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Gradient interpenetrating polymer networks: formation and properties

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Abstracts. The methods of preparation and physicochemical and mechanical properties of gradient interpenetrating polymer networks (IPN) are examined. The results of studies on the viscoelastic properties as well as the strength and other mechanical characteristics in layers of gradient IPN are presented. The properties of the usual and gradient IPN of the same chemical nature are compared. Data are presented on the layer-by-layer variation of the thermodynamic compatibility of the components in gradient IPN. The bibliography includes 64 references.

I. Introduction

One aspect of the chemistry of macromolecular compounds which is of current interest is the modification of finished polymers and preparation of materials based on them. From this standpoint, the study of mixtures and blends of linear polymers (interpenetrating polymer networks) is promising, since one can vary indefinitely the structures and properties of polymeric materials obtained on the basis of such systems. Interpenetrating polymer networks (IPN) are polymer–polymer compositions consisting of two or more three-dimensional polymers (or of network and linear polymers) in which the individual networks are not chemically linked but are indistinguishable owing to the mechanical intertwining of the chains determined by the conditions of the synthesis.

Interpenetrating polymer networks are obtained by modifying polymers with a three-dimensional structure. Since the appearance of the term 'interpenetrating polymer network'[1] much time has elapsed, but the principal studies in this field began in the 1980s[13–17] and have continued up to the present time.

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There are two monographs and several review articles[2–12] in which the methods of preparation, the nomenclature, and the structure and properties of IPN of different types are considered. Analysis of the literature shows that gradient IPN are some of the most interesting and promising polymers. Sperling,[4] Sergeeva and Lipatov,[10] and Sergeeva[11] have considered gradient IPN very briefly.

Gradient IPN are mixtures of three-dimensional polymers (or mixtures of a three-dimensional and a linear polymer), the concentrations of the components in which vary along the cross-section of the specimen. Gradient IPN constitute the basis for the synthesis of promising polymeric materials used, for example, in medicine, optoelectronics, wave optics, and instrument making, for vibration- and sound-proofing, and in other fields. The volume characteristics of polymeric materials based on IPN may remain unchanged. However, the overall characteristics of the composite are improved.

II. Methods of preparation and layer-by-layer analysis of the compositions of gradient interpenetrating polymer networks

The first studies involving the preparation and investigation of gradient IPN were associated with the search for and development of materials for medicine.[13–17] The interpenetrating polymer networks used for such purposes can be obtained only by the successive hardening method. This method consists of the following procedures: in the first stage, the preformed polymer (the first component) is kept in a monomer, which subsequently polymerises with formation of a second polymer. Swelling is interrupted at a certain stage, before the attainment of equilibrium, after which the second polymer is obtained, its concentration in the matrix polymer varying perpendicular to the surface as a consequence of the slowness of the swelling and diffusion processes in the matrix network. This results in the formation of an IPN, the properties of which differ both from those of the individual polymers and from the properties of the IPN of the same chemical nature but obtained by the successive hardening method under equilibrium conditions.

Since in the preparation of gradient IPN there is a stage involving the nonequilibrium swelling of the matrix network in the monomers, problems arise, associated with the influence of various factors on the rate of diffusion of the monomers into the matrix network and hence with the distribution of the second

polymer through the thickness of the matrix. In order to investigate the nature of the distribution of the polymers entering into the composition of the IPN as a function of thickness, use is made as a rule of the layer-by-layer elemental analysis. In the gradient IPN based on polystyrene (PS) and polyacrylonitrile (PAN) (with ethylene dimethacrylate as the cross-linking agent),[13] PS served as the matrix network and PAN was concentrated in the surface layer of PS with a definite concentration gradient. In order to establish the nature of the distribution of PAN in PS, layers 0.05 mm thick were removed and their nitrogen content assayed chemically. It was shown that the highest content of PAN ($\sim 50\%$) occurs near the surface of the specimen of the gradient IPN. The concentration of PAN near the surface is also confirmed by the finding that the specimens of the test IPN are more resistant to the action of hydrocarbons, for example benzene, in contrast to pure PS.[13] It has been suggested that the diffusion of the monomer into the matrix network in the test specimen generally obeys Fick's law, although there are certain deviations.[14] For systems such as poly(methyl methacrylate)–polymethacrylate, the layer-by-layer methods of chemical analysis proved unsuitable, since both polymers contain the same elements.

The rate of diffusion of the monomers during the preparation of gradient IPN and the subsequent distribution of the polymers probably depend on the monomer concentration in the solvent (if such is used), on the concentration of the cross-linking agent, and other factors. These problems have been examined in detail in a study of the gradient IPN based on polyester urethanes (PU) and cross-linked polyacrylamide (PAA).[15] The polyester urethanes were obtained by a two-stage method from diphenylmethane diisocyanate and poly(propylene glycol) using diaminoethane as the lengthening agent. The polyester urethane contained rigid domains — physical cross-links forming a network. The IPN specimens were obtained by swelling PU plates in a solution containing acrylamide (AA), a cross-linking agent (tetraethylene glycol dimethacrylate), and an initiator. This was followed by the polymerisation of the AA. The overall amount of the PAA was determined from the difference between the masses of the initial PU film and that obtained after its saturation by the PAA. It has been shown for this system that an increase in the monomer concentration in the swelling mixture leads to a steady increase in the PAA concentration in the IPN, although the dependence of its content on the AA concentration in solution is nonlinear. Naturally, an increase in the PAA content in the IPN leads subsequently to an increase in the degree of swelling of the specimen in water. An increase in the initiator concentration in the AA solution also leads to an increase in the PAA content in the IPN, but only up to a certain limit, beyond which the influence of the initiator concentration is insignificant. The change in the concentration of the cross-linking agent influences non-monotonically the PAA content in the IPN: there is an optimum concentration ensuring the maximum PAA content, but the capacity of the IPN for swelling in water decreases monotonically under these conditions.

The concentration of the monomer and its distribution in the matrix network are naturally to a large extent determined by the duration of the swelling of the initial network in the monomer. Thus, the influence of the swelling time (from 5 to 30 min) on the PAA content in the IPN has been investigated for the PU–PAA system.[16]

It has been established that the dependence of the fraction of PAA in the IPN ($\omega = W_{PAA}/W_{IPN}$) on the swelling time is described by the equation

$$\omega_t = \omega_\infty(1 - e^{-kt}),$$

where ω_t and ω_∞ are respectively the fractions of PAA in the IPN during polymerisation after swelling for a time t and after equilibrium swelling.

Apart from varying the swelling time, other procedures may be used to set up a concentration gradient along the thickness of the IPN layer, for example one can employ cross-linking agents with a higher molecular mass or the diffusion of the cross-linking agent.[16] The latter method can be described as follows: the matrix network is kept in the monomer solution with the initiator until the attainment of equilibrium, after which the swollen matrix network is placed for a time in a solution of the cross-linking agent. It was found that, when this procedure is employed, the fraction of PAA in the IPN based on PU and PAA is independent of the time during which the swollen PU is kept in the solution of the cross-linking agent.

The Fourier transform IR spectroscopic method[16] makes it possible to obtain more accurate information about the nature of the distribution of polymers in gradient IPN based on PU and PAA compared with chemical analysis.[14,15] It has been established[16] that, when the partial swelling method is employed (the method involving different exposure times), PAA concentrates mainly at the surface of the specimen (the depth of penetration by PAA does not exceed 10 μm). The PAA concentration gradient along the thickness has also been observed in the preparation of IPN after the attainment of the equilibrium swelling of the matrix network in the monomer, but it is not quite so distinct as in the previous case. Finally, the diffusion of the cross-linking agent and the variation of its molecular mass have virtually the same influence on the PAA concentration gradient in PU.

Like the usual IPN, 'direct' and 'reverse' gradient IPN may be synthesised. The system based on poly(methyl methacrylate) (PMMA) and poly(chloroethyl acrylate) (PCEA) have been obtained in two ways.[17] In the first case, the PMMA obtained beforehand was swollen in chloroethyl acrylate (CEA) and the CEA was then polymerised. The initiator was fluorobutyl ether from petrol and the cross-linking agent was ethylene glycol dimethacrylate. In the second case, PCEA was swollen in methyl methacrylate (MMA) and the latter was subsequently polymerised. Gradient IPN containing 30 mass % of PCA in a PMMA matrix and up to 50 mass % of PMMA in a PCEA matrix were obtained in this way. In order to determine the profile of the concentration gradient (in the present instance of chlorine) in the test system, chemical analysis was employed, as in certain other gradient IPN.

Fig. 1 presents the gradient in the distribution of PCEA in specimens obtained by the first method. Evidently the PCEA content decreases sharply on moving away from the surface, particularly when its concentration in the gradient IPN is low whereupon the main bulk of PCEA concentrates at the surface of the specimen.

It is noteworthy that in the usual IPN (Fig. 1, curve *4*) i.e. those obtained by the successive hardening method under the conditions of the equilibrium swelling of the matrix network in the monomer, the PCEA concentration does not change on moving away from the surface of the specimen. This conflicts with data obtained for the PU–PAA system,[14] where a concentration gradient with respect to the thickness was established even for the usual IPN. It is most likely that this may be induced by the time during which the PU specimens are kept in PAA, before the start of the polymerisation, being insufficient.

For specimens of the second series, the PMMA content does not diminish quite so sharply (judging from the growth in the PCEA content with increasing thickness) on moving away from the specimen surface.

Gradient IPN based on PU and polyacrylate copolymers have been obtained[18,19] by a method involving the swelling of a preformed network PU without attaining the equilibrium distribution of the diffusants and subsequent photopolymerisation of the reactants. The composition of the components in the layers was determined by comparing the glass points (T_g) of the

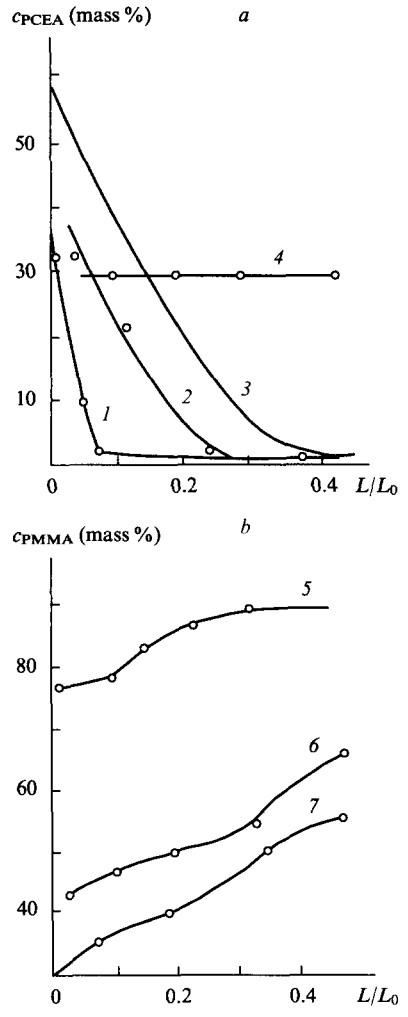


Figure 1. Distribution of PCEA and PMMA in specimens of gradient polymers (*1–3*) and IPN (*4–7*) with a PMMA matrix (*a*) and a PCEA matrix (*b*) for different PCEA and PMMA contents.
c_{PCEA} (mass %): (*1*) 10; (*2*) 20; (*3*) and (*4*) 30; c_{PMMA} (mass %): (*5*) 10; (*6*) 30; (*7*) 50; L/L_0 = relative thickness of the specimen.

usual IPN and gradient IPN of the same nature and also by elemental analysis.[20–33]

Free-radical initiation was used in the studies described above to obtain the second polymer with a concentration gradient in the first polymer-matrix. The use of polycondensation appears at first sight impractical, since the reaction can occur during the swelling process. After the attainment of equilibrium, the reactants must then be present in the matrix in almost equivalent proportions for the formation of a high-molecular-mass condensation polymer. Nevertheless, it has been shown [34] that polycondensation can be used extremely successfully for the preparation of gradient IPN. For this purpose, one of the reactants is initially kept in the preformed polymer-matrix and the matrix is then placed in the second reactant or its solution. Diffusion and the polycondensation reaction between the reactants take place simultaneously under these conditions. Such a process may be referred to as diffusion-controlled polycondensation occurring in the matrix in the mixing zone of the two components.

A gradient IPN, the matrix of which consisted of the 2-hydroxyethyl methacrylate–*N*-vinylpyrrolidone copolymer while the polymer with a concentration gradient was polyurethane based on a diol or a triol and 1,6-diisocyanato-2,4,4(2,2,4)-trimethylhexane, was obtained in this way.

III. Thermodynamic compatibility of the components in layers of gradient interpenetrating polymer networks

At a certain stage during the formation of the IPN, a microphase separation of the components begins as a consequence of thermodynamic incompatibility caused by the formation of heterogeneous three-dimensional structures.[3,20–22] The phase separation conditions are determined both by the composition of the IPN and by the rate of formation of the two networks. Apparently, the separation in each layer of the gradient IPN occurs to different extents, since the component ratio undergoes continuous layer-by-layer variation. It is noteworthy that the microphase separation is not completed in the IPN formed, which results in the formation of nonequilibrium 'frozen structures', which are nevertheless kinetically stable.[3,10]

The thermodynamic parameters which make it possible to infer the compatibility of the components in layers at different distances from the surface of the specimens have been estimated [23] in relation to the gradient IPN based on polyurethane and cross-linked poly(butyl methacrylate). The changes in the free energy of mixing of the network components Δg_x were estimated by analysing the isotherms for the sorption of benzene vapour by the IPN specimens. Fig. 2 presents the variation of Δg_x in IPN layers on moving away from the specimen surface (from the first to the fourth layer). Evidently, Δg_x is positive, so that the components are incompatible, as in the majority of the usual IPN.[3,24,31–36] The absolute value of Δg_x depends on the depth of the layer in the specimen. This fact is due not only to changes in the composition of the networks as the core of the specimen is approached but also to changes in the phase separation conditions in each layer of the IPN produced.

The different degrees of compatibility of the components in the IPN layers influence the structure formed and at the same time the properties of the component as a whole. Each layer in a gradient IPN can be regarded as an independent two-phase IPN with a different phase composition.[23] By considering each phase arising during the incomplete phase separation as an independent quasi-equilibrium IPN,[24] the authors [23] estimated the compositions and ratio for these phases. For this purpose, they used Fox's equation,[25] proposed for compatible polymer blends, and the glass points obtained by the dilatometric method both for the individual networks and for the networks in the layers of the gradient IPN. In the gradient IPN based on polyurethane, T_g refers to one of the phases enriched in PU or the copolymer. The volume fractions of PU in the PU-enriched phase and of the copolymer in the copolymer-enriched phase were calculated from the corresponding glass points in the IPN and in the layers of the gradient IPN.

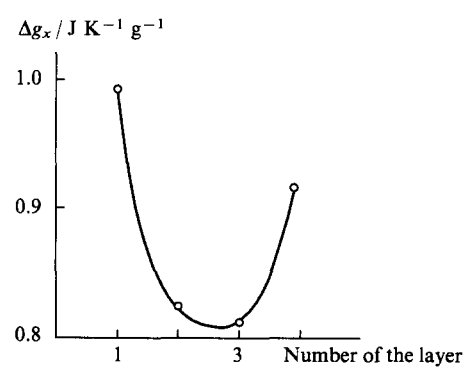


Figure 2. Variation of the free energy of mixing of the components in the layers of gradient IPN.

Analysis of the data obtained led to the conclusion that, as a consequence of the incomplete separation, two phases are formed in the layers of the gradient IPN, the composition of which depends on the phase separation conditions in each layer. As a result of the variation of the composition (and hence of the thermodynamic compatibility of both networks), the degree of segregation in each layer is different from that for the usual IPN having the same composition.[23]

Thus gradient IPN are multicomponent systems, the properties of which are determined by the presence not only of the composition gradient but also of the phase composition gradient and the phase ratio in the microphase systems.

IV. Relaxation properties and transition temperatures

A considerable proportion of the studies on gradient IPN have been devoted to dynamic mechanical properties. Information about the transition temperatures and the compatibility of the components in the test systems can be obtained from these data. Thus two transition temperatures have been observed for the IPN based on PMMA and PCEA (PMMA matrix)[17] in a study of the temperature dependence of the modulus of dynamic losses: one at 263 K, corresponding to PCEA, and the other at 383 K, corresponding to PMMA. This indicates unambiguously the occurrence of phase separation and the incompatibility of the components in the IPN.

However, a single transition in the region between the glass points T_g of the corresponding homopolymers has been observed for the same IPN but with a PCEA matrix. The transition temperature shifts to 323 K at a PMMA concentration up to 50%, which constitutes evidence, according to Martin et al.,[17] in favour of the absence of phase separation. As will be shown below, the latter conclusion is hardly legitimate.

The mechanical relaxation properties of a polymer with a composition gradient have been modelled for a qualitative estimation of the influence of the change in composition on the viscoelastic properties of a polymeric specimen with a glass point gradient.[26] A system consisting of eleven plates, differing in the glass points by a known number of degrees determined by the gradient, was adopted as the model gradient material for this purpose.

Fig. 3 presents the calculated temperature variations of the real component of the complex modulus of shear ($\lg G'$) of the model gradient material, the layers of the material being deformed in parallel. The presence of a glass point gradient leads to the appearance of characteristic temperature variations, which are less steep the higher the gradient. At the same time, with increase in the temperature gradient, the height of the maximum of the tangent of the angle of mechanical losses ($\tan\delta$) decreases, becomes broader, and shifts by 8–10° into the low-temperature region compared with the position of the $\tan\delta$ maximum corresponding to a high glass point. It was also established that, in the formation of the specimen in the direction coinciding with the direction of the gradient (i.e. for the consecutive deformation of the layers), the nature of the temperature dependences of $\lg G'$ and $\tan\delta$ is predetermined by the properties of the components having low glass points. However, the $\tan\delta$ maxima for the gradient materials are shifted towards higher temperatures by 5–7° relative to the $\tan\delta$ maximum corresponding to the 'lowest temperature' component and the changes in the height of the maxima are slight.

The theoretical data obtained led to the conclusion[26] that the temperature range of the transition state of the gradient materials expands significantly, increasing with increase in the temperature gradient. An important feature of materials of this kind is the anisotropy of the properties in different directions, which is manifested most strikingly in limiting cases where the direction of the deformation is parallel or perpendicular to the direction of the gradient.

Experimental studies[18,19] have confirmed to some extent the above theoretical conclusions. Gradient IPN based on PU with a network structure and the copolymer of butyl methacrylate with triethylene glycol dimethacrylate[18] or oligo(carbonate-methacrylate)[19] were obtained. The usual IPN having the same composition were also obtained for comparison.

Fig. 4 presents the temperature variations of $\tan\delta$ for the usual IPN based on PU and the butyl methacrylate–oligo(carbonate-methacrylate) copolymer and also for their components.[19] Similar variations have also been obtained for another IPN of a similar chemical nature.[18] Evidently the $\tan\delta$ maximum is observed at 248 K for PU and at 366 K for the copolymer. For the IPN with 10 mass % of the copolymer, the temperature dependence is characterised by the occurrence of the relaxation α-transition, corresponding to the acrylate

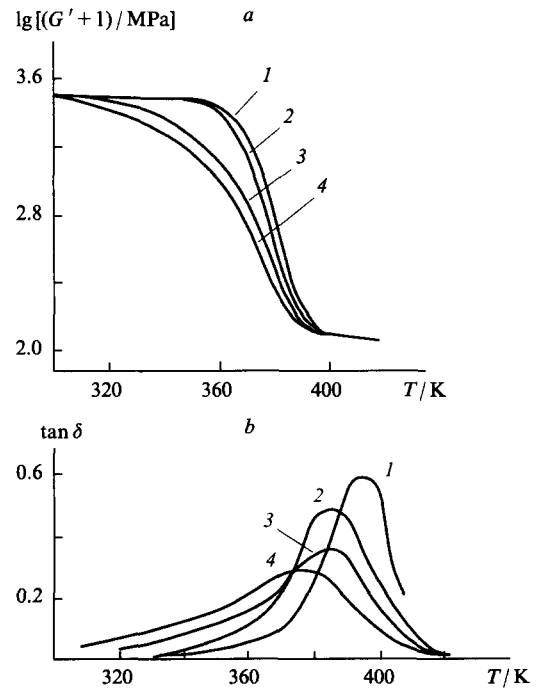


Figure 3. Calculated temperature variation of $\lg G'$ (*a*) and $\tan\delta$ (*b*) for a gradient model (n = 11) with different T_g gradients [(dT_g/dx)/K]: (*1*) <20; (*2*) 20; (*3*) 50; (*4*) 70 with parallel deformation of the components.

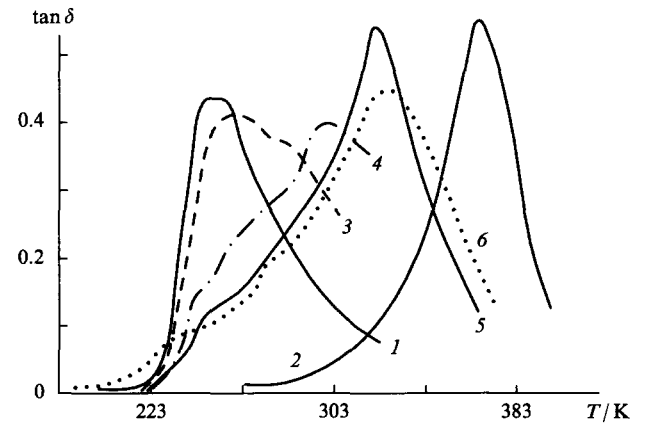


Figure 4. Temperature variations of $\tan\delta$ for PU, the copolymer, and the IPN based on them with different component ratios: (*1*) PU; (*2*) copolymer; (*3*)–(*6*) IPN containing 10, 20, 30, and 40 mass % of the copolymer respectively.

component, and is manifested by a distinct shoulder on the descending branch of the curve in the temperature range 273–303 K (Fig. 4, curve *3*). With increase in the fraction of the copolymer in the IPN, the relaxation maximum corresponding to the copolymer is manifested more distinctly and the temperature range where this transition occurs shifts, with increase in the copolymer concentration in the IPN, towards the temperature range of the relaxation α-transition of the initial copolymer (Fig. 4, curves *2–6*).

The nature of curves *3–6* in Fig. 4 shows that the IPN are two-phase systems in which both components form continuous phases.[27] The expansion of the temperature range of the α-transition of the copolymer indicates the generation of an extensive interfacial region in the IPN during the formation of the acrylate network under these conditions.

Calculation of the segregation coefficients of the components (α) by the method proposed by Rosovitskii and Lipatov[28] showed that α for all the IPN is in the range from 0.3 to 0.5 and tends to fall with increase in the fraction of the copolymer in the IPN, i.e. the degree of segregation of the components diminishes.

Thus the usual IPN are two-phase systems. However, the observed shift of the tan δ maximum along the temperature scale for the copolymer in the IPN compared with its position in the individual network and also its broadening indicate an incomplete phase separation of the components in the formation of the IPN. This confirms data indicating the thermodynamic incompatibility of the components in the IPN of the same chemical nature.

The gradient IPN-1 IPN-2 with different copolymer contents, 30% and 15% respectively, have been investigated layer-by-layer, both along the copolymer concentration gradient and at right angles to it.[19] Fig. 5 presents the temperature variations of tan δ for specimens obtained sections at right angles to the concentration gradient. Analysis of the family of curves and their shape as well as the intensity and relative positions on the temperature scale of the maxima corresponding to PU and the copolymer led the authors[19] to the conclusion that, firstly, a copolymer distribution gradient is indeed observed as one moves away from the surface of the specimen and, secondly, the continuity of both phases in the gradient IPN-1 containing a greater amount of the copolymer is observed at a greater distance from the specimen surface than for IPN-2.

The average concentrations of the copolymer in the layers of the gradient IPN were calculated from the observed linear dependence of the glass point of the copolymer (T_g is the temperature corresponding to the high-temperature tan δ maximum) on composition for the usual IPN. Thus the first three layers in IPN-1 contained 38.6, 26.9, and 15.3% of the copolymer, while the contents of the copolymer in the first and second layers in IPN-2 were respectively 38.6 and 10.6 mass %, i.e., for a greater average concentration of the copolymer in the specimen, a more uniform distribution with respect to the depth in the specimen is observed.

The study of the viscoelastic properties of sections obtained along the copolymer concentration gradient revealed certain differences (Fig. 6).[18,19] For specimens representing a complete section through the gradient system (Fig. 6, curves *2*), a

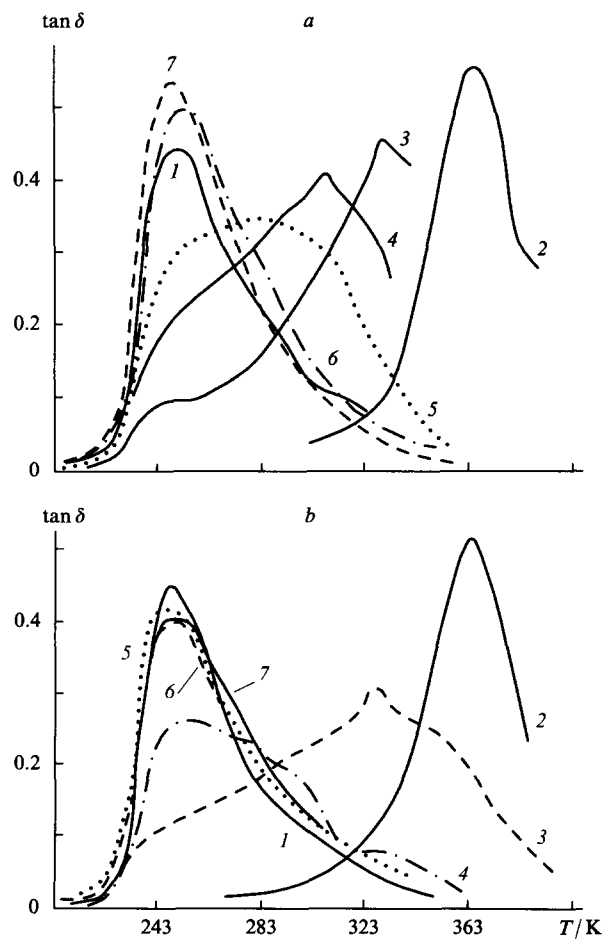


Figure 5. Temperature variations of tan δ obtained for perpendicular sections through gradient IPN-1 (*a*) and IPN-2 (*b*): (*1*) PU; (*2*) copolymer; (*3*)–(*7*) the first, second, third, fourth, and fifth sections respectively.

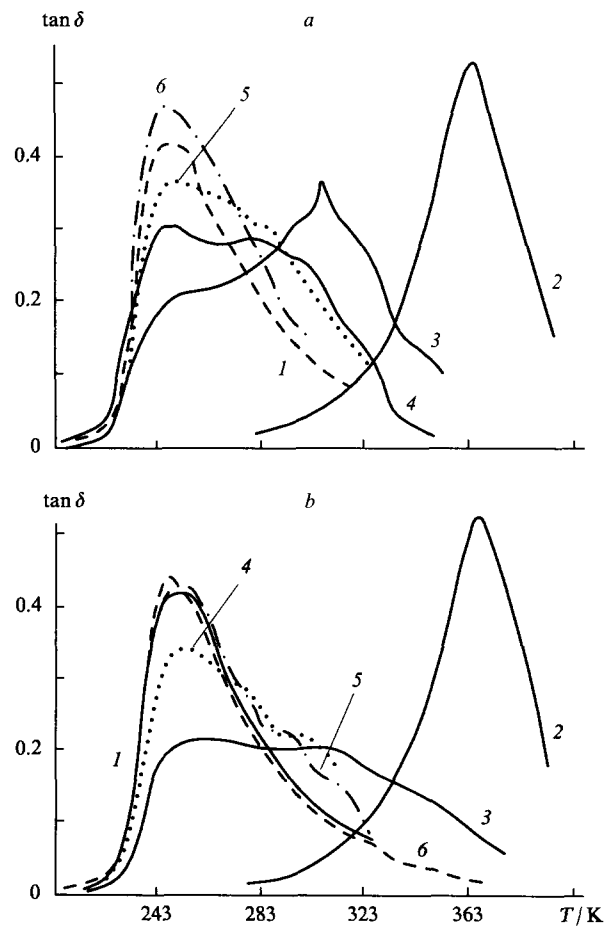


Figure 6. Temperature variations of tan δ for specimens obtained from longitudinal sections of gradient IPN-1 (*a*) and IPN-2 (*b*): (*1*) PU; (*2*) copolymer; (*3*)–(*6*) the first, second, third, and fourth sections respectively.

maximum is observed in the range 233–363 K. For IPN-1, the maximum is observed at 308 K in the region corresponding to the transition in the copolymer, while in the region of the relaxation α-transition in PU there is a distinct shoulder. A single broad maximum in the form of a plateau, overlapping the region of the relaxation transitions in both components, is observed for IPN-2.

The presence of broad maxima on the $\tan\delta - T$ curves is probably not a result of the compatibility of the components in the IPN but indicates a superposition of a large number of relaxation maxima in layers with gradually varying compositions.[18] These data agree with the results of modelling[26] and also account for the appearance of a single but broad transition for the PMMA–PCEA system, which has been erroneously regarded[17] as evidence for the compatibility of the components.

The damping properties of the gradient and the usual IPN based on PU and the butyl methacrylate–oligo(carbonate-methacrylate) copolymer have been compared[19] on the basis of the analysis of dynamic mechanical spectroscopic data for these systems. One of the integral parameters characterising the ability of a material to scatter mechanical energy is known[29,30] to be the area under the curve describing the temperature variation of the imaginary component of the complex modulus of elasticity ($S_{E''-T}$), which is determined by the intensity and width of the temperature range of the relaxation transition. For all the test specimens, this parameter has been calculated by the method of trapezia on a computer. For specimens of the usual IPN, the values of this parameter have been calculated assuming additivity.[19]

Examination of the results revealed that in general the damping properties of the IPN investigated are superior to those of the initial components (the $S_{E''-T}$ for the IPN are higher). For gradient IPN specimens sliced at right angles to the copolymer concentration gradient, $S_{E''-T}$ diminishes with decrease in the concentration of the copolymer, whereas for sections along the $S_{E''-T}$ gradient the values of $S_{E''-T}$ actually increase with decrease in the copolymer concentration, i.e. the anisotropy of the properties is observed, which confirms the conclusions reached by Lipatov et al.[26]

Furthermore, it was found that the variation of the damping properties of the usual and gradient IPN is not the same for chemically similar IPN specimens: thus the damping characteristics of the gradient IPN based on PU and the butyl methacrylate–ethylene glycol dimethacrylate copolymer[18] are superior to those of the usual IPN, whereas the opposite picture is observed for the IPN based on the same PU and the butyl methacrylate–oligo(carbonate-methacrylate) copolymer.[19]

Thus analysis of the results of the study of the relaxation characteristics of the usual and gradient IPN indicates a significant difference between their viscoelastic properties. Furthermore, the results of the modelling agree satisfactorily with the experimental data.

V. Mechanical properties of gradient interpenetrating polymer networks

The strength characteristics of gradient IPN have been investigated in some studies. Thus, in a study of the IPN based on PMMA and PCEA, Martin et al.[17] established that the gradient IPN differ from the usual IPN and the homopolymers by a higher decomposition energy and that the deformation of gradient IPN with a PMMA matrix and 30 mass % of PCEA increased by an order of magnitude on decomposition compared with the pure PMMA, while the strength of the IPN with a PCEA matrix and 50 mass % of PMMA is 10–15 times higher than that of PCEA.

The study of the mechanical characteristics of gradient IPN based on PMMA and methyl methacrylate (MMA) showed[13] that, whereas pure PMMA decomposes (at 373 K) on 2% extension, the gradient IPN containing ~10 mass % of MMA

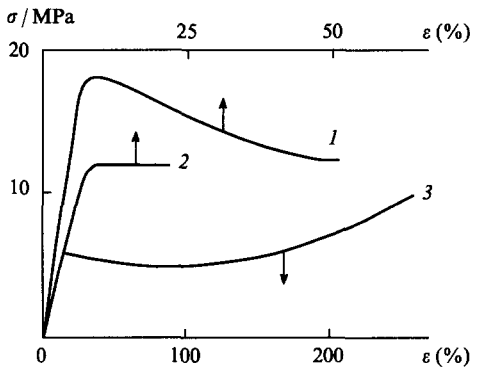


Figure 7. Stress–deformation curves for a gradient polymer (*1*), IPN (*2*), and a statistical methyl methacrylate–methyl acrylate copolymer (*3*).

breaks after 10% extension. The introduction of 19 mass % of MMA leads to the disruption of the IPN specimen only after 80% extension. Fig. 7 presents the stress–deformation relations for PMMA–MMA specimens obtained in the form of a gradient polymer, an IPN obtained by successive hardening, and a statistical copolymer.[13] Evidently, the gradient polymer is subjected to the highest stress at rupture and the area under the stress–deformation curve is greatest for this polymer.

Comparative study of the mechanical properties of the usual and gradient PU-based IPN and the butyl methacrylate–triethylene glycol dimethacrylate copolymer (for the same component ratios) showed (Fig. 8) that the highest strength parameters are observed for the gradient IPN:[18] the area under the stress–deformation curve increases and so does Young's modulus (the slope of the initial section of curve *3* is greater than that of curve *2*).

Thus when a gradient of the concentrations of the components is established in a polymeric material, there is a tendency towards an improvement in its mechanical properties. Several hypotheses have been put forward to account for these phenomena.[13,17] According to one of them, a gradient IPN is regarded as an assembly of an infinite multiplicity of layers, the compositions and moduli of elasticity of which vary monotonically on moving away from the surface the bulk of the specimen. On deformation of the specimen, all the layers are stretched to the same extent and the stress in each layer corresponds to its modulus. Such distribution of stresses promotes the development of plastic deformation, and not brittle rupture, and leads to an increase in the elongations at rupture and rupture energies.

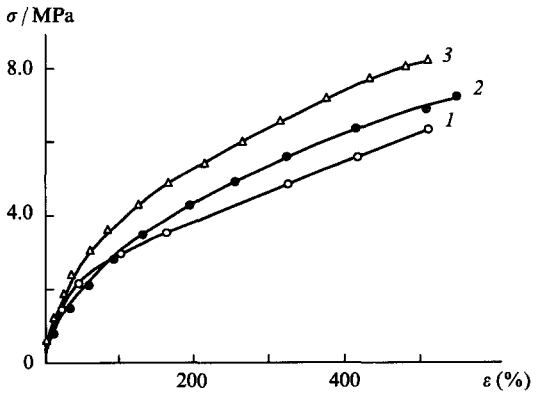


Figure 8. Stress–deformation curves for polyurethane (*1*), a usual IPN containing 33.7 mass % of the butyl methacrylate–triethylene glycol dimethacrylate copolymer (*2*), and a gradient IPN containing 33.7 mass % of the copolymer (*3*).

Another hypothesis attributes the increase in the strength of gradient IPN to a decrease in the defectiveness of the surface layers. One can postulate that the introduction of an elastomer into the surface layer of a 'rigid' matrix inhibits the growth of cracks and increases thereby the stress necessary to initiate cracks. The study of the morphology of the specimens confirmed that the presence of an elastic shell can increase the stress corresponding to the formation of 'cracks'.[17] The near-surface layers (after the rupture of the specimen) proved to be smoother than the internal regions of the specimen.

In order to confirm or reject the hypotheses proposed, further studies involving the use of a wider range of gradient IPN are needed.

VI. The use of the principle governing the formation of gradient interpenetrating polymer networks for the preparation of gradient lenses and other polymeric materials

Polymers with nonlinear optical properties have found extensive application in engineering at the present time,[35,36] in particular a series of polymeric materials based on IPN with nonlinear optical characteristics have been obtained.[37-39] These have definite advantages over both inorganic materials and polymers of other classes.[38,39] Studies on the creation of gradient or graded-index lenses — light-focussing elements based on transparent materials with a parabolic distribution of the refractive index — are of interest in this connection.[40-51] Such lenses have been used successfully in optoelectronics and wave optics (adjusting devices, light beam dividers), in instrument making, and medical engineering.

In most of the studies, the synthesis of graded-index lenses is accompanied by the formation of gradient IPN. The possibility of obtaining graded-index lenses from gradient polymers was first pointed out by Ohtsuka.[40] For this purpose, methyl methacrylate was allowed to diffuse into a cylindrical gel matrix consisting of a diallyl isophthalate (DAIP) prepolymer (70 mass % of the monomer + a mixture of linear and cross-linked polymers), the refractive index of methyl methacrylate being lower than that of DAIP. The distribution of the refractive index generated during the diffusion process was 'fixed' by additional polymerisation. Refractive index differences $\Delta n_D \approx \pm 0.04$ were then obtained, which is appreciably beyond the possibilities of the diffusion technology in inorganic glasses.[42]

A similar polymer system has been used[41,42,44] to obtain light-focussing elements (LFE). The physicochemical processes constituting the basis of the preparation of such elements were investigated in detail. Exchange diffusion processes in the DAIP–MMA system were examined using Fick's equation. The influence of various parameters (diffusion time, temperature, diffusant concentration, etc.) on the variation of the refractive index in the LFE was analysed.

Thus it has been established[41] that the variation of the diffusion coefficient with the diffusant concentration does not alter significantly the optimum diffusion conditions and in many instances impairs the distribution of n_D compared with the case in which there is a constant diffusion coefficient. In order to create the maximum change in n_D along the LFE cross-section, it has been suggested[40] that a polymerisation initiator (benzoyl peroxide) be added to the diffusant (MMA). Bearing in mind that Fick's equation cannot be used to calculate the n_D profile under conditions where polymerisation reactions take place, the authors[41] suggested that account be taken of the cessation of the diffusion of some of the MMA and DAIP molecules. They modified a series of equations for the calculation of the diffusion coefficient and calculated the changes in the MMA and DAIP concentrations during the preparation of the LFE and also the variation of the n_D profile along the specimen cross-section.

It was noted[41] that the use of monomers capable of forming a network in the early stages of the polymerisation is very important from the standpoint of the n_D distribution obtained. In the study of the influence of temperature on the variation of the n_D distribution along the LFE cross-section, it was shown that, up to certain temperatures, the polymerisation reaction has an insignificant influence on the n_D profile, but at high temperatures, for example at 353 K, the influence of polymerisation is reflected in a change in the distribution of n_D after only 20 min. In the preparation of polymeric LFE, account must also be taken of the disappearance of the n_D gradient along the LFE cross-section and its subsequent restoration.[41]

An important conclusion reached by Marturunkakul et al.[39] and Ohtsuka[40] is that it is essential to select systems capable of increasing sharply the rate of polymerisation after the attainment of a specified degree of conversion. This property, called the gel effect, is characteristic of many vinyl monomers during their radical block polymerisation. The gel effect plays an important role in the formation of gradient lenses from gradient IPN based on DAIP and MMA[44] and on styrene–triethylene glycol dimethacrylate (TGDM)–MMA.[43,45,50] A characteristic feature of the latter system is that, at a certain instant after the beginning of the diffusion of MMA into the polymerised matrix consisting of styrene and TGDM, rapid spontaneous copolymerisation of the matrix monomers and the diffusant up to virtually complete conversion takes place. After the diffusion process has ceased, the n_D profile generated at the given instant is fixed.

The problem is how to make sure that the fixation of the distribution of n_D should occur at the instant when it is closest to the ideal form[43,48] because one then rules out the separate stage involving the fixation of the distribution of the refractive index established during the diffusion process (characteristic of other systems[48]), in which it is difficult to avoid the diffusion-induced impairment of the distribution of n_D.

A mathematical model has been proposed[43,45] for the establishment of the n_D distribution profile and the following conclusion was reached on the basis of the analysis of the results of the modelling of the diffusion and copolymerisation processes in the styrene–TGDM–MMA system: if the chosen amount of initiator and the temperature are such that the gel effect begins for a distribution n_D close to that given by the expression

$$n_D(r) = n_0 \operatorname{sech}(\alpha r) \simeq n_0\left(1 - \frac{\alpha^2 r^2}{2}\right),$$

where n_0 is the refractive index along the axis of the lens, r is the radius of the graded-index lens and α is the distribution constant, then the distribution is preserved and the gradient lens obtained is of good optical quality. The results of the modelling have been confirmed experimentally and the optimum conditions for the preparation of polymeric gradient elements based on the copolymer of styrene with TGDM and MMA have been proposed.[43,45]

Further study of the molecular diffusional exchange in the DAIP–maleic anhydride (matrix)–MMA (penetrant) system established the occurrence of diffusional anomalies[52] when specimens having different diameters are employed. It was established that a disk model for the description of the molecular diffusional exchange in the system investigated is applicable to specimens having diameters between 5 and 12 mm. On the other hand, for specimens with larger diameters (from 12 to 30 mm), a sharpening of the diffusion was, as it were, observed and in addition the experimental refractive index distribution (RID) curves differed from the Fick RID.[53,54] Hui et al.[54] put forward ideas according to which the volume fraction of the penetrant on the surface may increase to an equilibrium value, the rate of change of the volume fraction of the penetrant (at any point on the surface) being determined by

the rate of deformation of the creep, which depends on the osmotic pressure arising in the polymer during swelling. Here it has been suggested that the longitudinal viscosity diminishes exponentially with increase in the concentration of the penetrant. Bukhbinder et al.[52] suggested that the concentration of the penetrant at the boundary increases fairly slowly, so that for short times (diffusion into specimens having small diameters) conditions are not attained under which there is a sharp decrease in viscosity accompanied by an abrupt increase in the diffusion coefficient. Thus the mechanism of the diffusion in specimens with small diameters is close to the Fick mechanism, whereas, on passing to specimens with a large diameter (an increase in the diffusion time), the equilibrium concentration reaches the threshold value. After the attainment of the threshold value, there is a sharp jump in the diffusion coefficient and a front begins to be formed on the RID curves. This front can be regarded as the moving boundary of the penetrant, which is equivalent to a decrease in the effective diameter of the specimen as a function of time. The proposed explanation for the diffusional anomaly is supported by the fact that a large change in n_D along the cross-section, virtually equal to the theoretical change, can be attained in large-diameter specimens, in contrast to specimens with a small diameter. Thus a reasonable explanation of the observed diffusional anomaly has been found and an interesting conclusion has been reached: the geometrical factor (the change in the dimensions of the specimens) is important in the preparation of graded-index lenses with a specified RID.

The possibility of using gradient IPN of different nature for the preparation of polymers with hard external, soft internal, and intermediate zones and with a continuously varying composition has been demonstrated.[55]

In order to obtain materials with a surface susceptible to hydration, which can replace protective coatings in arteriovenous shunts, a gradient IPN based on oxyethylene methacrylate monomers and a silicone rubber has been employed.[56]

The possibility of forming grains from hydrogels, the surface layer of which consists of a gradient IPN acting as a membrane permitting the regulation of the migration of the water-soluble medicinal substances absorbed by the grains, has been demonstrated in relation to gradient IPN based on polyurethane and cross-linked polymers consisting of 2-hydroxyethyl methacrylate and *N*-vinylpyrrolidone.[34,57-59] This makes it possible to create new forms of long-acting medicinal preparations.

Gradient IPN are promising for the preparation of vibration- and sound-proofing materials.[4,18] It is possible to apply the principle governing the formation of gradient IPN in other fields as well. Thus, the use of IPN as adhesives, especially for polymeric substrates, is promising. It has been shown[59] that in this instance an adhesion junction consisting of a gradient IPN is formed. The authors used the IPN based on polyurethane and the MMA–triethylene glycol dimethacrylate (TEGDM) copolymer for glueing vulcanised natural rubber (NR) to poly(vinyl chloride) (PVC). It was established that, as a consequence of the diffusion of the MMA and TEGDM monomers into the polymeric materials and subsequent hardening of the composition, two gradient IPN are formed: a three-component gradient IPN consisting of natural rubber, PU, and the copolymer is produced at the interface with natural rubber, whilst a three-component IPN, consisting of PVC, PU, and the copolymer, is formed at the interface with PVC. The thickness of the transitional layer at the interface with natural rubber reaches 30 μm, while that at the interface with PVC reaches 20 μm. The thickness of the transitional layers as well as the adhesive strength can be regulated by varying the duration of contact between the unhardened composition with natural rubber and PVC and also by employing different procedures for the preparation of the IPN-adhesive, namely by employing the prepolymerisation MMA or the simultaneous mixing of the components and subsequent hardening of the composition.

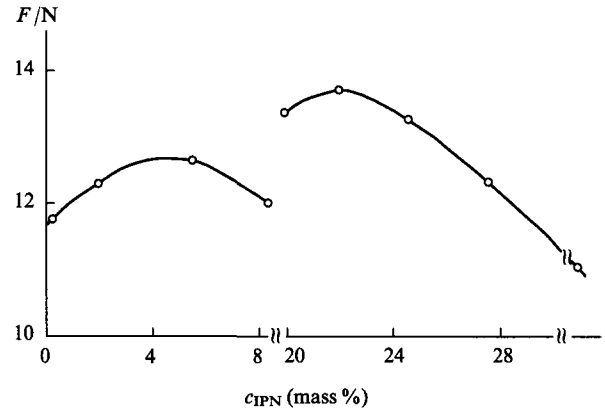


Figure 9. Dependence of the strength of a complex capron filament in the presence of an IPN in its surface layer at 373 K.

It has been shown[60] that the method for the preparation of gradient IPN for the improvement of the physicochemical characteristics of synthetic fibres and organic plastics based on the latter is promising. This has been demonstrated in relation to polyamide fibres, which were swollen for different times in an alcoholic solution of a phenol-formaldehyde oligomer containing a hardening agent with subsequent hardening of the binder. This resulted in the formation in the surface layer of the fibre of a gradient IPN, the matrix of which is the polyamide, while the hardened phenol-formaldehyde layer is distributed in it with a certain concentration gradient. Physicochemical study of the fibres obtained showed that the modified fibres are more effectively wetted by solutions of the phenolic oligomer and that their heat resistance is improved: the temperature of the onset of degradation increases to 373 K and the mass loss in the temperature range 373–473 K is smaller by a factor of 2 than for the initial fibres. The strength properties of the fibres at room and elevated temperatures also increase under these conditions. The strength of the hardened oligomer in the surface layer of the fibres (Fig. 9) varies non-monotonically. The curve has two maxima in the regions where the contents of the IPN are 1.8–4.5 and 22 mass %. The breaking stress on compression of organic phenoplastics, obtained from the modified fibres, is 50% greater than for the plastics obtained from the initial fibres, i.e. the application of the method for the preparation of gradient IPN is promising for the preparation of organic plastics with improved physicomechanical characteristics.

VII. Conclusion

The preparation of gradient IPN is a promising procedure for the specific modification of the surface layers of monomers with a three-dimensional structure, which makes it possible to impart to them new characteristics — to improve the optical and mechanical properties of composites based on them, to alter the relaxation behaviour, etc.

Variation of the degree of thermodynamic compatibility of the matrix network with the monomer or polymer diffusing in it and the conditions governing the diffusion process (diffusion time and temperature) makes it possible to regulate specifically the thickness of the layer with a composition gradient and at the same time to obtain polymeric composites with specified characteristics.

The number of gradient IPN obtained and investigated hitherto is unfortunately small. However, a series of materials based on IPN of this type have already found quite definite applications in various branches of engineering and biomedicine.

As is frequently the case, the studies on the preparation and practical employment of the gradient IPN have outstripped those on the mechanism of their formation, structure, and the relation between structure and physicochemical properties. Furthermore, during the formation of gradient IPN, there is a change not only in the ratio of the components in the layers but also in the formation conditions, in particular phase separation conditions in the layers of gradient IPN, which should alter the morphological characteristics and the properties of these layers compared with the IPN obtained by the usual methods.

Studies along these lines have only just begun. The available information about the layer-by-layer variation of the morphology in gradient IPN is limited. It is of interest to obtain multicomponent IPN with a composition gradient and to investigate their formation and properties. Analysis of the available data on gradient IPN does not as yet permit definite conclusions about the causes of their different properties. It may be that, for a certain change in the formation conditions, it is possible to obtain a particular gradient for the same polymer system. All the problems noted here and others listed above require further investigations in order to be able to create new gradient systems. The synthesis of gradient IPN leads to new prospects for the preparation of polymeric materials and it is so far difficult to predict what diverse combinations of properties these systems will possess. In addition, further studies on gradient IPN as well as other types of IPN are extremely important from the standpoint of the theory of the formation of multicomponent polymer systems and the principles governing the preparation of composite polymeric materials from them.

In conclusion, one should note that the synthesis of gradient IPN is only one of the ways of obtaining gradient polymeric materials. There are also other procedures. Recent investigations,[61-64] in which a fundamentally new aspect of the creation of gradient polymeric materials from network copolymers has been developed, are particularly interesting. In order to obtain other polymeric materials, in which the modulus of elasticity varies smoothly within the boundaries of one specimen in a specified direction (in the absence of transitional layers and interfaces), an approach based on the creation of dense-network structures containing bulky rigid nodes connected by flexible linear chains with a controllable length has been employed. The creation of such structures has been demonstrated experimentally in the synthesis of network polyisocyanurates, in which the role of the node was assumed by isocyanurate rings with the aromatic rings adjoining them and the role of the internodal fragment was assumed by fairly short but flexible organosilicon chains[61,62] or short chains based on the oligomeric tetrahydrofuran–epoxypropane copolymer.[64] This resulted in the formation of materials in which the modulus of elasticity varies smoothly within a single specimen in the specified direction from 4.5 MPa to 2.0 GPa, i.e. a smooth transition from a rubber to a plastic has been achieved. The following conclusion is of fundamental importance: despite the fact that the range of moduli for the materials synthesised overlaps the values characteristic of the region corresponding to the transition from the vitreous to the highly elastic state, the materials obtained exhibit elastic and not viscoelastic properties, behaving, for example, as glasses or rubbers.[64] Studies on these lines are being vigorously prosecuted.

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