Macromolecules 1982, *15*, 625–631

Phase Continuity in Sequential Poly(*n*-butyl acrylate)/Polystyrene Interpenetrating Polymer Networks

J. M. Widmaier[†] and L. H. Sperling*

Materials Research Center No. 32, Lehigh University, Bethlehem, Pennsylvania 18015.
Received September 15, 1981

ABSTRACT: Poly(*n*-butyl acrylate)/polystyrene sequential interpenetrating polymer networks, IPN's, of various compositions were made by UV photopolymerization. Poly(*n*-butyl acrylate) served as network I, and polystyrene as network II. Acrylic anhydride (AA) and divinylbenzene (DVB) were used as labile and permanent cross-linkers, respectively. Two series of IPN's were prepared depending upon in which network the cross-linkers were placed. After IPN formation, the AA-containing network was de-cross-linked and solvent extracted. The critical experiments had the AA in network I. After extraction of network I, the density of the remaining network II was in the range 0.7–0.9 g/cm^3. Scanning electron microscopy of network II revealed a porous but continuous structure formed by aggregates of fused spherical polystyrene domains. It was also concluded that network I was continuous, since it could be quantitatively and easily extracted. Hence, for compositions above about 20% by weight polymer II, dual phase continuity exists.

Introduction

The preparation and properties of various multipolymer combinations have received considerable interest in recent years. Among these materials, much attention has been given to interpenetrating polymer networks, IPN's.[1–4] IPN's are defined as a combination of two or more polymers in network form, at least one of which was synthesized and/or cross-linked in the immediate presence of the other. Preparation methods for IPN's can be classified as following two main routes: (1) Sequential IPN techniques entail the synthesis of network I, imbibing it with a second monomer and cross-linker, and finally polymerizing and cross-linking to form a network II. (2) In the second process, after mixing of two monomers or prepolymers, polymerization and cross-linking of both networks usually occur simultaneously through independent mechanisms.

Like other multipolymer materials, interpenetrating polymer networks have positive free energies of mixing, F, along with a positive second derivative with respect to mole fraction X_i, $\partial^2 F/\partial X_i^2 < 0$, and therefore phase separate. But, due to their interlocking phase configuration, the extent of phase separation is restricted, and domain dimensions are on the order of hundreds of angstroms, similar to block polymers. While the different morphologies in block polymers, spheres, cylinders, and lamellae (depending on the relative proportion of the two components) are well investigated, the exact prediction of the phase shape and phase continuity (if any) is still not possible in the case of IPN's.

Two theories, based on thermodynamic considerations, exist to determine the phase domain size[5,6] in sequential IPN's. Both models assume spherical domains of polymer II and hence a discontinuous polymer II phase. For the sequential IPN system poly(*n*-butyl acrylate)/polystyrene, extensively studied in this laboratory,[7,8] partial experimental confirmation of the theories has been achieved by transmission electron microscopy. The domains appeared spherical and were of the predicted diameter. However, the evidence for or against dual phase continuity was not satisfactorily established, since work was limited to a two-dimensional analysis of electron micrographs. Also, dynamic mechanical spectroscopy results suggested dual phase continuity.[4,7,8]

Table I
Polymer Molecular Weights

polymer	[AA], mol %	[1-dodecanethiol], mol %	$10^{-5}M_w$
PnBA	0	0	∞ [a]
PnBA	0	0.15	2.93
PnBA	0	0.3	1.75
PnBA	0	0.6	1.01
PnBA	1	0.3	1.59 [b]
PnBA	1	0.6	2.70 [c]
PS	0	0	3.77
PS	1	0	3.54 [b]

[a] Network. [b] After hydrolysis. [c] Some aggregate.

The use of selective chemical degradation[9] of the cross-links in one polymer followed by the extraction of the de-cross-linked material offered a new dimension in the analysis of IPN morphology by means of scanning electron microscopy.[10]

In this paper, the results of studies on sequential IPN's based on poly(*n*-butyl acrylate)/polystyrene, in which network I or network II contained labile cross-links formed by acrylic anhydride (AA), are reported. The AA in the network was hydrolyzed, leading to a linear polymer, which was then extracted out, leaving the pure second network. The remaining material was characterized by swelling and density measurements and examined by scanning electron microscopy.

Experimental Section

Synthesis. A series of poly(*n*-butyl acrylate)/polystyrene IPN's (PnBA/PS) with various compositions was prepared in bulk by photopolymerization at room temperature. Divinylbenzene (DVB) and acrylic anhydride (AA) were the permanent and labile cross-linkers, respectively.

Just before use, the *n*-butyl acrylate (Polysciences Inc.) and styrene (Aldrich) were dried and their inhibitor was removed by a column chromatographic technique using neutral alumina (Fisher Scientific). Divinylbenzene, 55% active (Polysciences Inc.) was purified similarly and stored over 4-Å molecular sieves. Acrylic anhydride (Polysciences Inc.) was used as received. The other polymerization reagents, benzoin (Kodak) and 1-dodecanethiol (Polysciences Inc.), were also used without further purification.

All IPN's were synthesized by a sequential technique previously described.[7,11] In brief, the sequential synthesis consists of the following steps: In a dry nitrogen atmosphere, a mixture of nBA monomer, chain transfer agent (1-dodecanethiol),[12] cross-linker (either DVB or AA), and photoinitiator (benzoin)[13] was poured in a rectangular glass mold formed by two glass plates (plus a thin Mylar sheet to prevent adhesion) separated by a 3-mm-diameter Viton O-ring and clamped together. The filled mold was exposed to ultraviolet light and the mixture allowed to polymerize and

---

[†] Permanent address: Université Louis-Pasteur, Ecole d'Application des Hauts Polymères, 67000 Strasbourg, France.

0024-9297/82/2215-0625$01.25/0

cross-link. The addition of a small amount (usually 0.3 mol %) of 1-dodecanethiol was necessary to avoid undesirable gel formation due to side reactions remaining after hydrolysis (see Table I).

After 96 h of UV exposure, the PnBA network was removed from the mold and dried in vacuo at 60 °C. The weight loss was usually less than 2%.

The PnBA network thus prepared was then swollen in a mixture of styrene monomer, cross-linker, and photoinitiator. The amount of solution added depended on the desired IPN overall composition. After all the monomer II had been absorbed, the sample was allowed to attain uniformity of composition via diffusion for 12 h and then weighed to determine the exact composition. Finally, the swollen network was again exposed to UV light for 36 h and the resulting IPN was dried to constant weight.

For all synthesis, the cross-linker level was constant at 1 mol % and the concentration of photoinitiator was 0.4% by weight.

For the present study, two series of IPN's, designated A and B, were prepared depending upon the position of the cross-linkers. The elastomeric PnBA was always polymerized first. In the A-type IPN's, acrylic anhydride (AA) was the cross-linker of polymer network I, and divinylbenzene the cross-linker of polymer network II. In the B-type IPN's, the order of the cross-linkers was exchanged: the DVB was for the poly(n-butyl acrylate) and AA was for polystyrene. A- and B-type IPN's are written PnBA(AA)/PS(DVB) and PnBA(DVB)/PS(AA), respectively.

For comparison purposes, polystyrene and poly(n-butyl acrylate) networks cross-linked by DVB and by AA, as well as linear polystyrene and poly(n-butyl acrylate), were synthesized under the same experimental conditions.

De-Cross-Linking. Samples of the homopolymer network and the IPN's with labile cross-links were soaked in a 10% aqueous ammonium hydroxide solution for about 12 h. De-cross-linking was effective, as shown by the complete dissolution of the treated homopolymer in the solvents of the corresponding linear polymer. Of course, the remaining DVB cross-linked network swelled, with only a small portion dissolving, as illustrated below.

In the case of IPN's, after de-cross-linking of the AA cross-links only, the resulting linear polymer was extracted from the other network in a Soxhlet extractor. The sample size was approximately 30 × 15 × 3 mm. The solvent used was either toluene or acetone. The experiment was continued for 10 days, after which no further material could be extracted.[14] The solution was evaporated to dryness and the amount of soluble material determined. The extracted network was dried at 60 °C under vacuum for at least 1 week. After this drying time, a constant weight was observed.

Characterization. Linear polymers were characterized by gel permeation chromatography; see Table I.

The homopolymer networks, including de-cross-linked and extracted IPN's, were characterized by a determination of their equilibrium swelling degree in different solvents. Densities of all materials were determined by a pycnometer. To achieve better precision, three samples of each solvent-extracted network were swollen in excess solvent for 2 weeks at room temperature until constant weight was achieved and an average value of the swelling ratio taken. It was assumed that the volumes were additive.

Ten-second shear moduli were measured with a Gehman torsion stiffness tester, as described elsewhere.[15,16] The IPN's density at 22 °C was determined before and after de-cross-linking and extraction.

IPN's were examined by scanning electron microscopy. Samples were cooled in liquid nitrogen and fractured with a sharp blow. Fractured samples were coated with Au/Pd by using a Polaron E S100 sputter coater in an argon atmosphere. Micrographs were obtained with an Etec Autoscan scanning electron microscope.

Results and Discussion

Homopolymer Networks. Four different networks (parent networks) were prepared by the combination of the two monomers with the two cross-linkers.

Table II
Extractable Materials for Homopolymer Networks

polymer	cross-linker[a]	sol fraction,[b] %
PnBA[c]	DVB	8
PnBA[c]	AA	13
PS	DVB	6
PS	AA	14

[a] 1 mol %. [b] In toluene. [c] 0.3 mol % 1-dodecanethiol added.

The parameters usually employed to characterize a polymer network are the amount of extractable polymer and the molecular weight between cross-links (M_c). The quantity M_c can be evaluated from swelling measurements through application of the Flory–Rehner equation:[17]

$$\frac{1}{M_c} = -\frac{\ln(1 - v_2) + v_2 + \chi_{12}v_2^{2}}{\rho V_1(v_2^{1/3} - \frac{1}{2}v_2)} \tag{1}$$

where v_2 is the reciprocal of the equilibrium volume swelling degree (q_v), V_1 is the solvent molar volume, ρ is the polymer density, and χ_{12} is the polymer–solvent interaction parameter. For polystyrene–toluene and polystyrene–methyl ethyl ketone (MEK), values of χ_{12} were 0.444 and 0.488, respectively.[18] As some surprisingly high χ_{12} values were recently reported[19] for poly(n-butyl acrylate) with various solvents (χ_{12} for MEK = 0.87; χ_{12} for acetone = 1.05), we thus calculated χ_{12} from the Hildebrand and Scott[20] solubility parameters δ_1 and δ_2

$$\chi_{12} = \beta + \frac{V_1}{RT}(\delta_2 - \delta_1)^2 \tag{2}$$

The constant entropic term β was taken as 0.32, a value which gives the best fit for self-consistent results for five different solvents. Hence χ_{12} was equal to 0.327, 0.332, 0.344, 0.358, and 0.473 for toluene, THF, benzene, MEK, and acetone, respectively.

The quanitity M_c can also be estimated from the shear modulus, G, measured well above T_g, by the application of the statistical theory of rubber elasticity:[21]

$$M_c = \frac{\rho RT}{G}\frac{\bar{r}^2}{\bar{r}_0^{2}} \tag{3}$$

Usually, $\bar{r}^2/\bar{r}_0^{2}$, the ratio of mean-square end-to-end distance of a chain segment between cross-link sites to the equivalent free chain end-to-end distance, is assumed to be equal to unity.

The amount of extractable polymer, i.e., the percent of polymer not incorporated into the network, is shown in Table II. With toluene, a good solvent for both polystyrene and poly(n-butyl acrylate), the sol fraction was relatively high, ranging from 6 to 14%. This may be due to the low cross-link density of the samples. However, for both homopolymer networks, higher amounts of extractables were obtainbed when AA is used as cross-linker.

In Table III, experimental values of M_c estimated from swelling measurements and shear modulus at 10 s, according to eq 1 and 3, respectively, are compared with the theoretical values calculated from the monomer/cross-linker ratio. The data confirm the difference in effectiveness between divinylbenzene and acrylic anhydride as cross-linkers. When DVB is used as the cross-linker, the experimental values agree well with the theoretical ones. The close agreement may be fortuitous, however, since one would expect physical cross-links to contribute to the experimentally measured cross-link level, especially when modulus was used. Apparently, network defects and physical cross-links nearly cancel each other out in this system.

Table III
Homopolymer Network Characterization Data

polymer network	av mol wt between cross-links, M_c						
	theor	from modulus data	from swelling data				
			toluene[c]	THF[c]	benzene[c]	MEK[c]	acetone[c]
PnBA(DVB)	13 000	14 400[a]	12 200	12 700	12 600	13 200	12 800
PnBA(AA)	13 000	38 100[a]	36 200	35 900	37 400	41 300	42 600
PS(DVB)	10 500	10 800[b]	8 300			11 000	
PS(AA)	10 500	27 700[b]	21 900			25 800	

[a] Room temperature. [b] At 160 °C. [c] Swelling solvent.

Table IV
Results of Soxhlet Extraction for De-Cross-Linked PnBA(AA)/PS(DVB) IPN's with Various Compositions

IPN wt composition PnBA/PS	sol fraction, %	
	toluene as solvent	acetone as solvent
0/100	6.1	
30/70	37.8	29.5
40/60	46.4	38.3
45/55	48.8	43.8
50/50	53.2	49.6
55/45	62.7	56.1
60/40	69.2	61.6
70/30	75.9	71.2
80/20	85.1	83.0
90/10	94.4	94.6
100/0	100	100

For AA on the other hand, the M_c values are much higher than expected, indicating lower cross-link formation. Partial hydrolysis of AA could not explain the results since less than 5% free acrylic acid was found in the AA by infrared analysis. An alternative explanation for the lower than expected cross-link densities for AA cross-linked networks may be the possibility of ring formation. It is well-known[22] that the cross-linking in diacrylate or dimethacrylate systems is not complete, due to competition between intermolecular cross-linking and intramolecular cyclization. In AA, the distance between the two vinyl end groups favors intramolecular cyclization. This data is helpful in understanding the differences in Table II and the domain sizes reported below.

After the de-cross-linking step, the soluble polymer thus obtained was found to have a molecular weight similar to that of the corresponding linear polymer prepared in the same experimental conditions, but without addition of cross-linker. As reported in Table I, the average molecular weight is around 3.5 × 10^5 for polystyrene, which is in accordance with previous results from this laboratory.[23] The difference in molecular weight between linear and de-cross-linked poly(*n*-butyl acrylate) is around 10% when 0.3% chain transfer agent was added. The GPC chromatograms show a minor broadening of the molecular weight distribution for the de-cross-linked polymer. This indicates that the major point of attack was a chemical degradation of the three-dimensional junction sites.

Sequential PnBA/PS IPN's. Sequential PnBA/PS IPN's were prepared with various compositions. Thus, the material was rigid when polystyrene was the major component and soft when poly(*n*-butyl acrylate) dominated, confirming previous studies by Yeo et al.[7,8] The exact compositions are shown in Tables IV–VII, and ranged from 30/70 to 90/10.

In the range 30/70 to 70/30, all the samples were opaque, whereas for the 80/20 and 90/10 PnBA/PS ratios, they were more transparent but still opalescent. This indicates a phase-separated, heterogeneous system, consistent with other studies.[24,25]

Table V
Density Measurements and Swelling Behavior for PnBA(AA)/PS(DVB) IPN's and De-Cross-Linked IPN's with Various Compositions

IPN wt composition PnBA/PS	IPN density, g/cm³	de-cross-linked and extracted IPN, PS remaining	
		ρ, g/cm³	q_v[a]
0/100	1.05[b]		4.70
30/70	1.053	0.984	5.78
40/60	1.022	0.781	6.43
45/55	1.079	0.845	6.33
50/50	1.067	0.795	7.04
55/45	1.059	0.818	10.37
60/40	1.052	0.744	15.35
70/30	1.023	0.965	18.96

[a] True swelling plus interstitial solvent held by capillary forces. [b] Literature value.

Table VI
Results of Soxhlet Extraction for De-Cross-Linked PnBA(DVB)/PS(AA) IPN's with Various Compositions

IPN wt composition PnBA/PS	sol fraction, %	
	theor[a]	toluene as solvent
0/100	100	100
30/70	72.4	69.9
40/60	63.2	61.2
45/55	58.6	54.2
50/50	54.0	45.1
55/45	49.5	41.6
60/40	44.8	37.5
70/30	35.6	33.5
80/20	26.4	27.0
100/0	8.0	8.0

[a] Estimated amount considering the IPN composition and the poly(*n*-butyl acrylate) network sol fraction.

Table VII
Density Measurements and Swelling Behavior for PnBA(DVB)/PS(AA) IPN's and De-Cross-Linked IPN's with Various Compositions

IPN wt composition PnBA/PS	IPN density, g/cm³	de-cross-linked and extracted IPN, PnBA remaining		
		ρ, g/cm³	q_v	M_c
30/70	1.023	0.964	7.24	11 800
40/60	1.032	0.999	7.54	12 800
45/55	1.030	1.001	7.84	13 800
50/50	1.044	1.021	7.92	14 100
55/45	1.029	1.039	8.09	14 700
60/40	1.013	1.018	8.46	16 100
70/30	1.007	1.016	8.18	15 100
80/20	1.011	1.023	8.35	15 700
100/0			7.3	12 200

A-Type IPN's: PnBA(AA)/PS(DVB). When soaked in ammonium hydroxide, network I is de-cross-linked and can be extracted; see Table IV. The amount of PnBA extracted with acetone roughly equals the amount in the

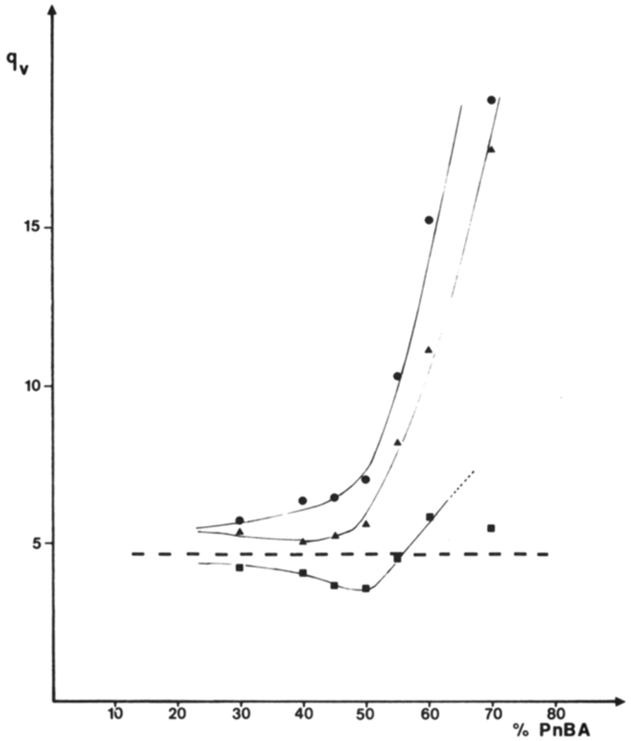

Figure 1. Equilibrium swelling degree of remaining polystyrene (polymer II network) vs. IPN composition: (●) apparent swelling; (▲) calculated from q_w using experimental details; (■) true swelling estimated by correction for extractibles. The dotted line is for homopolystyrene network.

IPN. With toluene, the amount of extractable material is higher than expected, especially for high polystyrene content samples.

Some PS (from imperfect cross-linking of the polymer network II) is also extracted. For example, analysis by UV spectroscopy at 262 mm reveals 11.0% of PS in the sol fraction of a 50/50 de-cross-linked IPN, which explains the high values obtained when toluene was employed as the extracting fluid.

With acetone, which is a good solvent for the PnBA phase but a bad one for the PS phase, the extraction data in Table IV show that at each composition the PnBA phase was quantitatively removed from the IPN. This means that (a) the de-cross-linking reaction occurs even when the PnBA network is in an IPN form (effective diffusion of the ammonium hydroxide in the network) and (b) the grafting level between polymer I and polymer II is low, probably less than 5%.

The optical properties and the macroscopic aspects of the samples in the dry state after extraction are of certain importance. Surprisingly, for every composition the de-cross-linked and extracted IPN was almost transparent. This must be caused by the partial collapse to a size where light scattering is reduced (see below). Note also that when the IPN had more than 30% PS, a monolithic sample remained in the thimble; at 30%, after drying, the material was very brittle. For the lower composition studies (10 and 20% PS), small grains were obtained. This means that for midrange compositions, polymer II was also continuous. Roughly speaking, the limit of polymer II continuity is between 70/30 and 80/20 PnBA/PS.

The remaining polystyrene network was characterized by swelling studies. For each composition, when possible, the equilibrium swelling degree in toluene was calculated, and the results are listed in Table V.

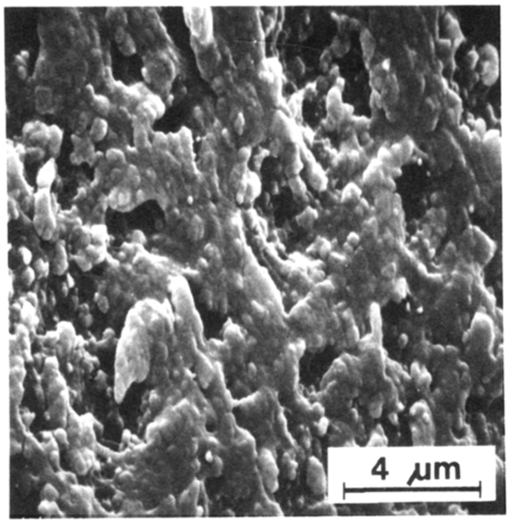

Figure 2. Low-magnification scanning electron micrograph of de-cross-linked and extracted A-type IPN [PnBA(AA)/PS(DVB), 50/50].

The change in q_v with percent PnBA needs explanation. One cannot consider the extracted and de-cross-linked IPN, i.e., the remaining polymer II, as a conventional PS network. The decrease in density (see Table V) together with electron micrographs presented below suggest a porous material. Some liquid is imbibed in the pores during swelling as a more or less pure phase. The materials that had a higher concentration of PnBA on swelling have more solvent imbibed and, hence, an apparently larger q_v.

Figure 1 shows the equilibrium degree of swelling of the de-cross-linked and extracted IPN as a function of the IPN composition. The apparent swelling volume was corrected by two procedures: (a) q_v was calculated from the equilibrium degree of swelling by weight, q_w, taken as the weight of the swollen sample divided by the weight of the dry sample, assuming additivity of polymer and solvent volumes, from the relation

$$q_v = (q_w - 1)\frac{\rho_N}{\rho_s} \qquad (4)$$

where ρ_N and ρ_s are the densities of the network and the solvent, respectively (the quantity ρ_N was taken as the measured density reported in Table V); (b) the amount of extractable was deducted from the volume of the sample; thus only the swelling of the compact PS was taken in account and hence true swelling was evaluated.

As mentioned above, the density of the de-cross-linked, extracted, A-type IPN's is in the range 0.8–0.9 g/cm^3, clearly lower than the bulk density of the IPN and indicating a partial (and variable) collapse of the structure. The invariance of the numbers is probably a consequence of the partial collapse of the porous structure.

It can be seen that for samples containing over 50% PnBA, i.e., when the PS phase is the swollen component in the IPN, q_v deviates from the homopolystyrene equilibrium swelling volume, thus indicating more and more effect of the pore volume.

Electron Microscopy. In general, all scanning electron micrographs of de-cross-linked and extracted IPN's revealed the internal appearance of a sponge with pores of 500 Å to 1 μm. The decrease in density (see Table V), although less than theoretical, confirms a porous structure. Figures 2 and 3 show micrographs for a midrange composition. In Figure 2, the lighter regions represent the remaining polymer, which is polystyrene, and the dark zones are voids where network I was located. Undoubtedly, the PS phase is continuous. The voids appear to be continuous, too, and hence the poly(n-butyl acrylate) phase

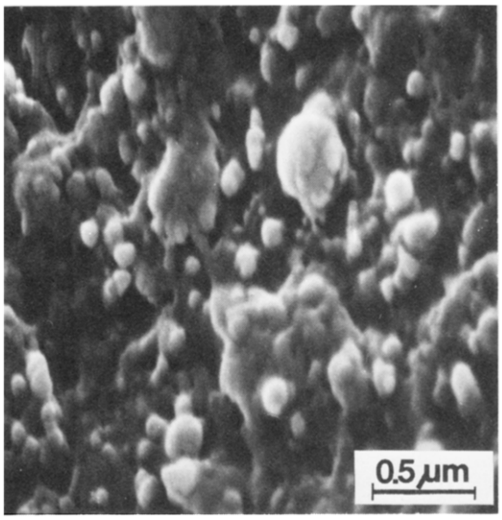

Figure 3. High-magnification scanning electron micrograph of de-cross-linked and extracted A-type IPN [PnBA(AA)/PS(DVB), 50/50].

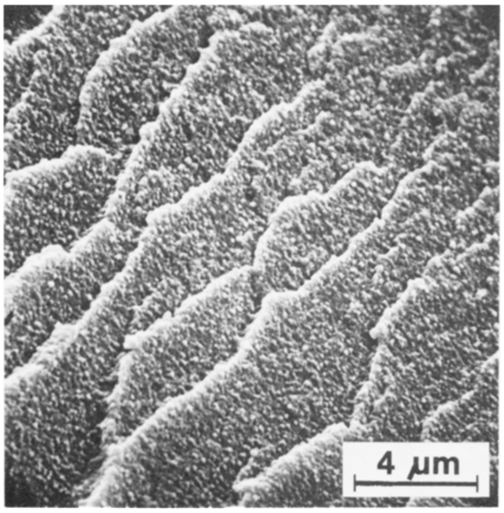

Figure 4. Scanning electron micrograph of de-cross-linked and extracted A-type IPN (PnBa(AA)/PS(DVB), 70/30]. Note polymer II network has collapsed.

must have been continuous before extraction. (This is reinforced by the ready extractability of the poly(*n*-butyl acrylate).) At a higher magnification, Figure 3, it can be seen that the continuous phase is formed by an agglomerate of spheres. The diameter of these spheres is approximately 100 nm. This is in accordance with the previous theoretical calculations[5,6,26] and transmission electron microscopy measurements.[8]

For IPN's with only 30% PS, the de-cross-linked material collapsed during the drying step after extraction of polymer I and revealed, Figure 4, a cracked structure with grooves. This was suggested by the value of the density found for that sample; see Table V.

It is of particular interest to examine the morphology of the remaining phase in the case of obvious macroscopic discontinuity (less than 20% PS in the IPN). Each individual grain exhibited a porous structure even from a 90/10 PnBA/PS IPN, Figure 5. At high magnification, for the 80/20 ratio, there is no doubt the voids are continuous to a certain extent, Figure 6. But for the 90/10 ratio, Figure 7, one observes individual particles (300–400 nm wide) formed by the aggregation of a few spheres.

B-Type IPN's: PnBA(DVB)/PS(AA). For the B-type IPN's, the order of cross-linker is reversed. As a consequence, after de-cross-linking, polymer I remains insoluble, whereas polymer II can be dissolved out of the

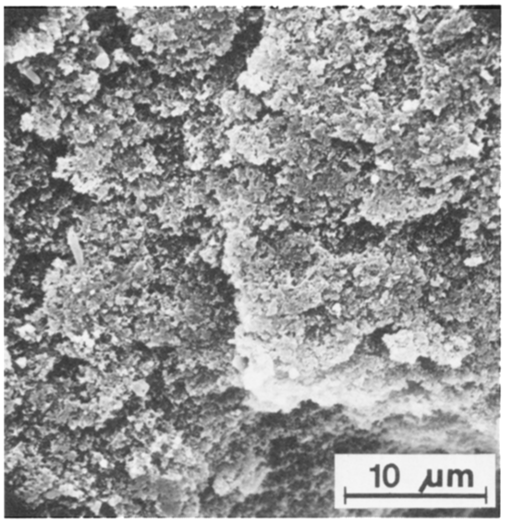

Figure 5. Low-magnification scanning electron micrograph of the remaining polymer II network granular powder after de-cross-linking and extraction of 90/10 PnBA(AA)/PS(DVB) IPN.

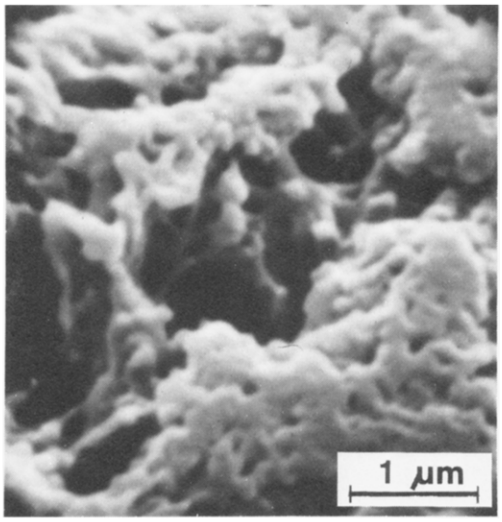

Figure 6. High-magnification scanning electron micrograph of de-cross-linked and extracted A-type IPN [PnBA(AA)/PS(DVB), 80/20].

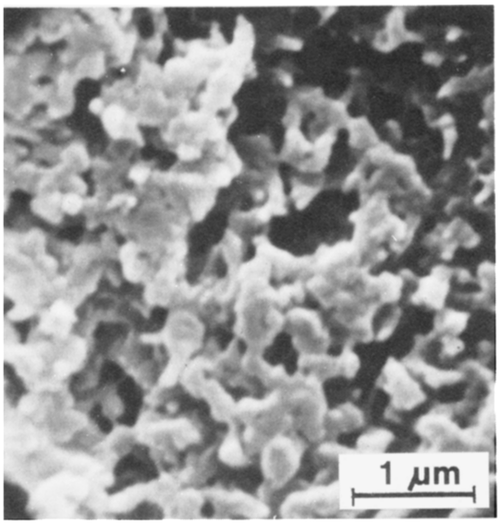

Figure 7. High-magnification scanning electron micrograph of de-cross-linked and extracted A-type IPN [PnBA(AA)/PS(DVB), 90/10].

IPN. In fact, by using toluene, a mutual solvent of the two linear polymers, the sol fraction of de-cross-linked IPN will contain polymer II plus about 8% of polymer I. For various compositions, the results of the extraction measurements are listed in Table VI. The amount of polymer removed from the de-cross-linked IPN is slightly lower than expected, except for the 80/20 PnBA/PS ratio. For midrange compositions, the difference between experimental and theoretical values is significant. Visual examination of the remaining gel revealed that the monolithic poly(n-butyl acrylate) sample was still hazy, indicating inclusion of some polystyrene in the network. While small pores can obviously cause haziness, the density data in Table VII reveal substantially a fully dense product. Hence, it may be assumed that the fully dense material is collapsed around the remaining PS inclusions.

Table VII gives the equilibrium swelling degree of the de-cross-linked and extracted B-IPN's and the corresponding molecular weight between cross-links, assuming pure poly(n-butyl acrylate). There is a slight variation of q_v and M_c with IPN composition, which may be due to incomplete extraction of the PS network. (Some polymer I chains could also have been broken during the synthesis of polymer II, which would lead to higher swelling values than for homopolymer network. If damage to polymer I had been significant, one should expect an increase of q_v and consequently of M_c with increasing polystyrene content, but this was not observed. The increase in q_v in Table V was attributed to void space, absent here.)

Contrary to de-cross-linked and extracted A-type IPN's, the density of the remaining network in B-type IPN's was close to that of the homopolymer. Scanning electron micrographs of all compositions do not show a porous material, but rather a smooth matrix of PnBA with some cracks, probably caused by drying stresses. Homopoly(n-butyl acrylate) exhibited almost the same aspect. Apparently, the remaining network, PnBA, being above its glass transition temperature, collapses and tends to occupy the empty space where polymer II was located, and consequently, no further information relative to the morphology of the second network can be obtained from the micrographs.

In type-B networks, the extracting solvent is toluene, a good solvent for both PnBA and PS. So it follows that once the PS is extracted, the remaining PnBA network will by highly swollen and flow together so that upon solvent removal and drying, all aspects of the morphology developed during the polymerization will be erased. Hence, one should not expect to see much change in the density or any reliable information on morphology in the SEM. The time scale of the extractions of both the A-type and the B-type IPN's was 10 days. Obviously, somewhat more material may have been extracted from the B-type IPN's, had the experiment been continued longer.

The driving force for the collapse of the B-type IPN's is rubber elasticity. The chains are relaxed in the fully dense state. The opposite is true for the A-type IPN's, where the relaxed state is the porous structure for polymer II, as formed.

Discussion

The immediately preceding work[24] describes the modulus–temperature behavior of PnBA(TEGDM)/PS(DVB) IPN's, where TEGDM is tetraethylene glycol dimethacrylate, a permanent cross-linker like divinylbenzene, DVB. The cross-link levels are of the same order of magnitude as those of the present paper. Values of the glass transition temperatures, T_g, of these materials are shown in Table VIII. In general, the glass transitions of the IPN's are shifted inward and broadened, making an exact determination difficult. Such data indicate a significant extent of molecular mixing between networks I and II.

Table VIII
Glass Transition Data of PnBA(TEGDM)/PS(DVB) IPN's from Ref 24[a]

	full IPN		semi-I IPN	
composition	PnBA	PS	PnBA	PS
0/100		+95		+95
13/87		+80		+88
25/75	−35	+75	−40	+85
40/69	−40	+40	−45	+40
51/49	−40		−45	
58/42	−45			
68/32			−50	
72/28	−45			
87/13	−55		−55	
100/0	−55[b]		−55[b]	

[a] T_g's in °C. [b] Estimated.

For the semi-I IPN case (PS not cross-linked), corresponding to the case after de-cross-linking but before extraction, the two individual glass transition temperatures become more sharply defined and are closer to the corresponding homopolymer transition. Values are also shown in Table VIII. This indicates that on the relaxation of network constraints, the phases separate to a greater extent. Probably such a separation is also taking place in the de-cross-linked IPN's before extraction. Tables V and VII show a slight maximum in the density for the IPN's before extraction. This may be a consequence of the extent of phase mixing, which would bear greater study.

Conclusions

The use of a labile cross-linking agent allows a different approach to the study of interpenetrating polymer networks. With acrylic anhydride as the cross-linker, hydrolysis leads to a linear polymer, easy to extract and characterize, and to a pure homopolymer network whose characteristics can be compared with similar networks prepared by classical methods.

In the A-type IPN's, AA was used to cross-link PnBA, i.e., polymer I, and DVB to cross-link PS, i.e., polymer II. In the B-type IPN's, the cross-linking agents were reversed, keeping the order of polymer synthesis the same. For both types and for various overall compositions, nearly the whole amount of de-cross-linked polymer can be extracted, indicating a low level of chemical grafting between polymer I and polymer II. In the B-type PnBA(DVB)/PS(AA) IPN, after swelling of the monolithic poly(n-butyl acrylate) network in monomer II, polymerization, de-cross-linking, and extraction, one still recovers polymer I without substantial damage as shown by its density, equilibrium swelling degree, and scanning electron micrographs.

Interesting morphological details heretofore not available were found for A-type PnBA(AA)/PS(DVB) IPN's: the remaining network II presents a porous structure as indicated by density measurements and scanning electron microscopy. The void regions, which correspond to the location of the poly(n-butyl acrylate) phase before extraction, are interconnected in the composition range studied.

Most interestingly, the extent of continuity of the remaining polystyrene depends on its concentration in the IPN. For midrange compositions, high-magnification scanning electron micrographs showed dual phase continuity. When the amount of polymer II in the A-type IPN was decreased below 30%, the sample crumbled by itself, indicating a macroscopically discontinuous second phase. However, at a microscopic level some of the spheres were still interconnected. It is only when polymer II is around 10% that the discontinuity is evident and only a few individual particles are connected.

The major conclusion from this paper relates to the dual phase continuity of PnBA/PS in sequential IPN's:

(1) Above 20% of polymer network II, its phase domain structure was continuous.

(2) Throughout the composition range studied, polymer network I was continuous.

In a forthcoming paper,[27] a further analysis of the domain sizes will be given, especially with regard to the theory by Yeo et al.,[6] and data on semi-IPN's containing AA will be presented.

Acknowledgment. We thank the National Science Foundation for financial support through Grant No. DMR-8015802, Polymers Program.

References and Notes

(1) Klempner, D.; Frisch, K. C., Eds. "Polymer Alloys"; Plenum Press: New York, 1980; Vol. II.
(2) Manson, J. A.; Sperling, L. H. "Polymer Blends and Composites"; Plenum Press: New York, 1976.
(3) Lipatov, Yu. S.; Sergeeva, L. M. "Interpenetrating Polymeric Networks"; Naukova Dumka: Kiev, 1979.
(4) Sperling, L. H. "Interpenetrating Polymer Networks and Related Materials"; Plenum Press: New York, 1981.
(5) Donatelli, A. A.; Sperling, L. H.; Thomas, D. A. *J. Appl. Polym. Sci.* **1977**, *21*, 1189.
(6) Yeo, J. K.; Sperling, L. H.; Thomas, D. A. *Polymer*, submitted.
(7) Yeo, J. K.; Sperling, L. H.; Thomas, D. A. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1980**, *21* (2), 53.
(8) Yeo, J. K.; Sperling, L. H.; Thomas, D. A. *Polym. Eng. Sci.* **1982**, *22*, 190.
(9) Neubauer, E. A.; Thomas, D. A.; Sperling, L. H. *Polymer* **1978**, *19*, 188.
(10) Kresge, N. E. In "Polymer Blends"; Paul, D. R., Newman, S., Eds.; Academic Press: New York, 1978; Vol. 2.
(11) Sperling, L. H.; Friedman, D. W. *J. Polym. Sci., Part A-2* **1969**, *7*, 425.
(12) Yomoda, S.; Sperling, L. H. *J. Appl. Polym. Sci.* **1977**, *21*, 2609.
(13) Heine, H. G.; Rudolph, H.; Rosenkranz, H. *J. Appl. Polym. Symp.* **1975**, *26*, 157.
(14) Widmaier, J. M. *Makromol. Chem.* **1978**, *173*, 1743.
(15) Gehman, S. D.; Woodford, D. E.; Wilkinson, C. S. *Ind. Eng. Chem.* **1947**, *39*, 1108.
(16) American Society for Testing and Materials, ASTM D 1052-73T, 1974.
(17) Flory, P. J.; Rehner, J. *J. Chem. Phys.* **1943**, *11*, 512, 521.
(18) Frank, H. P.; Mark, H. *J. Polym. Sci.* **1951**, *6*, 243.
(19) Walsh, D. J.; McKeown, J. G. *Polymer* **1980**, *21*, 1335.
(20) Hildebrand, J. H.; Scott, R. L. "The Solubility of Nonelectrolytes", 3rd ed.; Reinhold: New York, 1950.
(21) Flory, P. J. "Principles of Polymer Chemistry"; Cornell University Press: Ithaca, N.Y., 1953.
(22) Tobolsky, A. V.; Katz, D.; Takahashi, M.; Schaffhauser, R. *J. Polym. Sci., Part A* **1964**, *2*, 2749.
(23) Sperling, L. H.; Ferguson, K. B.; Manson, J. A.; Corwin, E. M.; Siegfried, D. L. *Macromolecules* **1976**, *9*, 743.
(24) Yeo, J. K.; Sperling, L. H.; Thomas, D. A. *Polym. Eng. Sci.* **1981**, *21*, 696.
(25) Yeo, J. K.; Sperling, L. H.; Thomas, D. A. *J. Appl. Polym. Sci.* **1981**, *26*, 3283.
(26) Michel, J.; Hargest, S. C.; Sperling, L. H. *J. Appl. Polym. Sci.* **1981**, *26*, 743.
(27) Widmaier, J. M.; Sperling, L. H. *J. Appl. Polym. Sci.*, submitted.

Stress Relaxation of a Polyelectrolyte Network As Affected by Ionic Strength

Carlos A. Kienzle-Sterzer, Dolores Rodriguez-Sanchez, Diane Karalekas, and ChoKyun Rha*

Biomaterials Science and Engineering Laboratory, Department of Nutrition and Food Science, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139.
Received November 10, 1981

ABSTRACT: Stress relaxation behavior of polyelectrolyte films under simple tension is affected by the ionic strength (NaCl) of the swelling medium. In this study, the cationic polyelectrolyte chitosan [(1→4)-2-amino-2-deoxy-β-D-glucan] was used to prepare films. Swelling at 24 °C showed a salting-in effect up to ionic strength 0.4, reaching an equilibrium volume of approximately 180% (w/w). Linear stress relaxation behavior indicated a predominant first elastic component in a two-component Maxwell model, with a first relaxation time of approximately 10^{-4} s. The apparent Young's modulus increased, with an inflection point at ionic strength between 0.4 and 1.0. Internal stress of the polycationic films, calculated from linear stress relaxation experiments, decreased as the ionic strength increased. The internal stress changed from positive to negative at ionic strengths between 0.4 and 1.0. Nonlinear stress relaxation measurements at extension ratios between 10 and 40% showed that the instantaneous stress–strain relationships can be represented by the Mooney–Rivlin equation, where both C_1 and $|C_2|$ decrease with time, showing a marked dependence on ionic strength. The results indicate a rearrangement of the molecular chains in the network under tensile stress and also the electrostatic nature of the interactions responsible for the network integrity in the polyelectrolyte films.

Introduction

Interchain interaction in random coil polyelectrolytes is largely electrostatic and thus is strongly affected by ionic strength. Consequently, the mechanical properties of any polyelectrolyte network is affected by ionic strength. In order to evaluate the effect of ionic strength on interchain interactions, a cationic polyelectrolyte, chitosan [(1→4)-2-amino-2-deoxy-β-D-glucan], deacetylated chitin, was selected for this study. The removal of some or all acetyl groups from chitin imparts the polycationic nature to chitosan.[1] We selected chitosan since it is the only known available high molecular weight cationic polysaccharide.

The film-forming qualities of chitosan, methods of film preparation, and some mechanical properties such as breaking stress and tensile elongation have been reported.[1]

Previously, we examined the network-forming mechanism of polyelectrolytes using films cast by the evaporation of solvent from chitosan solutions.[2–4] The results revealed the electrostatic mechanism of interaction and nonideal rubber-like elasticity of the films. The non-Guassian be-

0024-9297/82/2215-0631$01.25/0 © 1982 American Chemical Society