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Gradient interpenetrating polymer networks

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The methods of synthesis and properties of gradient interpenetrating polymer networks (IPN) are discussed based on literature and authors' own experimental data. Gradient IPN can be treated as a sequence of an infinite number of layers of IPNs, whose composition and properties vary gradually from the surface to the core of specimens. These are analysed the most important properties of gradient IPNs: temperature transitions, thermodynamic and physico-mechanical characteristics and the main direction of practical application of gradient IPN-based materials.

1. Introduction

Among the wide variety of polymeric composite materials that have been developed recently, compositions with a gradient of physical or chemical properties have attracted great interest. These materials include the gradient interpenetrating polymer networks (IPNs), whose preparation and investigation was begun in the 1970s [1, 2].

Distinct from traditional IPNs [3], gradient IPNs have compositions which vary as a function of position in the sample. Such systems are sequential IPNs. The term refers to the time-order of polymerization. They are formed as a result of the swelling of a preformed first (host) network in the monomers forming the second (guest) network. The swelling is terminated at a certain stage before equilibrium is established, and then polymerization is carried out to produce the guest network (or a linear polymer in the case of a semi-IPN). In this case, the concentration of the guest network in the host (or matrix) network has a gradient. As a result, the properties of the system differ from those of both individual networks and IPNs prepared by the traditional method.

Gradient IPNs can be treated as a sequence of an infinite number of layers of IPNs, whose compositions and properties vary gradually from the surface to the core of samples.

A number of reviews have been published [4–6] in the field of IPNs; however, this paper is the first to review specifically the gradient IPNs.

2. Preparation of gradient IPN and estimation of the component distribution

Apart from the non-equilibrium swelling of the host polymer in a monomer, attempts to use other methods to attain a gradient of properties across the sample thickness have also been undertaken. Elsabee *et al.* [7] employed differential diffusion of the cross-linking agent. The host polymer, polyurethane (PU) was swollen to equilibrium in an ethanolic solution of acrylamide with an initiator, after which the swollen samples were immersed for different times in a cross-linking agent solution. This method, however, failed to yield a significant gradient of polyacrylamide (PAM) in the PU matrix. The PAM concentration in the polyurethane–polyacrylamide IPN was found not to depend on the holding time of the samples in the cross-linking agent solution.

An attempt was also undertaken to use a cross-linking agent of a higher molecular weight to produce a gradient distribution of PAM in poly(ether urethane) (PEU), but this method also proved to be ineffective.

Elsabee *et al.* [7] investigated gradient IPN samples prepared by the three above-described methods using total internal reflection infrared Fourier transform spectroscopy, which yields quite accurate information on the character of the PAM distribution in the host PU. They showed that, in the systems where PU swelling times in the solution of acrylamide had been short, the latter concentrated mainly at the surface of the sample, penetrating up to 10 μm within the former. An insignificant PAM concentration gradient across the thickness was also found for IPNs prepared ordinarily, i.e. by equilibrium swelling of PU in acrylamide, followed by a partial diffusion of the cross-linking agent. They exhibited a variation of PAM concentration across the sample, but a less significant one than from the first method.

By exploring the morphology of prepared systems, differences between the outer and deep layers of gradient IPNs have been revealed [7, 8]. Ultrathin sections of samples, stained by OsO_4, were studied by electron microscopy. The influence of monomer, initiator, and cross-linking agent concentrations, of the nature of the solvent and of the sample heating method in polymerizing the guest component on the structure of gradient systems, were examined. It was demonstrated that surface layers of a PU/grad.PAM IPN contain PAM domains of 30–40 nm, dispersed in the PU matrix. Increasing the PAM content in the system increased the size of its domains. A low content of PAM at deeper than 10 μm and its complete absence in the core of samples were observed.

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The method of non-equilibrium swelling of the host polymer in a monomer, employed to prepare gradient IPNs, gives rise to problems involved with the effects of various factors on the monomer diffusion rate and consequently on the distribution of the guest component across the sample thickness.

Akovali *et al.* [1] prepared two series of gradient IPNs: polystyrene with a gradient of polyacrylonitrile (PS/grad.PAN) and poly(methyl methacrylate) with a gradient of poly(methyl acrylate) (PMMA/grad. PMA). The host PS and PMMA were prepared with the use of a cross-linking agent, ethylene dimethacrylate (1.2 vol%); polymerization was effected by ultraviolet radiation with benzoin isobutyl ether as the photosensitizer. When obtaining a gradient of acrylonitrile in PS, the cross-linking agent and photosensitizer were added to the monomer in the same proportions as for the host polymer. Akovali *et al.* [1] explored in detail the acrylonitrile diffusion into the host PS. They supplemented experimental data by computing gradient profiles for diffusion obeying Fick's law with a constant diffusion coefficient (Fig. 1). To determine the profile of the PAN distribution in PS, they resorted to the layer-by-layer elementary chemical analysis used in most studies [1, 9, 10]: 0.05 mm thick layers were removed and then analysed for nitrogen content by combustion, which showed the highest PAN content (around 50%) to occur near the sample surfaces. The best fit of the computed curves to experimental data was obtained with a diffusion coefficient of $1.10 \times 10^{-8}\ \mathrm{cm^2\,s^{-1}}$.

Akovali *et al.* [1] studied the hydrocarbon penetrability of prepared IPNs and demonstrated that the higher PAN concentration in the PS surface layers enhances the resistance of the IPNs to solvents, such as benzene, over that of a pure PS. In their opinion, such materials can be used for construction of plastic gasoline tanks.

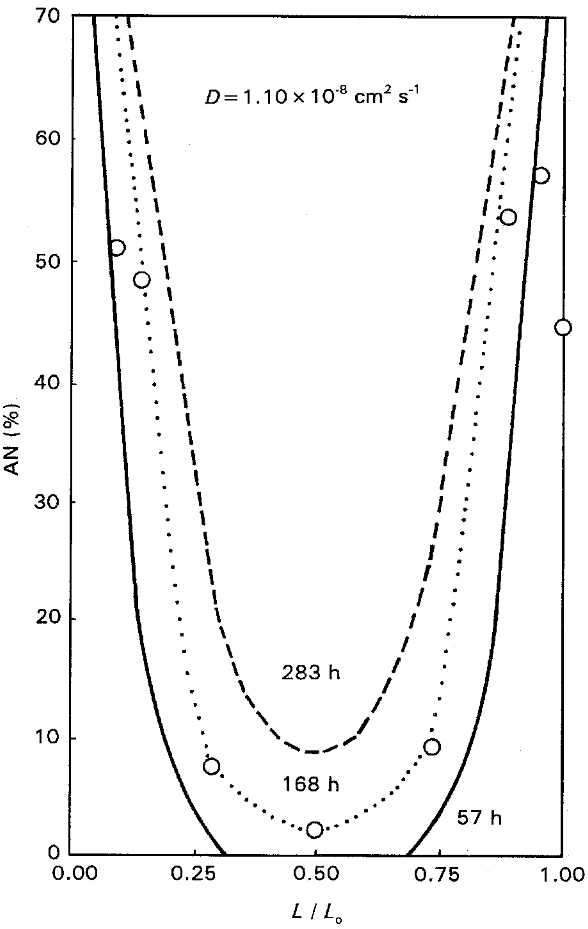

Figure 1 Gradient profile of PS/grad.PAN system prepared by immersing cross-linked PS sheet into acrylonitrile monomer at 323 K. (○) Experimental data determined from chemical analysis. Curves were computed by Fick's equation with diffusion coefficient of $1.10 \times 10^{-8}\ \mathrm{cm^2\,s^{-1}}$ for immersion times of 57, 168, and 283 h [1].

The rate of diffusion of the monomer in the course of preparing a gradient IPN and the resulting distribution of the guest polymer throughout the host polymer are, to a great extent, dependent on the monomer concentration in solvent (if used), on the concentration of cross-linking agent, initiator, etc. Dror *et al.* [8] explored this issue in detail when studying an IPN of poly(ether urethane) with a gradient of polyacrylamide (PEU/grad.PAM). The PEU contained hard domains serving as physical links to form a network. Gradient IPN samples were prepared by swelling PEU films in an ethanolic solution of acrylamide, cross-linking agent (tetraethyleneglycol dimethacrylate), and initiator (AIBN), followed by acrylamide polymerization. The amount of PAM formed was determined as the difference between masses of the initial PEU and the IPN after acrylamide polymerization, samples having been washed in ethanol to remove linear PAM before weighing. Dror *et al.* [8] determined the influence of the PEU swelling time in acrylamide solution and of the acrylamide concentration in the solution on the composition of resulting IPNs. Increasing the monomer concentration in the swelling solution resulted in a regular growth of PAM concentration in the gradient IPN, although the variation of the PAM content with the acrylamide concentration in the solution was non-linear. Increasing the initiator concentration in the solution also increases the PAM content in the IPN, but only up to concentration of 0.05–0.09 M, after which its variation ceased to exert an appreciable effect. Varying the cross-linking agent concentration affected the PAM content in a gradient IPN non-monotonically; there exists an optimum concentration, at which the PAM concentration in the host PEU is a maximum.

Dror *et al.* [8] also demonstrated the effect of the PEU swelling time in the monomer solution on the PAM concentration and distribution in the host polymer network. Having explored the influence of the PEU swelling time (from 5–30 min) on the PAM content in the gradient IPN, they showed the content to be described by the equation $W_t = W_\infty(1 - e^{-kt})$, where W_t and W_∞ are, respectively, the mass fractions of PAM in the IPN at polymerization after swelling for a time t and after swelling to equilibrium.

3. Temperature transitions, thermodynamic and physico-mechanical characteristics of gradient IPNs

Temperature transitions, sorption properties of layers of the IPNs, and variation of the thermodynamic compatibility of their components throughout the sample volume have been studied [10] for IPNs based on polyurethanes with a gradient of butyl methacrylate–triethyleneglycol dimethacrylate copolymer (PU/grad.(BMA–TrEGDMA)).

As is known, at a certain stage of the reaction in the course of IPN formation, microphase separation occurs caused by the appearance of the thermodynamic incompatibility of the constituent networks and determined by the influence of the system composition on the IPN formation reaction kinetics. It is obvious that if a gradient IPN is conventionally divided into layers, the composition of every such layer will differ from the average for the IPN. Hence, conditions for the microphase separation will differ from layer to layer, resulting in differences in morphology and properties. In view of this, Lipatov *et al.* [10] investigated the differences in the properties in the various layers.

Studies were carried out on 0.6 mm thick sections sliced from gradient IPN samples perpendicular to the copolymer concentration gradient. The contents of components in the sections were determined by elementary chemical analysis. The amount of PU in a section was determined by measuring the nitrogen content. Nitrogen is present in the PU chain, but absent in the BMA + TrEGDMA copolymer. For a gradient IPN with an average copolymer mass fraction of 33.6%, the fraction in the first, surface, layer amounted to 39.4%, and in the fourth layer to 26.75%.

Transition temperatures of sections of gradient IPNs have been studied in detail for a series of ordinary IPNs made of the same components, i.e. PU and BMA + TrEGDMA copolymer, with various ratios between the latter [10].

Temperature dependences of the specific volume of ordinary IPNs exhibited transitions in the regions of glass transition temperatures of the two components, which indicated the presence of two-phases. The glass transition temperatures were, however, shifted from those for the pure components due to an incomplete phase separation of the components and the formation of two varying-composition regions [10]. The glass transition temperature shifts regularly with varying IPN composition. In the composition region of 10%–60% copolymer, there occurred a linear increase of the glass transition temperature of one phase and a decrease of that of the other phase.

The data obtained when studying transition temperatures of gradient-IPN sections, sliced perpendicular to the copolymer concentration gradient, are shown in Fig. 2. The specific volume–temperature curves for four successive sections exhibit two transition temperatures, corresponding to the glass transition of the PU and of the BMA + TrEGDMA copolymer in the system. The points beds corresponding to the glass transitions of the components in the layers are shifted along the temperature scale. The glass transition temperature of the PU decreases in the layers in the direction from the surface to the core of the gradient block: in the first, surface, layer it is 264 K; in the second, 262 K; in the third, 259 K; and in the fourth, 256 K. The glass transition temperature of the copolymer also decreases: T_g copolymer in the first, surface, layer is 325.5 K; in the second, 322 K; in the third, 318 K; and in the fourth, 314.5 K. Comparison of these values with glass transition temperatures of the copolymer in IPNs of the given compositions has allowed the content of the BMA + TrEGDMA copolymer in the layers of the gradient IPN to be determined. The resulting copolymer-content profile across the gradient-sample thickness turned out to be close to that determined by elementary analysis of the same system.

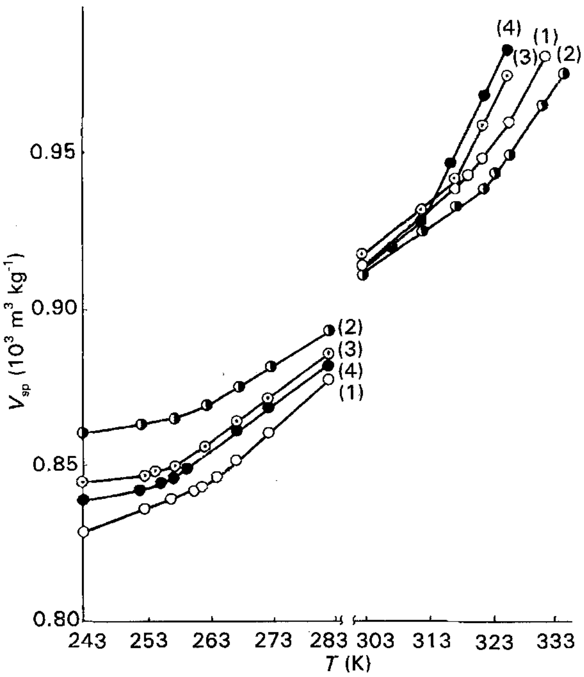

Figure 2 Temperature dependence of specific volume for gradient IPN sections sliced off perpendicular to the BMA + TrEGDMA copolymer concentration gradient. Sections are numbered from surface to core of the gradient system [10].

Lipatov *et al.* [10] also explored sorption properties of gradient-IPN layers and calculated the free energy of mixing of PU and BMA + TrEGDMA copolymer in them. Sorption studies of the PU-copolymer gradient-IPN demonstrated the isotherms of benzene vapour sorption by the PU and the copolymer to be rather close to each other and, therefore, the sorptive capacities of layers of the PU-copolymer IPN differed little as well. Using thermodynamic calculations from experimental data on benzene vapour sorption by gradient-IPN layers, Lipatov *et al.* computed a number of thermodynamic parameters: partial free energies of the solvent and polymeric components; the mean free energy of mixing of individual components and of the gradient IPN with the solvent; and, as a result, the free energy of mixing of PU and the copolymer in gradient-system layers spaced at different distances from the surface and containing different amounts of the copolymer. The calculations demonstrated (Fig. 3) the free energy of mixing of PU and the copolymer to be positive, which indicated a thermodynamic incompatibility between the components of the system under consideration. The free energy of mixing decreased in absolute value towards the centre of the gradient sample, increasing only in the fourth layer, i.e. in the core. The authors ascribed the phenomena to the following factors. When the gradient

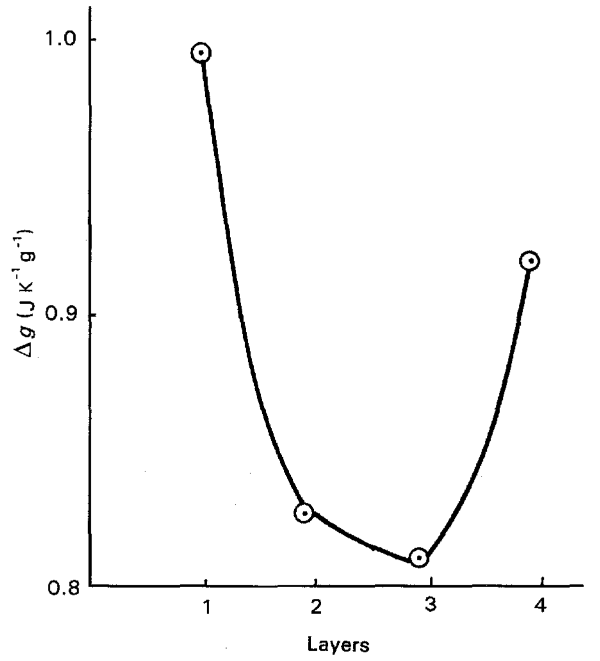

Figure 3 Variation of free energy of mixing of components in gradient-IPN layers [10].

IPN is being formed, the conditions for transition from the one-phase region to the two-phase state vary throughout the sample because the ratio between the host polymer and the monomers forming the guest network at the polymerization varies with the distance from the sample surface. In the course of the polymerization, owing to kinetic reasons, there occurs "freezing" of the non-equilibrium state rather than separation of components into two phases. Non-equilibrium states of the system at different depths from the surface differ from one another because initial conditions for the phase separation have been dissimilar.

The degrees of deviation of the system from the equilibrium state in gradient IPN layers spaced at different distances from the surface is supposed to be dissimilar as well.

Physico-mechanical characteristics of gradient systems were explored in a number of studies [1, 11, 12]. Lipatov *et al.* [12] investigated viscoelastic and mechanical properties of gradient IPNs containing a polyurethane with a gradient of butyl methacrylate–triethyleneglycol dimethacrylate copolymer (PU/grad.(BMA + TrEGDMA)). The host polymer, PU, was swollen in a mixture of BMA and TrEGDMA with polymerization initiators. After that, photopolymerization of monomers was performed.

Lipatov *et al.* [12] also prepared and studied a series of ordinary IPNs from the same components in various ratios, which allowed a comparative analysis of properties. Temperature dependences of viscoelastic functions, E' and tan δ for this IPN series and their individual components PU and BMA + TrEGDMA copolymer, are shown in Fig. 4. As can be seen, in the region of glass transition of the components, the curve for the copolymer (1) exhibits a distinct tan δ maximum at 347 K, while for the PU (2) the tan δ maximum occurs at 238 K. The curves for the IPNs with the large content of copolymer feature a pronounced maximum in the region of the α-transition of the BMA–TrEGDMA copolymer (Fig. 4b, curves 3, 4), and for IPNs with a small content of copolymer, the curves feature low and wide maximum (Fig. 4b, curves 5, 6). In the region of the α-transition of the PU, the curves feature a small maximum or a bulge (depending on the composition) (Fig. 4b, curves 3–6). The shape of the temperature dependences of the elastic modulus (Fig. 4a) is typical for two-phase polymer systems with incompatible components. The elastic modulus drops significantly in the region of the glass transition of each of the components (PU and the copolymer). The investigated systems are two-phase ones, but the shift of the maximum tan δ for the copolymer in the IPN on the temperature scale from its position for pure copolymer, as well as its broadening, indicate an incomplete phase separation in the IPN formation. Lipatov *et al.* noted that the shift of the copolymer's tan δ maximum varied regularly with the IPN composition. The glass transition temperature variation with composition in the range 10%–60% copolymer was linear.

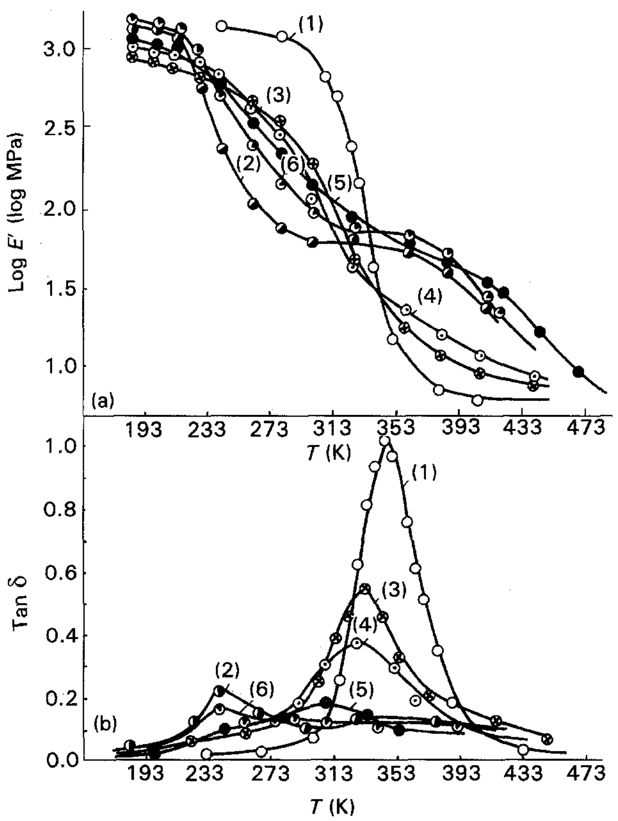

Figure 4 Temperature dependences of (a) elastic modulus and (b) mechanical loss angle tangent for ordinary IPNs and their individual components: (1) BMA + TrEGDMA copolymer; (2) PU; (3) IPN containing (by mass) 54.70%, (4) 47.02%, (5) 33.70%, and (6) 9.00% of copolymer [12].

When studying the PU/grad.(BMA + TrEGDMA) IPNs, Lipatov *et al.* [12] prepared sections sliced from a 5 mm thick sample in two directions: along and perpendicular to the copolymer concentration gradient. Four, approximately 0.6 mm thick sections were cut perpendicular to the successive sections of a gradient IPN containing 33.76% (by mass) the BMA + TrEGDMA copolymer, are shown in Fig. 5.

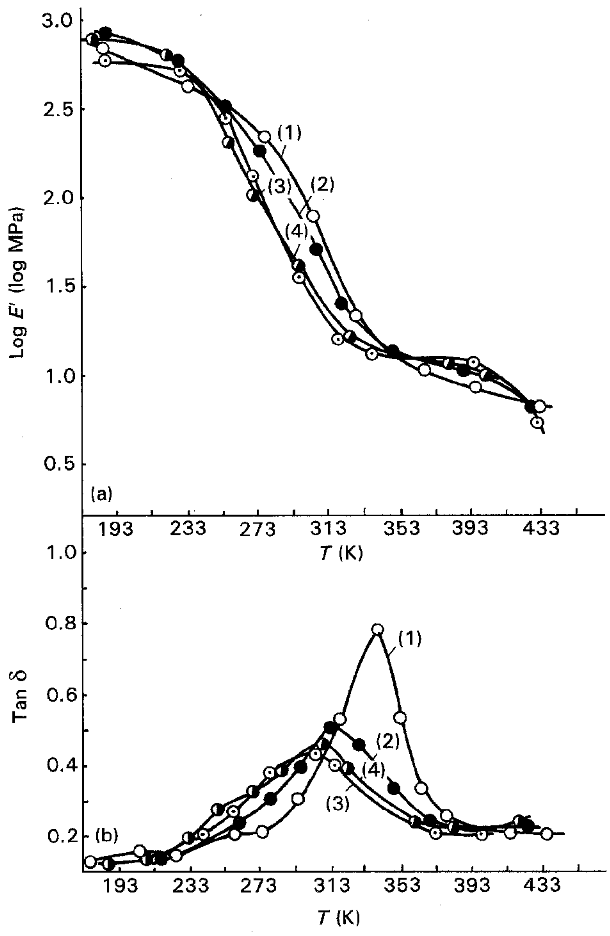

Figure 5 Temperature dependences of (a) elastic modulus and (b) mechanical loss angle tangent in sections of a gradient IPN, sliced perpendicular to the BMA + TrEGDMA copolymer concentration gradient. Sections are numbered from surface to core [12].

The curves of mechanical loss angle tangent for the four layers of the gradient system differ significantly from each other. The curve for the first (i.e. surface) layer exhibits a pronounced narrow peak, characteristic of the copolymer glass transition in the region of 339 K and a transition, characteristic of the PU, in the region of 253 K (Fig. 5b, curve 1). For the second layer, the copolymer's tan δ peak is lower, broader, and shifted towards lower temperatures. For the third and fourth layers the copolymer's tan δ maximum is further shifted towards lower temperatures and the relaxation in the PU glass transition region increases (Fig. 5b, curve 4). The results show that the copolymer is concentrated mainly in the first layer, its concentration in subsequent layers declining progressively. The temperature dependences of the elastic modulus, E', of the same four sections of the gradient IPN (Fig. 5a) indicate that at 293 K, for example, the modulus of the first and fourth sections differ by more than half an order of magnitude, which also indicates a significant difference of copolymer concentration.

Lipatov *et al.* [12] have also examined viscoelastic functions of four gradient IPN sections cut along the BMA + TrEGDMA copolymer concentration gradient. The first section was a full one across the whole gradient. Approximately 0.6 mm thick surface layers were removed from the second section, and an additional 0.6 mm from the third section at both ends. The fourth section was from the core of the gradient sample. The tan δ–temperature dependence curve for the first (full) section exhibited a broad maximum spanning a temperature range from 273–373 K and a small maximum in the region of glass transition of the host PU network. The broad maximum was accounted for by the authors as the result of a superposition of a plurality of maxima, characteristic of layers with different copolymer contents (which is proved by the results of studying the IPN series with various host-to-guest polymer ratios, Fig. 4). Changing the composition also changed the copolymer's tan δ maximum position on the temperature scale. It follows that it is the superposition of the copolymer's tan δ maxima from different-composition layers that brought about the broad maximum of the tan δ versus temperature curve.

As the outer layers, containing the greatest amount of the BMA + TrEGDMA copolymer, were removed, the tan δ maximum decreased and shifted towards lower temperatures. On the tan δ curve for the third section, where layers with a high content of the copolymer were absent, the broad maximum became still lower and shifted by a further 15 K towards lower temperatures, while the relaxation in the PU glass transition region rose.

For the fourth section, the core of the gradient sample, the PU's tan δ maximum and the broad maximum of transitions of the copolymer in layers merged into a broad plateau in the temperature range 233–313 K. Lipatov *et al.* [12] emphasized that the broad maximum of mechanical losses for the PU/grad.(BMA + TrEGDMA) IPN are not a consequence of the compatibility of the IPN components, but a result of superposition of a great number of relaxation maxima in layers with progressively varying compositions. This opens up broad possibilities for manufacture by this method of promising noise- and vibration-damping materials.

Studying mechanical characteristics of gradient IPNs based on PU and BMA + TrEGDMA copolymer [12] demonstrated their tensile strength to be much higher than that of ordinary IPNs and of the individual component networks; the area under the stress–strain curve, determining the work of fracture, is greater for a gradient IPN. The slope of the initial part of the curve, characterizing the Young's modulus, for a gradient IPN is greater than for an ordinary IPN as well as for a polyurethane.

Akovali *et al.* [1] investigated the mechanical properties of gradient IPNs (PMMA/grad.MA), of ordinary IPNs and of a random copolymer of the same overall composition to compare the results. They obtained stress–strain curves for temperatures of 353, 363 and 373 K and demonstrated that at 373 K pure PMMA fractures at a tensile strain of about 2%; a gradient IPN containing 10.3% methyl acrylate, at a strain above 10%; and a gradient IPN with 19% MA, at a strain of almost 80%. Comparison of their data for an ordinary IPN, a gradient IPN, and a copolymer of the same overall composition, demonstrated that the gradient IPN featured the highest rupture stress and the largest area under the

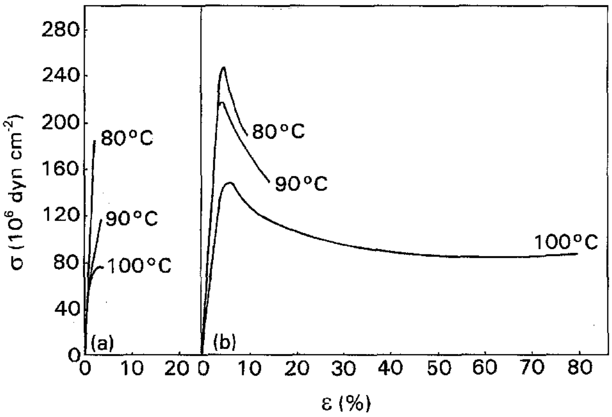

Figure 6 Stress–strain curves for (a) ordinary and (b) gradient IPNs at various temperatures. Total methyl acrylate content in PMMA is 20% in both samples [1].

stress–strain curve. The stress–strain curves from [1] are shown in Fig. 6. As can be seen, the impact strength of gradient IPNs is much higher than that of ordinary IPNs.

Lipatov *et al.* [11] have modelled mechanical relaxation properties of a complex composite material with gradients of composition and properties. There exists no procedure for calculating the glass transition temperature and temperature dependences of viscoelastic function of materials for an infinite number of layers, and therefore models with the number of layers increasing from 2–11 were studied successively in comparison with calculation results. The data indicate that as the number of layers is increased, curves of viscoelastic functions tend rather rapidly to a limit, and when the number of layers is more than 10, its further increase exerts practically no effect on the character and position of the curves. Lipatov *et al.* [11] therefore decided on a gradient composite material model consisting of 11 layers each differing from the preceding one in the glass transition temperature by a definite number of degrees. Three gradient versions were calculated, namely a 2, 5 and 7 K change per layer, with the total number of layers and their thickness unchanged.

The calculated temperature dependences of the real part of the complex shear modulus and of tan δ of the gradient polymeric material models are shown in Fig. 7. Calculations were based on the assumption that deformation of the layers occurs perpendicular to the gradient direction. The existence of a glass transition temperature gradient in the composite material results in a characteristic form of lg G' versus temperature curves, which have a broader transition region as the gradient becomes higher. As the glass transition temperature gradient increases, the heights of the maxima of tan δ decrease and shift by 8–10 K towards lower temperatures and broaden in the same direction. For the deformation in the direction of the gradient (i.e. successive deformation of layers) the character of temperature dependences of lg G' and tan δ was primarily determined by the components having a low glass transition temperature. The maxima of tan δ of the gradient materials shifted by 5–7 K towards higher temperatures with respect to the maximum of tan δ of the "lowest-temperature" component, but did not change significantly in height. Lipatov *et al.* [11] emphasize that a gradient structure of a composite polymeric material should bring about an extension of the temperature range of a transition of such a material and the extension can be the greater, the higher is the composition gradient. Another important feature of gradient composite materials, shown by calculations, is anisotropy of properties, especially pronounced in limiting cases, i.e. where the direction of deformation is parallel or perpendicular to the direction of gradient.

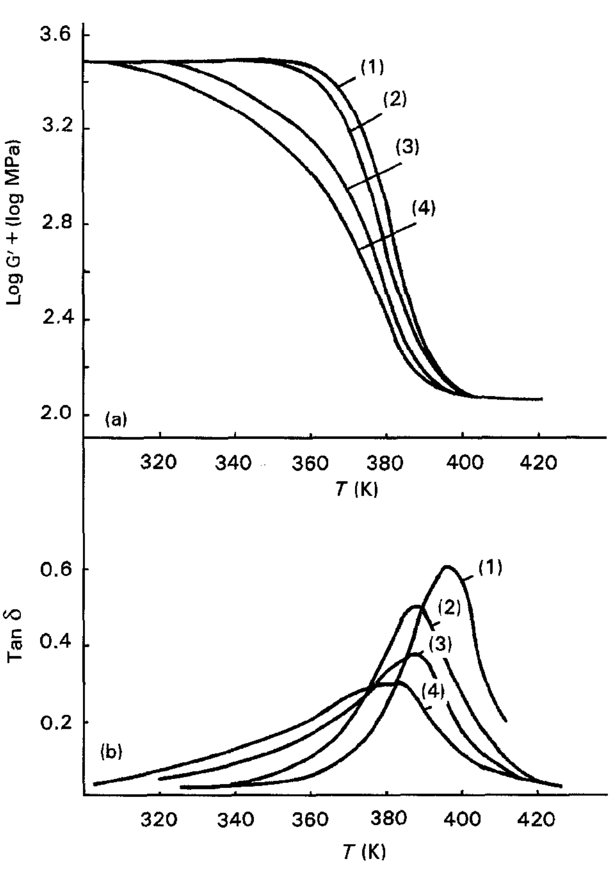

Figure 7 Calculated temperature dependences of (a) log G' and (b) tan δ for a gradient model with number of layers $n = 11$ and various T_g gradients: layer with highest T_g (1); ΔT_g/layer = 2 K (2), 5 K (3), and 7 K (4), for the parallel deformation of layers [11].

Martin *et al.* [9] investigated mechanical properties of gradient systems formed from PMMA and poly(2-chloroethyl acrylate) (PClEA) in two "reciprocal" versions. The first one had the host polymer of hard PMMA, which was subjected to a non-equilibrium swelling in 2-chloroethyl acrylate that was then photopolymerized. The second version was prepared by synthesizing PClEA, swelling it in MMA, and then polymerizing the latter. The resulting gradient compositions contained up to 30% PClEA in a PMMA matrix and up to 50% PMMA in a PClEA matrix. To determine the gradient profile of the guest component, the authors carried out chemical analysis of the chlorine concentration across the thickness of samples; the gradient profiles are shown in Fig. 8. For the first series, with a PMMA matrix, the PClEA content dropped steeply with distance from the surface, especially at the lowest PClEA content, where a major amount of PClEA concentrated at the very surface (Fig. 8, curve 1). For samples of the second series, with

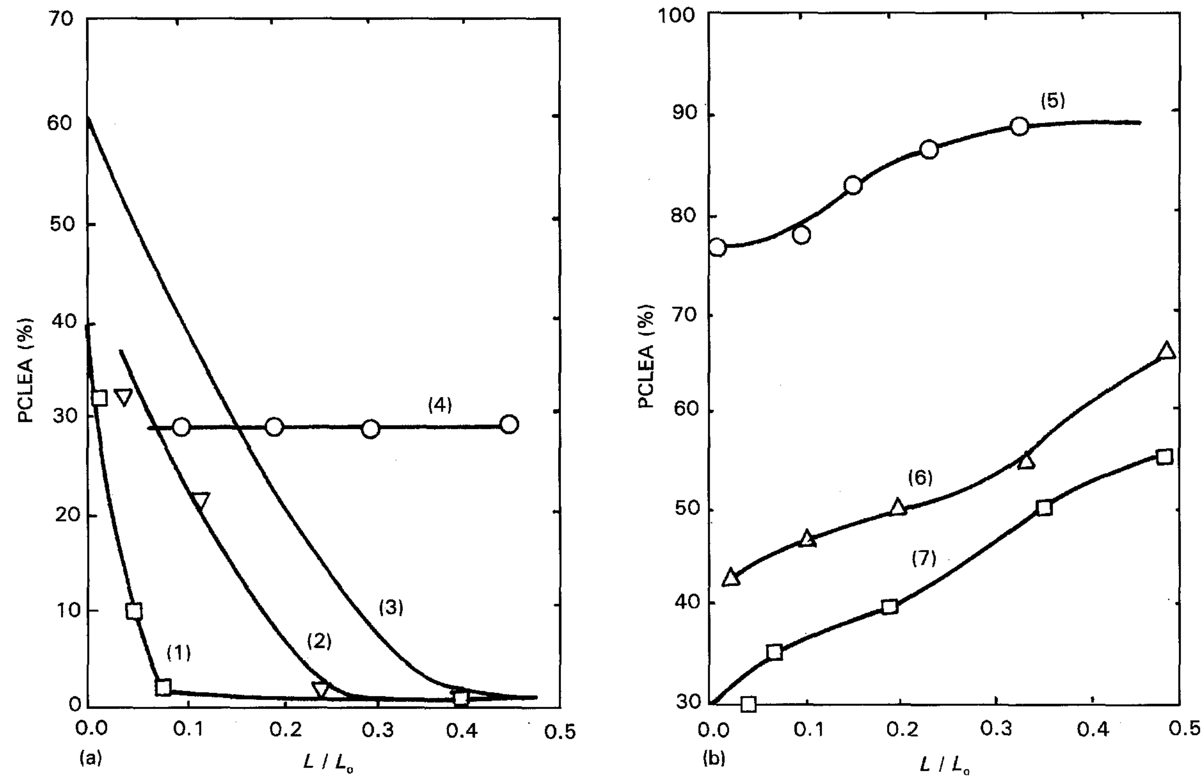

Figure 8 PClEA gradient profiles in gradient IPNs with (a) PMMA and (b) PClEA matrices at various contents of components (by mass): PClEA (1) 10%, (2) 20%, (3) 30%; (4) ordinary IPN, 30% PClEA; (5) PMMA: 10%; (6) 30%; (7) 50%. L/L_0 = reduced sample thickness [9].

a PClEA matrix, the PMMA content decrease with depth into the sample was not so steep.

When exploring viscoelastic functions, Martin *et al.* [9] found two glass transition temperatures in the dynamic loss modulus curves for the first (PMMA-matrix) series of gradient IPNs, at 263 K for PClEA and at 383 K for PMMA, which indicated the phase separation and incompatibility of the IPN components. In contrast, the gradient IPN with an elastic PClEA matrix exhibited a single transition, disposed between the glass transition temperatures of the components; with increasing PMMA fraction, the temperature shifted and at 50% PMMA was 323 K. As claimed [9], this fact evinced no phase separation in the second series of gradient IPNs. However, viewing the results of the detailed layer-by-layer investigation of viscoelastic properties by Lipatov *et al.* [12], it can be supposed that the single maximum is not the result of compatibility, as for the PU/grad.(BMA + TrEGDMA) system. Superposition of the ranges of the glass transition in layers with different PMMA contents could occur, resulting in a single broad maximum between the glass transition temperatures of the pure components.

Mechanical tests [9] demonstrated that gradient IPNs offer a higher fracture energy than homopolymers and ordinary IPNs. The rupture strain for a gradient IPN with a PMMA matrix and 30% PClEA was an order of magnitude higher than for pure PMMA (Fig. 9) and the strength of a gradient IPN with a PClEA matrix and 50% PMMA turned out to exceed 10–15 times that of the initial PClEA.

Thus, as shown, creating a gradient structure in a polymeric material can markedly improve its mechanical properties. Martin *et al.* [9] as well as Akovali *et al.* [1] put forward a number of hypotheses to account for this phenomenon. One of them treats gradient IPNs as collections of an infinite number of layers whose compositions and elastic moduli change progressively. When a sample is strained, all layers are stretched to one and the same degree, and the stress in every layer corresponds to its modulus. Such a stress distribution promotes plastic deformation rather than brittle fracture and thereby increases breaking elongation and fracture energy.

Another hypothesis relates the higher strength of gradient IPNs to a reduction of imperfections in surface layers. In gradient IPNs with a PMMA matrix [9], a high elastomer concentration in the surface layer prevents craze and crack initiation. This hypothesis is favoured by morphological studies of the fracture surface, which clearly indicate differences between the outer and inner layers of gradient IPNs [9]. Inner regions generally feature distinct characteristic parabolas, traces of the propagation of secondary fracture cracks initiating at imperfections. Subsurface layers turned out to be smoother, i.e. the extension of fracture cracks in them is inhibited.

All the above-described advantages in the mechanical properties of gradient systems over ordinary IPNs and initial matrices have been attained with the use of components sharply differing in properties, thus creating a hard gradient in a soft matrix or, conversely, a soft gradient in a hard matrix. By contrast, gradient IPNs containing a hard gradient in a hard matrix exhibit no substantial gain in mechanical properties. Thus, Akovali and Labban [13] investigated gradient IPNs with a hard gradient in a hard matrix

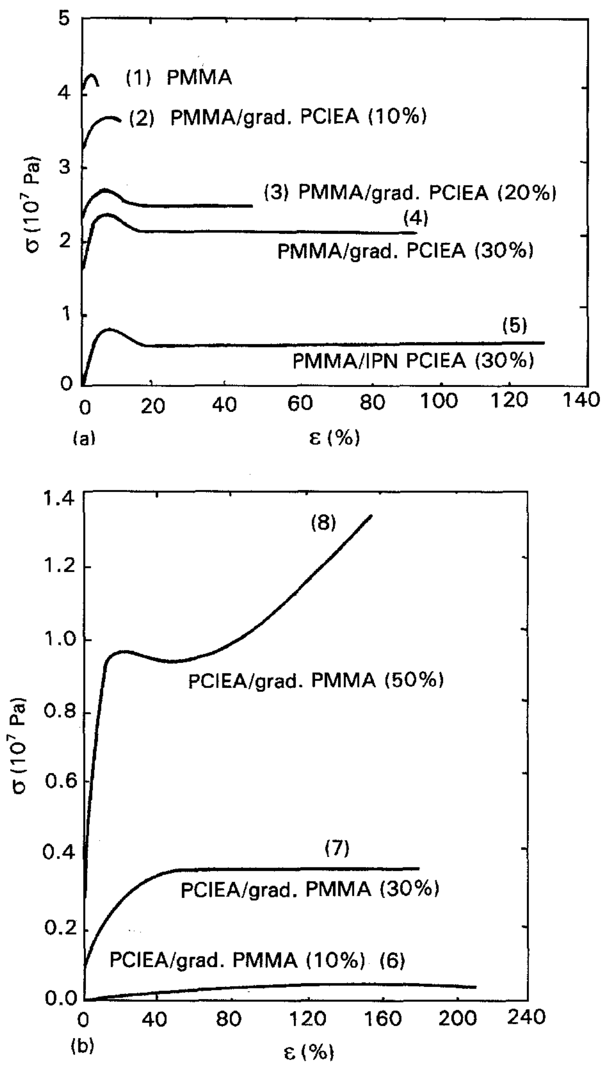

Figure 9 Stress–strain curves for: (a) PMMA (1); gradient IPNs (2–4) and ordinary IPN (5) with PMMA matrix, containing (2) 10, (3) 20, and (4, 5) 30 mass% PCIEA; (b) gradient IPNs with PCIEA matrix, containing (6) 10, (7) 30, and (8) 50 mass% PMMA. Strain rate = 0.042 s^{-1}; temperature = 60 °C [9].

(PMMA/grad.PAN and PMMA/grad.PS). Having measured stress–strain curves and determined other mechanical characteristics, they demonstrated that for gradient IPNs only dynamic loss moduli are higher, whereas in other mechanical properties, gradient IPNs, as well as ordinary IPNs, exhibit no significant advantages over the initial matrix.

4. Practical applications of gradient IPN-based materials

Gradient IPN-based materials can find applications in diverse fields. Sperling and Thomas [2] prepared gradient IPNs with the aim of creating hard outer and soft inner zones interposed with intermediate layers with a progressively varying composition for use as noise- and vibration-dampening materials.

Berry *et al.* [14, 15] produced a series of physico/chemical IPNs, based on a block copolymer of poly (ether urethane) with urea and acrylamide, 2-oxyethyl methacrylate, or *N*-vinyl-2-pyrrolidone. The materials, capable of forming high-strength water-absorbing hydrogel surfaces and offering a good compatibility with blood, have been used for biomedical purposes.

Predecki [16], by swelling silicone rubber in oxyethyl methacrylate, obtained materials with a hydratable surface, which can be used as protective coatings in arteriovenous shunts.

Lipatov *et al.* [17] demonstrated the attractiveness of gradient IPNs for upgrading physico-mechanical properties of synthetic fibres and organoplastics based on them. They swelled polyamide fibres for different times in an alcoholic solution of phenolformaldehyde oligomer, containing a curing agent, after which the oligomer was polymerized in the fibre matrix. As a result, a gradient IPN whose host polymer was polyamide, and phenolformaldehyde resin, distributed with a gradient, was formed in the surface layer of the fibre. Physico-chemical studies indicated that the modified fibres are better wetted by phenolic binder solutions and their thermal stability is upgraded; the initial temperature of destruction rises by 30 K, and the mass loss within the range 373–473 K is twice as low as for the initial fibres. The strength of the fibres is also improved. The strength of the fibre varies non-monotonically with the content of polymerized phenolformaldehyde oligomer in the surface layers, with two maxima in the regions of 4 and 22 mass%.

Using the modified fibres, Lipatov *et al.* [17] prepared organophenolic plastics and conducted comparative physico-mechanical tests. The breaking compressive stresses for plastics prepared from fibres with gradient IPNs turned out to be 50% higher than for those prepared from unmodified fibres.

Gradients of various types, such as linear, sigmoidal, and parabolic, can be created depending on the application of the gradient material. Creation of such gradients involves problems associated with the influence of various factors on the rate of diffusion into the host polymer network, distribution of the diffusate according to the required pattern, and fixation of the produced distribution.

The gradient-IPN method has been applied successfully to produce gradans, or optical gradient elements [18–22], employed in optoelectronics, integrated optics, and medical engineering. Gradans find application in optoelectronic and integrated optic devices, in medical engineering.

The processes of preparation of optical gradient elements, or gradans, were examined in detail elsewhere [18–22].

Gradans are produced using styrene–ethyleneglycol dimethacrylate copolymers or diallyl isophthalate as the matrix and methyl methacrylate as the guest component [20–22].

Gradans are most often produced in the form of cylindrical rods with radial profiles of composition which ensure parabolic decreases of refractive index from the axis to the surface. The best method for producing polymeric gradans [18, 19] involves three stages. The first stage consists of preparing a prepolymer matrix in the form of a cylindrical rod from a bifunctional monomer having a high refractive index, *n*, which, owing to formation of a cross-linked structure, is capable of retaining the shape imparted to it at a low degree of polymerization. In the second stage, the prepolymeric rod, containing up to 80% monomer, is immersed in a bath of another monomer, having a lower refractive index. A diffusion exchange of the matrix and diffusate monomers takes place, which is interrupted as a parabolic profile of the composition is established. The third stage consists of the copolymerization of the monomers in the prepolymer network. When a compatible pair has been selected, then a transparent light-focusing element, which is a gradient IPN, is formed.

The optimum optical characteristics are exhibited by gradient lenses where the refractive-index profile is described by the equation

$$n(r) = n_0 \mathrm{sech}(\alpha r) \approx n_0(1 - \alpha^2 r^2/2) \qquad (1)$$

where n_0 is the refractive index along the lens axis, r the gradan radius, and α the profile constant.

Producing in a gradan, an index refraction, n_D, profile close to Equation 1 is governed by a number of competing, concurrent physico-chemical and chemical processes; copolymerization, polymerization, mutual diffusion, and cross-linking, which makes the production exceedingly complicated and hard-to-control. Because of this, Krivchenko *et al.* [22] combined an experimental study of the refractive index profile in gradans with a computer experiment based on the developed mathematical model of the refractive-index profile formation process. The model is a set of equations, the first of which has been derived from Fick's law, allowing that diffusion proceeds in an inhomogeneous medium and the concentration of diffusing particles decreases due to polymerization. The second and third equations describe the build-up of cross-linked polymer because of polymerization of the components. The fourth equation serves as the basis for conversion from the concentration profile to the refractive-index profile. Based on the modelling of formation of the refractive-index profile across a section, the authors succeeded in selecting the optimum gradan manufacturing conditions.

A very difficult problem is to fix the created parabolic profile of the diffusate. Thermal fixation unavoidably leads to transformations of the produced profile because copolymerization does not occur instantaneously; the mutual diffusion of monomers in the matrix continues, but now under changed boundary conditions. These processes have been studied in detail by Krivchenko *et al.* [20, 22].

One way for preventing the undesirable transformation of the composition profile across a section is to select systems which exhibit a steeply increasing polymerization rate once a certain conversion has been reached. This property, called the gel effect of a polymerization, is featured by a number of vinyl monomers in radical polymerizations in bulk. The gel effect was successfully used [19, 20] in making gradans based on styrene, ethyleneglycol dimethacrylate, and methyl methacrylate as well as diallyl isophthalate and methyl methacrylate.

Krivchenko *et al.* [20] have determined the resulting refractive-index profile in prepared gradient elements using thin sections and a Mach-Zehnder interferometer. Profiles of the refractive indices of gradans for various guest component diffusion times are shown in Fig. 10. A parabolic profile, which provides light-focusing properties, is generally retained only over a part of the radius, amounting to 0.5–0.8 of the full radius of a sample.

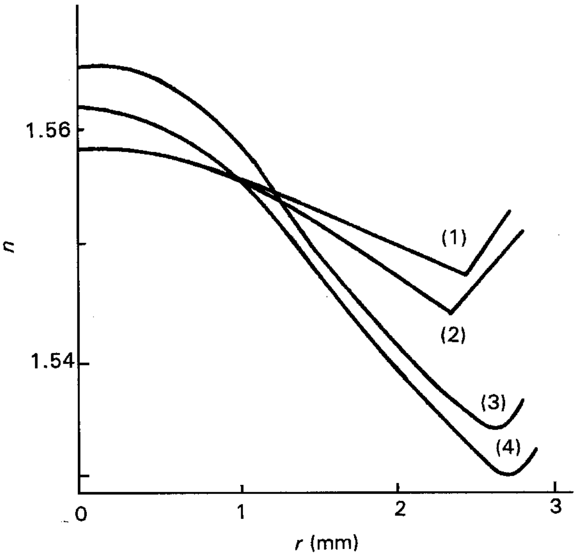

Figure 10 Refractive index profiles for four samples of diallyl isophthalate–methyl methacrylate gradans for diffusion times of (1) 9, (2) 11, (3) 13, and (4) 15 min [19].

5. Conclusion

The present review shows gradient IPN-based materials to be undoubtedly promising and be of great practical interest.

Gradient IPNs should be looked upon as systems with two heterogeneity levels, the first one being due to the existence of a composition gradient (macroheterogeneity), and the second to microphase separation in the course of formation of the systems (microheterogeneity). It is obvious that in gradient IPNs, where the composition of every conventionally defined layer differs from the average one, the microphase separation conditions will differ from layer to layer, resulting in varying morphology and properties. The microphase separation in gradient IPNs at various depths in samples is substantially different. As a result, properties of gradient IPNs will be determined not only by the existence of the intrinsic composition gradient, but also by the separation into microphases, which creates heterogeneity, produces various morphologies, and hence determines the physical properties.

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