are based on theoretical models).

The modulus-composition behavior of the polyurethane acrylic copolymer IPN's appear in accord with the expected behavior of two-phase systems composed of perfectly adhering phases and a spherical inclusion ("filler") geometry. The Mooney (22) (GM), Kerner (23) (GK<sub>1</sub>, GK<sub>2</sub>) and Dickie (24) (GD<sub>1</sub>, GD<sub>2</sub>) equations for the modulus predicted the modulus fairly well within a narrow range of concentration. However, over the entire concentration range, as can be seen in Figs. 1 and 2, the experimental values fit the Budiansky equation (25) (GB) best. This was expected since the Budiansky model can represent the modulus response of a system exhibiting phase inversion. The experimental modulus values of the FIPN's are slightly higher than the Budiansky predictions, while the other materials show lower values than the model, suggesting that a reinforcement effect is achieved only with the full IPN's.

The density-composition curve (Fig. 3) shows increased density in all cases, maxima occurring at 80% PU. The IPN's exhibited the largest increase at all concentrations. This

increase seems to indicate increased molecular mixing in full IPN's. This can be verified by the glass transition temperature behavior. Kim et al (14) explained the increased density of IPN's qualitatively by means of chain entanglements at the domain boundaries. However, it is possible to quantitatively correlate it with  $T_g$  shift. As the glass transition temperatures of the blends shift inward (from  $T_{gA}$  and  $T_{gB}$  to  $T_{gA'}$  and  $T_{gB'}$ , respectively),

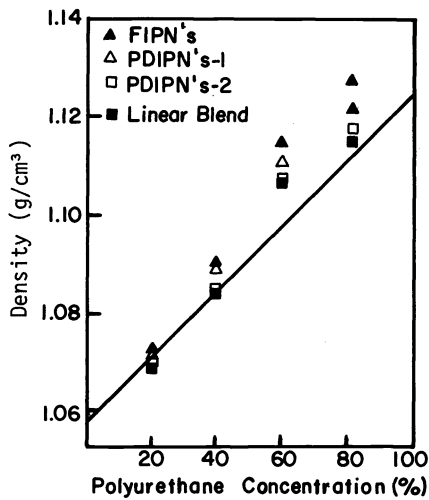


Fig. 3. Density vs. polyurethane concentration for PU-PA (straight line is based on volume additivity).

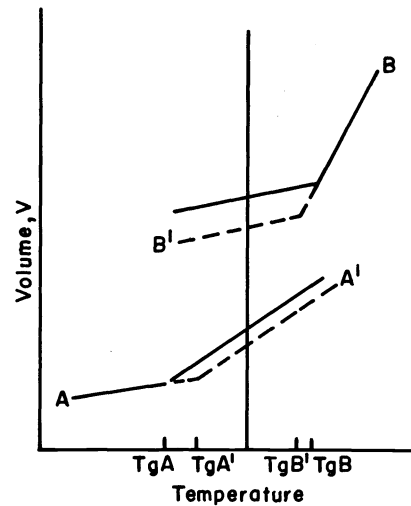


Fig. 4. Volume vs. temperature curves of pure homopolymers and polymer blends.

the volume-temperature curves (Fig. 4) of the components in the blends follow the dotted lines instead of the solid lines. Thus, the volume of each component becomes smaller than that of the pure component, which results in higher density at room temperature. Note that the densification of the IPN's is due to interpenetration, which produced the  $T_g$  shift and that the effect was the greatest with full IPN's in agreement with glass transition behavior and electron microscopy. Thus, it may be possible to predict the glass transition behavior of the polymer blends by measuring the densities at several temperatures.

The tensile strengths and breaking elongations of the IPN's as a function of composition are shown in Tables 2 and 3, respectively. The IPN's show a significant enhancement in tensile strength, particularly at PU/AC = 80:20. The PDIPN's and the linear blends show effectively no enhancement. In all cases measured, the tensile strengths of the IPN's are greater than those of the pseudo-IPN's and the linear blends at the same compositions. In addition, the tensile strengths of both of the pseudo-IPN's are greater than those of the linear blends at the same compositions. The enhancement in tensile strength is most likely due to the higher level of mixing in the IPN's and to greater adhesion between the dispersed and continuous phases. The IPN's should exhibit more complete mixing (less phase separation) and greater phase adhesion due to the permanent entanglements (interpenetration) at the phase boundaries.

TABLE 2. Tensile Strength of IPN's (PSI).

	PU 100%	80	60	40	20	0
	AC 0%	20	40	60	80	100
Full IPN	6100	7100	6525	5000	3715	2571
PDIPN-1	6100	5875	6300	3127	2227	1613
PDIPN-2	5600	4428	5215	3602	3018	2571
Linear Blend	5600	1828	3617	3413	2118	1610

TABLE 3. Elongation of IPN's (% at break).

	PU 100%	80	60	40	20	0
	AC 0%	20	40	60	80	100
Full IPN	640	780	540	270	180	15
PDIPN-1	640	540	250	138	120	12
PDIPN-2	610	553	520	276	211	15
Linear Blend	610	640	357	130	195	12

The elongation, as shown in Table 3, shows a slight increase from 100% PU to 80% PU in the IPN's, indicating the exceptional toughness of this IPN. No increase occurs for the PDIPN's and the blends. A sharp drop in elongation takes place at 60% PU, which indicates that a phase inversion occurs around this composition. The Shore A and D hardnesses shown in Table 4 show a rapid increase between 80% PU and 40% PU, which again indicates the phase inversion between 80% and 40% PU content.

TABLE 4. Hardness of IPN's (Shore A).

	PU 100%	80	60	40	20	0
	AC 0%	20	40	60	80	100
Full IPN	68(32)*	70(35)	80(38)	92(53)	94(63)	100(72)
PDIPN-1	68(32)	78(33)	86(38)	94(49)	95(55)	100(68)
PDIPN-2	73(31)	81(37)	91(43)	93(53)	96(65)	100(72)
Linear Blend	73(31)	75(30)	87(35)	92(48)	95(58)	100(68)

\*Hardness in parentheses are measured by Shore D.

The gel times of the polymers, shown in Table 4, show the expected trend, i.e., increasing catalyst concentration decreases the gel time. The glass transition behavior of these IPN's (Table 6) shows that as the rate of the respective polymerizations increases, the  $T_g$ 's shift

TABLE 5. Gel times of crosslinked polymers at different catalyst concentrations (min.).

AC	Time	PU	Time
AC-1	4.25	PU-1	12.30
AC-2	4.00	PU-2	7.25
AC-3	3.20	PU-3	3.15
AC-1 (0.5% BPO)		PU-1 (0.02% T-12)	
AC-2 (1% BPO)		PU-2 (0.1% T-12)	
AC-3 (2% BPO)		PU-3 (0.5% T-12)	

TABLE 6. Glass transition temperatures of IPN's: kinetic results.

	AC 40 - PU 60 $T_g$ ( $^{\circ}$ K)		AC 60 - PU 40 $T_g$ ( $^{\circ}$ K)	
IPN 1.1*	212.2	318.5	212	319
IPN 1.2	211	318	210	318
IPN 1.3	215	314	214	314
IPN 2.1	212	317	211	318
IPN 2.2	212.5	316	214	315.5
IPN 2.3	216	313	215	315
IPN 3.1	211	314	211.5	316
IPN 3.2	214	308	215	307
IPN 3.3	219	293	220	298

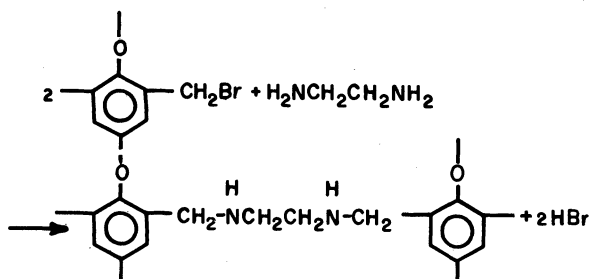
\*IPN 1.1 (IPN from AC-1 and PU-1).

inward, indicating less phase separation. This is most likely due to the fact that increasing the reaction rate lowers the diffusion time allowed for phase separation. The initial prepolymer mixture is single phase, since the molecular weights are low enough to allow complete mixing. As the polymers are cured, they phase separate due to their thermodynamic incompatibility. This phase separation is naturally diffusion controlled and requires time. If the curing reactions are accelerated, less time will be available for diffusion and subsequent phase separation to occur. When fully crosslinked, further phase separation cannot take place due to topological constraints imposed by the crosslinking of the component polymers. Thus, faster crosslinking would be expected to yield less phase separation. The maximum shift in  $T_g$  occurs in the IPN 3 series, in particular, 3-3. In this case, both polymers gel at almost the same time. This is in agreement with Sperling's, et al (13) results, which showed that the smallest domain size of epoxy-acrylic IPN's occurred when the respective curing reactions were closest to simultaneity. The degree of phase mixing, as deduced by the shifts in  $T_g$ , are confirmed by the transparency of the IPN films. The transparency increases as the reaction rate increases.

The behavior of this system is quite typical of behavior of IPN's prepared from relatively incompatible polymers. In the next section we show for the sake of contrast an IPN system prepared from two components whose linear blends are compatible over the whole composition range.

POLY (2,6-DIMETHYL-1,4-PHENYLENE OXIDE) - POLYSTYRENE INTERPENETRATING POLYMER NETWORKS

IPN's, pseudo-IPN's (PDIPN's - only one polymer crosslinked), and linear blends of polystyrene (PS), and poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) (whose compatibility has been reviewed elsewhere (26) were prepared, using for the IPN's and PDIPN's the simultaneous interpenetrating network (SIN) technique described in the previous section. The polystyrene was crosslinked by incorporating divinylbenzene. Several methods have been reported to synthesize crosslinked PPO using materials such as polysulfonazides and hydromethyldiphenyl oxide (27,28). However, these methods were found to be difficult to employ for simultaneous IPN's in which these two polymer networks are formed *in situ*, at about the same time. In this study the PPO was first directly brominated with bromine and subsequently crosslinked with ethylene diamine (experimental details can be found in reference (19)):



To confirm that crosslinking did indeed occur, solubility studies and elemental analyses were performed. The cured polymers did not dissolve in either tetrahydrofuran or trichloroethane (both good solvents for PPO); however, swelling did occur to about twice the initial dimensions. The elemental analyses (N, Br) (carried out at the Schwartzkopf Microanalytical Laboratory) showed that only 10% of the bromine in PPO was involved in the crosslinking reactions, the remaining bromine being inactive (most likely as aromatic bromine). Based on the amount of bromine reacted, the number average molecular weight between two crosslink sites ( $\bar{M}_c$ ) in PPO was 17,000. The theoretical  $\bar{M}_c$  of the crosslinked polystyrene was 7,260. After the IPN's, both types of PDIPN's (one with linear PS and one with linear brominated PPO), and linear blends were formed and were studied as described in the previous section by electron microscopy, ultimate tensile stress to break (TS) measurements on dumbbells 0.08 inches x 0.25 inches x 2 inches, dynamic mechanical spectroscopy (Rheovibron, temperature range 20 -260°C), and differential scanning calorimetry (DSC, temperature range 300 -500°K under nitrogen).

The electron micrographs of all the IPN's, PDIPN's and linear blends showed the presence of only one phase. The pure brominated PPO phase appears darker in these electron micrographs (due either to extra staining by osmium tetroxide and/or the presence of the bromine) than the lighter pure PS phase. The electron micrographs in all cases did not show any domains of either components.

The  $T_g$ 's of the full IPN's (FIPN's), PDIPN's and linear blends are listed in Table 7. The two glass transition temperatures measured by DSC and Rheovibron are within experimental error. In all cases one single broad  $T_g$  was observed, indicating complete segmental mixing of the two polymers, in agreement with the electron microscopy. The glass transition temperature in all cases varied systematically with the composition. The FIPN's showed higher  $T_g$ 's than the PDIPN's and the linear blends at the corresponding compositions. This is undoubtedly due to the higher  $T_g$ 's of the pure (crosslinked) components and does not relate to the morphology differences. The maximum of the difference in absolute value of the measured FIPN  $T_g$  from the corresponding weight average of the pure polymer networks occurs at 75% (brominated) PPO/25% PS. It is believed that this indicates (11) that near that composition occurs the greatest extent of additional chain entanglement.

TABLE 7. Glass transition temperature ( $T_g$ ) of the PPO-PS blends by DSC and Rheovibron ( $^{\circ}\text{C}$ ).

Wt. % (PPO/PS)	100/0	75/25	50/50	25/75	0/100
FIPN's (CPPO/CPS)	226 (232)*	172	149 (145)	120	83 (82)
PDIPN's-1 (CPPO/LPS)	226 (232)	226	234 (235)	113	75
PDIPN's-2 (LPP0/CPS)	213 (222)	162	138 (142)	117	83 (82)
Linear Blends (LPP0/LPS)	213 (222)	152	130 (128)	99	75

\*Measured by Rheovibron  
C = crosslinked; L = linear

This is confirmed by the behavior of the ultimate tensile strengths (TS) of the FIPN's. These are shown in Fig. 5 together with the data on the PDIPN's and linear blends. The FIPN's showed an enhancement in the TS (presumably due to the extra entanglement) with a maximum at or near 25% PS (75% brominated PPO). The PDIPN's and linear blends of the brominated PPO and PS do not exhibit any maximum. The TS of the pure PS is somewhat lower than expected from the theoretical degree of crosslinking. The tensile strengths of the FIPN's are higher than those of the PDIPN's and the linear blends at the same composition. There is no significant difference in the tensile strength, in general, between the PDIPN's and linear blends. The enhancement in tensile strength is most likely due to the permanent chain entanglements in the FIPN's. In the case of PDIPN's and linear blends, the entanglements are only temporary and "untangling" can occur at large deformations because one or both polymers are linear (topological constraints do not exist).

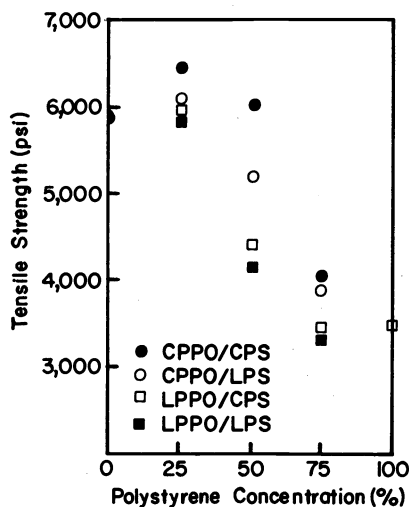


Fig. 5. Tensile strength vs. polystyrene concentration.

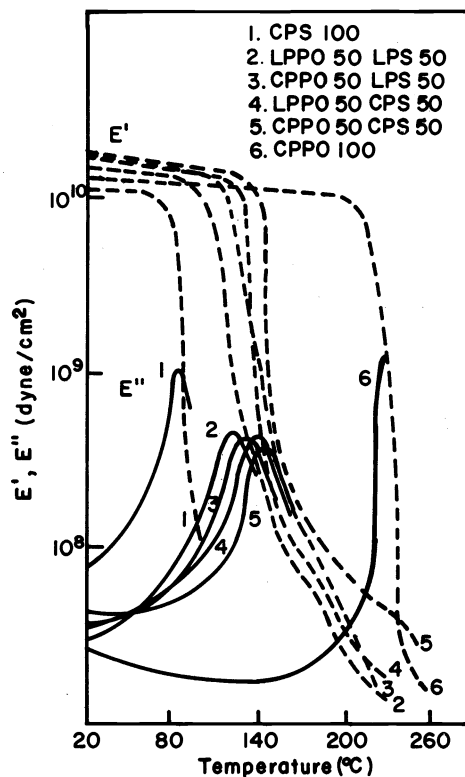


Fig. 6. Temperature dependence of storage ( $E'$ ) and loss ( $E''$ ).



The storage modulus,  $E'$  of FIPN, PDIPN's and linear blends with 50% PS as a function of temperature are shown in Fig. 6. From room temperature up to the respective  $T_g$ 's, the moduli of all the IPN's are higher than those of the pure components with the modulus of the FIPN being the greatest. This synergism in modulus has been noted before in compatible PPO-PS blends (29) and has been ascribed to increase in packing density due to blending. One would therefore expect the FIPN's to exhibit the greatest increase in modulus, since there should be a greater amount of permanent chain entanglements between the two networks which would result in a greater increase in packing density. The moduli sharply decrease near the  $T_g$ 's of each blend, respectively, as usual. The loss modulus,  $E''$ , of this sample as a function of temperature is also shown in Fig. 6. The loss modulus data shows a single  $T_g$ , indicating extensive phase mixing. The  $T_g$ 's, however, are broader than those of the pure components.

## DISCUSSION

The examples discussed in the previous two sections reveal some of the major aspects of behavior in IPN systems. Current work in our laboratories focuses on producing (1) poly-electrolyte IPN's of opposing charge components, synthesized under conditions when such charges would be at least partially present; (2) IPN's with three or more chemically different component networks and (3) IPN's in which one component is a very stiff linear polymer. The most serious open problems are a direct proof of interpenetration (such as available, e.g., electron microscopically for circular, catenated DNA decorated with cytochrome-c), and a sufficiently sensitive means of establishing chemically or physically the true extent of grafting of the component networks.

We are currently investigating (jointly with Professor G. Gillispie) the application of laser photo-luminescence spectroscopy as a function of temperature to resolve the separate molecular motions of the component networks. The PPO-PS IPN described in the previous section would have been an ideal candidate for such a study; unfortunately trace amounts of unreacted bromine in the polymer have largely obscured the luminescence bands of the aromatic rings in both networks.

Acknowledgement - This work was supported by NSF Grants DMR 780593802, ENG 76-10066, and an ARO Grant DAAG 2977G0273.

## REFERENCES

1. A comprehensive monograph in this field is Lipatov, Yu. and Sergeeva, L., "Vzaimopronikayushchie polimerovye setki" (Interpenetrating Polymer Networks), Naukova Dumka, Kiev, 1979 (in Russian).
2. Early citations to one-component IPN's are: Millar, J.R., *J. Chem. Soc.* 1311 (1960); Shibayama, K. and Suzuki, Y., *Kobunshi Kagaku* 23 (249), 24 (1966); Shibayama, K., *Zairyo* 12, 362 (1962); Shibayama, K., *Kobunshi Kagaku* 19, 219 (1962), *ibid.* 20, 221 (1963).
3. Frisch, H.L., Klemper, Daniel and Frisch, K.C., *J. Polymer Sci., Polymer Letters* 7, 775 (1969); Frisch, H.L., Klemper, D. and Frisch, K.C., *J. Polymer Sci. (A-2)* 8, 921 (1970); Matsuo, M., Kwei, T.K., Klemper, D. and Frisch, H.L., *Polymer Eng. and Sci.* 10 (6), 327 (1970); Klemper, D. and Frisch, H.L., *J. Polymer Sci. (B)* 8, 525 (1970).
4. Sperling, L.H. and Friedman, D.W., *J. Polymer Sci. A-2*, 7, 425 (1969); Sperling, L.H., Taylor, D.W., Kirkpatrick, M.L., George, H.F. and Bardman, D.R., *J. Appl. Polym. Sci.* 14, 73 (1970); Sperling, L.H., George, H.F., Huelck, Volker and Thomas, D.A., *J. Appl. Polymer Sci.* 14, 2815 (1970).
5. Frisch, H.L. and Klemper, D., *Adv. Macromol. Chem.* 2, 149 (1970).
6. Frisch, H.L. and Wasserman, E., *J. Amer. Chem. Soc.* 83, 3789 (1961).
7. Schill, G., "Catenanes, Rotaxanes and Knots", Academic Press, New York, 1971.
8. Sperling, L.H., Thomas, D.A., Covitch, M.J. and Curtius, A.J., *Polymer Eng. Sci.* 12, 101 (1972); Sperling, L.H., Thomas, D.A. and Huelck, V., *Macromolecules* 5, 340 (1972); Sperling, L.H., Chiu, T.W. and Thomas, D.A., *J. Appl. Polym. Sci.* 17, 2443 (1973).
9. Klemper, D., Frisch, H.L. and Frisch, K.C., *J. Elastoplastics* 3, 2 (1971).
10. Sperling, L.H., Thomas, D.A., Lorenz, J.E. and Nagel, E.J., *J. Appl. Polymer Sci.* 19, 2225 (1975); Grabes, J.A., Thomas, D.A., Hickey, E.C. and Sperling, L.H., *J. Appl. Polymer Sci.* 19, 1731 (1975).
11. Frisch, K.C., Frisch, H.L., Klemper, D. and Mukherjee, S.K., *J. Appl. Polymer Sci.* 18, 689 (1964); Frisch, K.C., Klemper, D., Antzak, T. and Frisch, H.L., *ibid.* 18, 683 (1974); Frisch, K.C., Klemper, D., Migdal, S. and Frisch, H.L., *J. Polymer Sci. (A-1)* 12 (4), 885 (1974); Frisch, K.C., Klemper, D., Migdal, S., Frisch, H.L. and Ghiradella, H., *Polymer Eng. Sci.* 14, 76 (1974); Frisch, H.L., Frisch, K.C. and Klemper, D., *ibid.* 14, 562 (1974).
12. Frisch, K.C., Frisch, H.L., Klemper, D. and Kim, S., Paper B-4.2, SIM, IUPAC Conf., Brazil, 1974; Kim, S.C., Klemper, D., Frisch, K.C., Frisch, H.L. and Ghiradella, H., *Polymer Eng. Sci.* 15, 339 (1975).

13. Sperling, L.H. and Arnts, R.R., J. Appl. Polymer Sci. **15**, 2731 (1971); Touhsaent, R.E., Thomas, D.A. and Sperling, L.H., J. Polymer Sci. **46C**, 175 (1974).
14. Kim, S.C., Klempler, D., Frisch, K.C., Radigan, W. and Frisch, H.L., Macromolecules **9**, 258 (1976); Kim, S.C., Klempler, D., Frisch, K.C. and Frisch, H.L., ibid. **9**, 263 (1976); ibid. **10**, 1187 (1977); ibid. **10**, 1191 (1977); Kim, S.C., Klempler, D., Frisch, K.C. and Frisch, H.L., J. Appl. Polymer Sci. **21**, 1289 (1977).
15. Flory, P.J., Chem. Rev. **35**, 51 (1944).
16. Prager, S. and Frisch, H.L., J. Chem. Phys. **46**, 1475 (1967).
17. Frisch, K.C., Klempler, D., Migdal, S., Frisch, H.L. and Dunlop, A.P., J. Appl. Polymer Sci. **19**, 1893 (1975); Kim, S.C., Klempler, D., Frisch, K.C., Frisch, H.L. and Ghiradella, H., Polymer Eng. Sci. **15**, 339 (1975); Kim, S.C., Klempler, D., Frisch, K.C. and Frisch, H.L., J. Appl. Polymer Sci. **21**, 1289 (1977).
18. Klempler, D., Yoon, H.K., Frisch, K.C. and Frisch, H.L., in "Polymer Alloys II" (ed. by Klempler, D. and Frisch, K.C.), Plenum Press, New York, N.Y., 1979, p. 185.
19. Frisch, H.L., Klempler, D., Yoon, H.K. and Frisch, K.C., Macromolecules (in press) and also in "Polymer Alloys II" (ed. by Klempler, D. and Frisch, K.C.), Plenum Press, New York, N.Y., 1979, p. 203.
20. Kato, K., Japan Plastics **2**, 6 (1968).
21. Such intermediate  $T_g$ 's were previously reported by Yu, Lipatov, Kramova, T., Sergeeva, L. and Karabanova, E., J. Polymer Sci. **15**, 427 (1977).
22. Mooney, M., J. Colloid Sci. **6**, 162 (1951).
23. Kerner, E.H., Proc. Phys. Soc. (London) **B69**, 808 (1956).
24. Dickie, R.A., J. Appl. Polymer Sci. **17**, 45 (1973); Dickie, R.A., Cheung, M.F. and Newman, S., ibid. **17**, 65 (1973); Dickie, R.A. and Cheung, M.F., ibid. **17**, 79 (1973); Dickie, R.A., ibid. **17**, 2509 (1973).
25. Budiansky, B., J. Mech. Phys. Solids **13**, 223 (1965).
26. MacKnight, W.J., Karasz, F.E. and Fried, J.R., in "Polymer Blends" (ed. by Paul, D.R. and Newman, S.), Vol. I, 185, Academic Press, New York, N.Y., 1978.
27. Bostick, E.E. and Gilbert, A.R., Fr. Pat. No. 1,518,441,22, March 1968.
28. Schmukler, S., U.S. Pat. No. 3,396,146,06, August 1968.
29. Kleiner, L.W., Karasz, F.E. and MacKnight, W.J., SPE 36th Annual Technical Conference, Washington, D.C., April 24, 1978, pp. 243-248.