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Characteristic features of the chemical kinetics of the formation of interpenetrating polymer networks

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ABSTRACT. Data on the kinetics of the formation reactions of interpenetrating polymer networks (IPN) are surveyed. They are formed in the course of the simultaneous cross-linking in the reaction system of two three-dimensional networks which do not react chemically. It was established that the kinetics of the formation of the network components forming part of the IPN differ from those for the "pure" networks. The mutual influence of the networks formed on the kinetics of their formation depends on the composition of the IPN, the ratio of the rates of the component reactions, and the order in which the reactions are carried out.

A characteristic feature of the formation of the IPN is that, even in the early stages of the reactions of the system, a thermodynamic incompatibility of the molecular fragments of the component networks arises as a rule.

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I. Introduction

It has now been established that the properties of polymeric materials based on interpenetrating polymer networks (IPN) depend on the thermodynamic compatibility of the constituent networks and the kinetics of the chemical reactions which establish the microphase separation at a particular level.

Analysis of the literature data shows that an increasing number of studies are now being published on this problem. Whereas the structure and properties of the IPN were previously studied mainly in the laboratories of Frisch, Sperling, and Lipatov, which led to the discovery of their principal structural features and a set of properties determined by the microheterogeneity of the IPN, nowadays Hourston, Meyer, Widmaier, and Hsu are engaged in the problem of the creation and study of the IPN. Investigations by Japanese and Chinese investigators have been published. Many polymer compositions for the production of IPN have been tested. For example, Kim et al.[1] investigated modern IPN based on polyurethane–polystyrene or polyacrylates, Hourston and co-workers[2] studied by the ^{13}C NMR method the structure and properties of IPN based on polyurethane-polyphenylsiloxane, Djomo, Morin, and co-workers[3] investigated the mechanical properties of IPN based on polyurethane–poly(methyl methacrylate), Bi Xiping, Li Binyao and co-workers[4,5] studied those based on poly(vinyl acetate)–poly(methyl methacrylate), and Burford et al.[6] investigated by mechanical dynamic spectroscopy IPN based on a cross-linked butadiene or butadienestyrene elastomer and polystyrene. Visscher et al.[7] studied by differential scanning calorimetry and IR spectroscopy new class of IPN based on polyorganophosphazenes and poly(methyl methacrylate), which are biocompatible and resistant to oil. The majority of studies were devoted to the synthesis and investigation of the mechanical and viscoelastic properties[8–11] and the morphology[12–14] of the materials obtained. However, in order to be able to employ the IPN in different technologies, it is essential to understand in detail the kinetics of the hardening reaction and the microphase separation processes in polymeric two-phase systems and the influence of these parameters on the viscoelastic and mechanical properties of such systems.[15,16]

A characteristic feature of interpenetrating networks is that the phase separation processes occur as a result of the formation of heterogeneous networks from an initially single-phase system, so that the degree of microphase separation is determined by the kinetics of the formation of the components. IPN can be obtained in two ways: with simultaneous and consecutive formation of polymer networks. The initial system is usually single-phase—in the simultaneous formation process it is a solution of components forming two networks, while in the consecutive formation process it consists of a swollen gel. Since microphase separation begins simultaneously with the chemical reaction at a certain degree of conversion, the properties of the IPN are determined by the differences between the rates of formation of individual networks, which can be varied within wide limits by altering the hardening temperature for each component, the catalyst concentration, the concentration of the cross-linking agent, the hardening sequence using thermo- or photohardening, and the component ratio in the IPN formed. It is also essential to take into account the fact that in the case of both consecutively and simultaneously formed IPN the formation reactions of one of the networks take place in the matrix of the other.

In the simultaneous formation of IPN, the kinetics of the formation reactions of the constituent networks are different and the reactions proceed via different mechanisms (polyaddition–polymerisation), one of the networks being formed usually at an earlier stage and serving as the matrix for the formation of the other. The network formed first (the matrix network) alters significantly the

conditions in the formation reaction of the second network, becoming segregated as a microphase as a consequence of the resulting thermodynamic incompatibility of the chains of the constituent networks. This affects the diffusion parameters of the formation reaction of the second network.

Although the factors listed above provide grounds for the hypothesis that there are differences between kinetics of the formation of the interpenetrating networks and the individual polymer networks, sufficient attention has not yet been devoted to the study of this problem. Vigorous investigation of the kinetics of the reactions, occurring simultaneously and consecutively via different mechanisms and influencing one another, has begun only in recent years.

II. The influence of the components of one network on the kinetics of the formation of the second network during the consecutive generation of interpenetrating networks

Studies on the formation of IPN began comparatively recently. This is associated primarily with the fact that, on passing from the study of individual polymer networks to IPN, the kinetics become more complex, apparently as a consequence of the rapid increase in the viscosity of the reaction medium during both polycondensation and radical polymerisation and the mutual influence of the two processes occurring in the IPN produced.

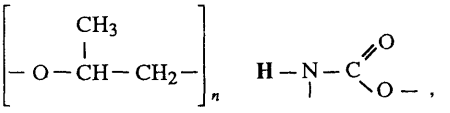
The first studies on kinetics of the formation of IPN were carried out by Djomo et al.[3] in relation to two network polyurethane–poly(methyl methacrylate) polymers. The polyurethane (PU) network was formed from a flexible polyoxypropylene glycol (POPG) block with a molecular weight of 2000 and an aromatic triisocyanate adduct. The catalyst was tin octanoate (OcSn). The poly(methyl methacrylate) (PMMA) network was obtained by copolymerising methyl methacrylate (MMA) and tri(hydroxymethyl)-propane trimethyacrylate using a radical polymerisation initiator 2,2-azobisisobutyronitrile (AIBN). The PU network was formed first at room temperature and this was then followed by the formation of the PMMA network at 50 °C. The influence of all the components of the PMMA network on gel formation in the PU network was studied in succession and a similar study was made of the influence of the components of the PU network on gel formation in the PMMA network. The influence of the OcSn catalyst on the rate of formation of the PMMA network was investigated. It was observed that the components of the PMMA network do not affect the gel formation in the PU network, whereas the components of the PU network diminish the gel formation time from 180 to 30 min. This is induced by the increase in viscosity of the reaction medium, which increases the rate of formation of the PMMA network (V_p) in the presence of the components of the PU network as a result of the decrease in the termination rate constant (K_t) in accordance with the equation[17]

$$V_p = \frac{K_p[M]\sqrt{V_{in}}}{\sqrt{K_t}}, \qquad (1)$$

where [M] is the monomer concentration, K_p the chain propagation rate constant, V_p the rate of chain propagation, V_{in} the rate of initiation, and K_t the termination rate constant.

The influence of the OcSn catalyst on the rate of formation of the PMMA network was studied in greater detail by Meyer.[18] Data for the electrical conductivity of the system led the author to the conclusion that the catalyst does not affect the rate of decomposition of the initiator but does accelerate the polymerisation and copolymerisation of the methacrylates as a result of the polarisation of the monomer double bonds and facilitates the addition of radicals to the latter, inducing thereby an acceleration of the formation reaction of PMMA in the presence of the OcSn catalyst.

The possibility of the formation of a chemical bond between the PU and PMMA networks has also been studied. The presence in the reaction medium of two components of the PU network–polyoxypropylene glycol and the triisocyanate adduct, i.e.



containing a mobile hydrogen atom which can be abstracted by a radical, suggests a possible way in which the reaction may be transmitted, which can be represented schematically as follows:

Stage I:

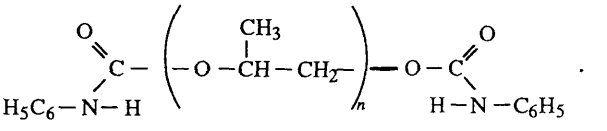
$$Ac^{\cdot} + T \longrightarrow Ac + T^{\cdot}.$$

Stage II:

a) $T^{\cdot} + Ac \rightarrow T \sim Ac^{\cdot}$;

b) $T^{\cdot} + Ac^{\cdot} \rightarrow T \sim Ac$,

where Ac is the MMA monomer, T the component containing the oxypropylene or urethane group, and $Ac^{\cdot}$ and $T^{\cdot}$ are the corresponding radicals. If reactions (IIa) and (IIb) occur, then a chemical bond is formed between PU and PMMA. To confirm this hypothesis, a mixture of methacrylate monomers with different amounts of the α,ω-phenylurethane–POPG adduct was polymerised under the experimental conditions described above:



The products were extracted with a solvent and were analysed by IR spectroscopy. It was observed that the PU component is extracted to an extent greater than 90% (of the amount introduced). For the system containing 20% PU and 80% PMMA, 1.8% PU remained after extraction in the poly(methyl methacrylate) network. This is a low value, so that even if a chemical graft does exist, it is so small that its influence on the macroscopic properties of the IPN is insignificant.

The above study[18] constituted the first step in the investigation of the complex IPN systems. The author showed that it is essential to take into account the influence of each component of one network on the formation of the second network, and conversely, as well as the possibility of side reactions, which may disturb or prevent the formation of one of the networks.

The influence of the concentration of the cross-linking agent and the initiator for the polyacrylate network, of the NCO/OH ratio, and of the component ratio PU/PMMA on the transparency and the viscoelastic properties of the resulting IPN and semi-IPN was demonstrated in subsequent studies.[19–22] Fourier transform IR

spectroscopy[23] was used to investigate the kinetics of the formation of IPN and semi-IPN based on PU and PMMA, obtained as described by Meyer.[3] The method makes it possible to study the kinetics of the simultaneous formation of IPN (the NCO group absorbs in the region of 2275.5 cm^{-1}, while the C=C bond absorbs at 1639 cm^{-1}). The authors[23] studied the influence of the various factors (temperature, concentration of the cross-linking agent, concentration of PU in solution) on the formation of individual PU and PMMA networks forming part of the composition of the IPN. In the study of the PU network in ethyl acetate (EA) with the concentration ratio PU/EA = 25/75 wt.%, the rate of formation of PU increased with increase in the OcSn catalyst concentration from 0.38 to 1.0 wt.% but a further increase in catalyst concentration to 2 wt.% did not affect the rate of formation of PU. It has also been shown that an increase in the PU content in ethyl acetate for a constant catalyst content increases the rate of formation of the PU network and that the temperature at which the PU network is formed has a similar effect. In the study of the formation of PMMA it was observed that the cross-linking agent accelerates the formation of the network structure of the PMMA compared with the linear polymer and that under these conditions the onset of autoacceleration shifts towards shorter times, whilst the presence of the OcSn catalyst intensifies the copolymerisation effect.

The study of the simultaneously formed IPN having the composition PU/PMMA = 34/66 (wt.%) by Fourier transform (FTIR) IR spectroscopy showed that the nature of the PU and PMMA kinetic curves does not differ from the initial curves and it was concluded on this basis that there is no chemical interaction between the two IPN networks.

Subsequently the IPN network based on the same PU–PMMA system was investigated by FTIR spectroscopy[24] under conditions of stepwise polymerisation. Polyurethane was polymerised at room temperature, while PMMA was polymerised at 60 °C. The influence of the catalyst concentration and of the PU/PMMA ratio on the rate constants for the urethane formation reaction in the IPN at room temperature was investigated. In the study of the kinetics of the formation of the PU network in the IPN for the component ratio PU/PMMA = 34/66 (wt.%) with the reactions occurring simultaneously, it was observed that the rate of urethane formation increases by a factor of 8 when the temperature is raised to 60 °C. The order of the reaction was found over a wide range of NCO conversions. The authors believe that the equation

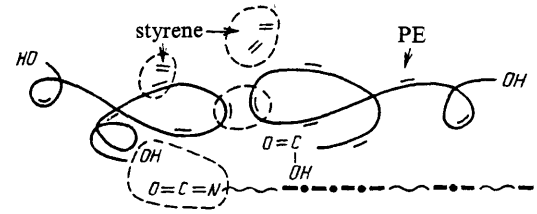
$$d[NCO]/dt = K[OcSn][NCO]^{1.5},$$

describes satisfactorily the formation of the PU network in the IPN under the conditions of both stepwise and simultaneous formation of both networks.

The search for new ways of synthesising IPN led Derrough et al.[25] to a simple but novel solution of the problem of synthesising IPN via a radical mechanism *in situ*. The butyl acrylate or methyl methacrylate (MMA) and diallyl carbonate–bisphenol A (DACBA) monomers were used to repair the IPN. The novelty of the method of synthesis consists in the choice of compounds which initiate the reaction only in a specific temperature range. AIBN, which operates at temperatures above 50 °C, was chosen for butyl acrylate or methyl methacrylate, while t-butylperoxy-3,5,5-trimethylhexanoate (TBPTMH), which initiates the reaction above 95 °C, was chosen for bisphenol A. The polymerisation mixture of MMA and DACBA in proportions of 50/50 (wt.%), containing the AIBN and TBPTMH initiators, was investigated by FTIR spectroscopy. The degree of conversion in the reaction was calculated from the change in the absorption band in the region of 1639 cm^{-1} characteristic of the C=C bond in MMA, with a shoulder at 1649 cm^{-1}, which corresponds to the allyl monomer. At 50 °C, the intensity of the 1639 cm^{-1} peak diminishes and reaches the base line, which corresponds to more than 95% conversion of the C=C bond in methyl methacrylate over a period of 2 h. With increase in temperature, the shoulder is unexpectedly transformed into an isolated peak, the intensity of which does not change so long as the temperature of the reaction medium does not reach 95 °C. After the attainment of this temperature, the peak intensity diminishes, indicating the polymerisation of the second component. After the introduction of the cross-linking agent, it is also possible to obtain the full IPN.

The influence of the methacrylate radicals on DACBA in the polymerisation of methyl methacrylate at 50 °C was investigated. UV analysis did not reveal the presence of the aromatic DACBA rings in the PMMA polymer chain. The nature and concentration of the radicals produced during the formation of the IPN were also investigated by the EPR method.[25] The results of this investigation agreed with the IR spectroscopic data. Consequently the authors clearly showed that the half-IPN or IPN can be obtained via a single mechanism (a radical mechanism) using different initiators. It would be of interest to have information about the phase state of the given IPN.

Hsu and Lee[26] investigated experimentally and theoretically the kinetics of the formation of IPN from polyurethane and an unsaturated polyester (PE). The PU component was obtained from a diisocyanate, a polyol, and a diol containing rigid and flexible segments; the PE component was obtained from an unsaturated polyester with styrene as the cross-linking agent involving the C=C bond in the polyester. The formation of a graft between the two PU and PE phases via the reaction of the NCO groups with the terminal OH or COOH groups of the PE molecules is possible. Such systems can be classified as graft IPN, which are illustrated schematically below.



The studies were carried out on an DSK-2S differential scanning calorimeter under isothermal and adiabatic conditions. The kinetics were studied for IPN obtained as a result of the RIM process (reaction injection moudling) and the usual casting. The kinetic measurements on the formation of the IPN by differential scanning calorimetry under isothermal conditions demonstrated that, as a consequence of different reaction mechanisms (polyaddition and radical polymerisation), the formation of urethane always begins after mixing the components and takes place under conditions where the PE phase does not yet react or only partly reacts, the PU being formed in solution in the components of the PE network, while the PE phase is frequently formed under conditions where the PU has been already fully or partly formed, i.e. the radical polymerisation of the polyester takes place fully or partly in the polymerised PU phase. However, the question of phase separation was not considered in the above study.

Fig. 1 shows that, with increase in the PU content in the IPN from 25/75 to 75/25 (wt.%), the peak for the PE reaction shifts to the right, which characterises the increase in the induction period due to the formation of the PE network, while the broadening of the peak indicates an increase in reaction time. This means that the diffusion of the PE reagents becomes hindered as the content of the PU network increases.

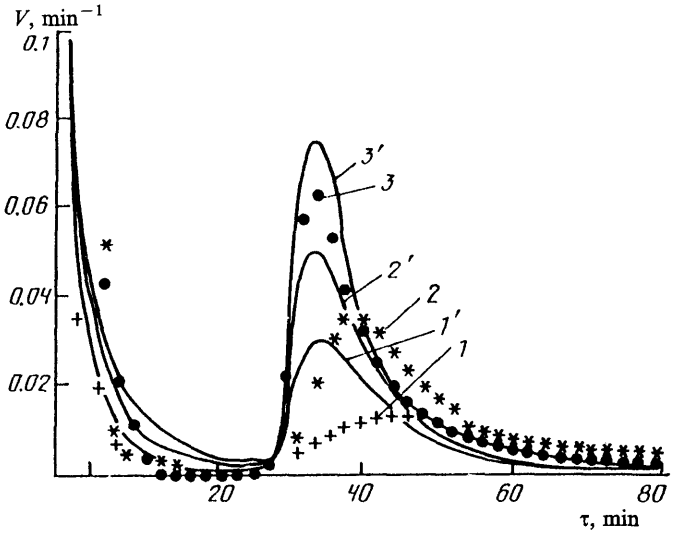


Figure 1. Time (τ) variation of the rate of reaction (V) for different ratios PU/PE in the IPN at T = 80 °C obtained experimentally (curves *1*–*3*) and calculated theoretically (curves *1'*–*3'*); PU/PE (wt.%): *1*, 75/25; *2*, 50/50; *3*, 25/75.[26]

The study of the formation of IPN under adiabatic conditions, modelling the RIM process, showed that the reaction takes place consecutively and the time variation of the degree of conversion of the components has the S shape characteristic of radical polymerisation for the component ratio PU/PE = 50/50 (wt.%). With increase in the fraction of the PU component in the IPN to 75/25 wt.%, the form of the curve changes, since the urethane formation reaction predominates in the overall process.

Using models based on the additive contributions of the initial components of the IPN, the authors[26] carried out a theoretical calculation for the model reaction under isothermal and adiabatic conditions involving the IPN investigated. In the calculation for the model reaction, use was made of the Arrhenius equation and a number of assumptions which disregarded the mutual influence and interaction of the two polymer network structures formed in the system, were made.

The kinetic parameters of the PU reaction were calculated from the increase in the temperature of the reaction system under adiabatic conditions using the equation

$$\ln\frac{dT_u}{dt} = \ln\left[\frac{\Delta H_u A_u}{P_u C_{pu}}\right] + \frac{E_u}{RT_u} + n\ln\left[\frac{T_{ad} - T_u}{T_{ad} - T_{uo}}\right] ,$$

The variables dT_u/dt, $1/T_u$, and $[(T_{ad} - T_u)/\Delta T_{ad}]$ can be calculated from the time variation of the temperature in the adiabatic polymerisation. Using the multilinear regression method, the order of the reaction n, the activation energy E_u, and the pre-exponential factor of the rate constant A_u were calculated.

The kinetic parameters of the radical polymerisation of the polyester were calculated by Lee's method[27] from the equation

$$\left(2fI_0A_p\right)\exp\left(-\frac{E_p}{RT}\right) = \frac{K_d\exp[-K_d(t_m - t_z)]}{1 - \exp[-K_d(t_m - t_z)]} ,$$

where f is the effectiveness of the initiator, I the concentration, K_d the decomposition rate constant, and t the induction period.

The authors concluded that the theoretical calculations for the reactions of pure PU and PE agree well with experimental data obtained by differential scanning calorimetry under isothermal conditions. Slight discrepancies between the theoretical calculation and experiment are observed for the IPN having the composition PU/PE = 25/75 (wt.%), while an increase in the content of the PU network in the system to 50/50 (wt.%) increases the discrepancies, which become appreciable for the ratio PU/PE = 75/25 (wt.%). The authors attribute this to the fact that in the theoretical calculations no account was taken of the interaction between the components. Discrepancies with experiment are observed particularly for the PE polymerisation, which is probably associated with the effect of diffusion in the region of high conversions. The mathematical description of the model reaction for the IRM process under adiabatic conditions agrees well with experimental results, which can be explained by the high rate of the reaction under adiabatic conditions.

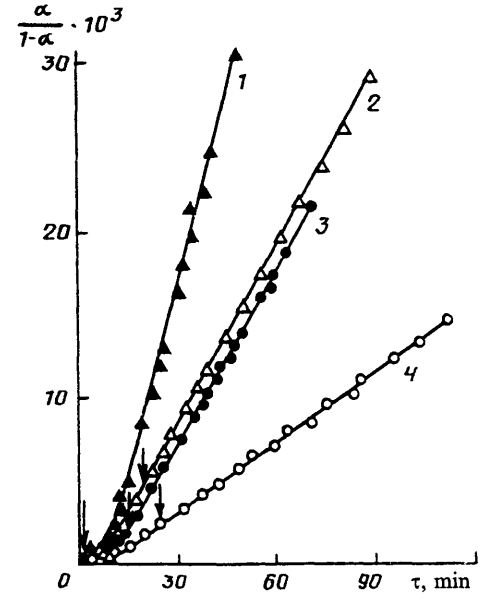


Figure 2. Transformed kinetic curves for the copolymerisation of styrene with divinylbenzene in a semi-IPN; the arrows indicate the onset of phase separation; PBMA content at T = 90 °C (wt.%): *1*, 40; *2*, 15; PBMA content at T = 80 °c (wt.%): *3*, 30; *4*, 15.[28]

III. Kinetics of the formation of interpenetrating polymer networks taking into account the interrelation between the processes and the influence on the microphase separation

The mutual influence of the kinetics of the formation of the polystyrene–divinylbenzene copolymer in the presence of poy(butyl methacrylate) (PBMA) and the microphase separation in the resulting IPN was investigated for the first time[28] in relation to a semi-IPN. Fig. 2 illustrates the linear forms of the kinetic curves for the copolymerisation of styrene with divinylbenzene in the semi-IPN for different proportions of the PBMA. The authors explain the absence of a break in the kinetic curves at the phase separation point by the fact that the microphase separation process in the semi-IPN produced proceeds via a spinodal mechanism, whereupon no visible volume effects are observed[29] and under such conditions the microphase separation (MPS) does not affect the rate of reaction. It has been established that, with increase in the content of PBMA in the mixture, the time of the onset of the MPS diminishes significantly, while an increase in temperature by 30 K likewise shortens the time of the onset of the MPS, the degree of conversion of the copolymer increasing under these conditions. It has also been shown that phase separation begins for low conversions of styrene in the range 0.1–8.0%. The authors conclude that there is a close relationship between the reaction kinetics, the degree of conversion, and the MPS in the system, the kinetics of the formation of the IPN exerting a significant influence on MPS processes, determining the onset of MPS.

Table 1. Physicochemical characteristics of the polyurethane network in the semi-IPN with the composition PBMA/PU = 15/100 (%).[30]

No. of specimen	Composition	T_h, °C	c_{ct}, wt.%	$10^4 K_r$, kg mol^{-1} s^{-1}	τ_{MPS}, min	α_{MPS}
1	PU	60	0.005	3.46	—	—
2	PU	60	0.010	7.63	—	—
3	PU	40	0.010	1.90	—	—
4	semi-IPN	60	0.005	1.30	100	0.13
5	semi-IPN	60	0.010	2.62	43	0.23
6	semi-IPN	60	0.050	8.10	28	0.39
7	semi-IPN	80	0.010	7.05	30	0.56
8	semi-IPN	40	0.010	0.73	290	0.48

Notation: T_h is the hardening temperature, c_{ct} the catalyst concentration, K_r the reaction rate constant, τ_{MPS} the time of the onset of the MPS, and α_{MPS} the degree of conversion at the instant of the onset of the MPS.

A study[30] of the formation of polyurethane in the presence of 15% PBMA was devoted to the establishment of the relationship between the kinetics of the hardening of the half-IPN and the MPS during the formation of the polymeric two-phase system. Analysis of the results, presented in Table 1, shows that the onset of the MPS depends directly on the rate constant of the urethane formation reaction. Variation of the rate of reaction achieved by varying the catalyst concentration alters the degree of conversion at which phase separation begins from 23 to 39%, while variation of the rate of reaction effected by varying the temperature (40–80 °C) leads to the considerable scatter in the degrees of conversion (from 23 to 56%). The transformed kinetic curves presented in Fig. 3 are characterised by the presence of two sections, which indicates a change in the rate of reaction in the system after the attainment of a definite degree of conversion. Comparison of experiments 1 and 4, 2 and 5, 3 and 8 reveals a decrease in the rate of urethane formation by a factor of 3 in the presence of PBMA, but the nature of the transformed kinetic curves remained qualitatively the same as before. The degree of conversion at which MPS begins does not agree with the degrees of conversion at which a break is observed in the transformed curves (except for experiment 8). The results do not indicate a change in the reaction kinetics when MPS begins or in the vicinity of the degree of conversion corresponding to this process, which indicates the occurrence of MPS via the spinodal mechanism in the half-IPN formed.[31] Consequently the results agree with those of Lipatov and Grigor'eva,[28] confirming unambiguously that the MPS depends significantly on the reaction kinetics, regardless of the type of reaction (radical polymerisation or polyaddition) and that a change in the kinetics of the formation of the two-phase system influences its viscoelastic properties.

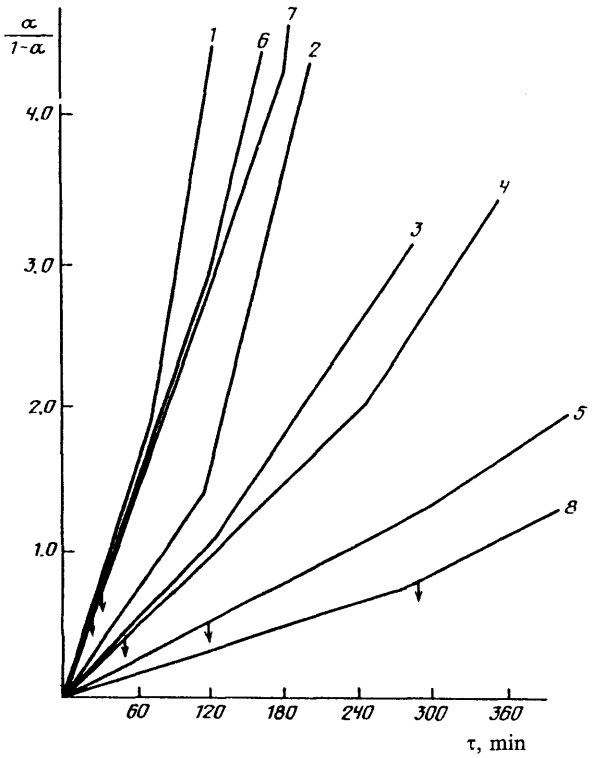


Figure 3. Transformed kinetic curves for the polyurethane network (curves *1–3*) in the semi-IPN based on polyurethane and PBMA (curves *4–8*); the significance of the symbols is indicated in Table 1.[30]

The kinetics of the formation of IPN based on polyurethane and polyurethane acrylate (in the IPN) were investigated for the first time by the method of distorted total internal reflection (DTIR) in the IR region with simultaneous hardening for different PU/OUA ratios (OUA = oligourethane acrylate). The transformed kinetic curves for the formation of polyurethane were linear up to a degree of conversion of 50%, which shows that the urethane formation reaction obeys a second-order equation. The initial slope of the curves (Fig. 4) depends significantly on the amount of oligourethane acrylate in the reaction mixture. Differentiation of these curves yielded the dependence of $|\partial\alpha/\partial\tau|$ on the composition, characterising the influence of the component ratio in the reaction mixture on the rate of the urethane formation reaction (Fig. 5). Fig. 5 shows that small amounts of added OUA play the role of an inhibitor of this reaction. For comparable amounts of the components in the OUA mixture, the formation of polyurethane is initially accelerated sharply, but, after the elapse of 45–60 min, the rate of formation of PU in the presence of PUA falls to values lower than in the individual PU.

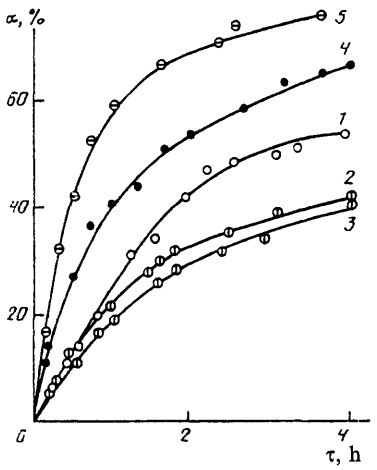


Figure 4. Kinetic curves for the hardening of pure polyurethane (curve *1*) and polyurethane in the IPN system; PUA (wt.%): *2*, 1; *3*, 5; *4*, 50; *5*, 70.[32]

Spectroscopic studies showed that the observed effect is not associated with the chemical interaction between unlike networks, since the spectra of the hardened IPN of different composition can be obtained by superimposing the spectra of the individual networks. On the other hand, some deviations from additivity, observed in the region of the stretching vibrations of the C=O and NH groups, indicate a redistribution of the network of physical bonds as the composition of the IPN is altered.

In IPN with comparable amounts of the components, the MPS process begins usually before the onset of gel formation in the individual networks, is fairly rapid, and is characterised by a high extent of completion. For both low and high OUA contents in the mixture, gel formation begins during the first 5–6 min of the reaction. The rapidly growing PUA network, segregated in the course of the MPS, displaces the reacting components of the first network (PU), intensifying their self-association and increasing the concentration of the reactants in the microregions, which accelerates the formation of polyurethane. Furthermore, the PUA segregated as a separate phase can play the role of a filler, which exerts an orienting influence on the components of the first network adsorbed on its surface, which can also accelerate its formation. The retardation of the polyaddition reaction at later stages of the formation of the IPN having this composition can apparently be explained by the fact that, as the reacting components are exhausted in the PU microregions, the process is controlled by the rate of diffusion of the components through the interface.

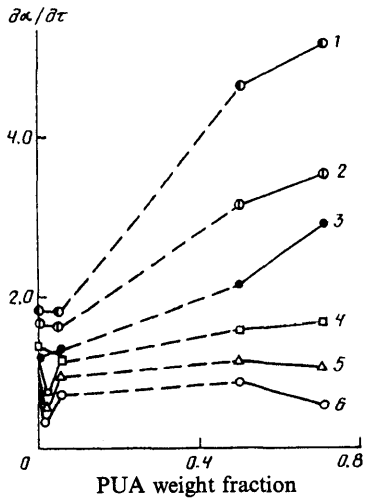


Figure 5. Concentration variation for the IPN; hardening time (min): *1*, 10; *2*, 20; *3*, 30; *4*, 45; *5*, 60; *6*, 90.[32]

For low contents of one of the components of the IPN, the MPS process is much slower. During the period investigated, the OUA has insufficient time to become segregated as a separate phase and the weakening of the bonds between the urethane groups and the appearance of free C=O groups (shoulder at 1740 cm^{-1}) indicates a significant redistribution of the intermolecular interactions after the introduction of small amounts of OUA.

These investigations showed that, in the formation of the IPN, the same component (OUA) can accelerate or retard the formation of the PU network depending on its fraction in the reaction mixture. We believe that this phenomenon is based on the dependence of the rate and the degree of completion of the MPS process on the composition of the reaction mixture. However, it has been shown[28,30] that the degree of MPS is a function of the rate of reaction. The onset of the MPS has been determined[30] during the reaction by the method of the appearance of turbidity points on an FPS-3 photocalorimeter. The experimental data (Table 1) show that, with increase in the rate constant for the formation of the PU network, the time of the onset of the MPS diminishes synchronously, which confirms unambiguously the dependence of the MPS on the reaction kinetics, whereas no breaks, which would indicate a change

in the rate of urethane formation at the instant of the onset of the MPS, are observed on the transformed kinetic curves for the formation of polyurethane at the point corresponding to the onset of the MPS (indicated by an arrow in Fig. 3).

The mutual influence of the kinetics of the formation of two unlike interpenetrating networks has been investigated in recent studies.[33–36]

Interpenetrating networks based on network polyurethane and an unsaturated polyester with styrene in molar proportions of 1 : 2 have been studied by FTIR spectroscopy[33] for simultaneous and consecutive reactions at 60 °C. Styrene served as an agent cross-linking polyester chains via the C=C bonds. Fig. 6 presents typical curves for the time variation of the degree of conversion for two phases (PU and PE) in the case of simultaneously produced IPN with a low-temperature radical polymerisation initiator for the component ratios PU/PE = 50/50 and 30/70 (wt.%). Similar kinetic curves are presented in Fig. 7 for the stepwise polymerisation of IPN with a high-temperature initiator.

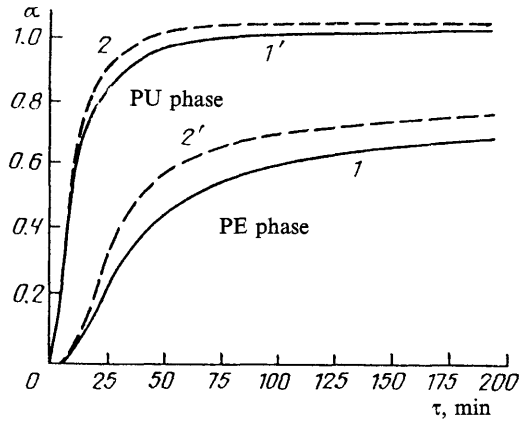


Figure 6. Time variation of the degree of conversion (α) for different PU/PE in the case of simultaneously formed IPN at T = 60 °C: *1*, 50/50; *2*, 30/70 (wt.%) (for polyurethane); *1′*, 50/50; *2′* 30/70 (wt.%) (for polyester).[33]

The use of the latter at 60 °C decreases the rate of reaction of the polyester component with the consecutive formation of IPN. It is of interest to note that, for both consecutively and simultaneously formed IPN, both reactions are accelerated with increase in the content of the polyester component 50 to 70 wt.%. The authors attribute this effect on the reaction of the polyester phase to the increased concentration of double bonds and, for the reaction of the polyurethane phase, to the fact that the rate of consumption of the NCO groups increases with the increase in the amount of the polyester component, since the NCO groups react with the OH groups of the polyol in the polyurethane phase and with the terminal OH groups of the unsaturated polyester. Consequently the degree of conversion in the polyurethane phase increases in proportion to the concentration of the polyester in the IPN, which indicates chemical interaction between the unlike polyurethane and polyester network structures and the given system can be classified as a graft IPN.

The polymerisation of the polyurethane in the IPN takes place in solution in the initial components of the polyester which have not yet reacted or have only partly reacted. On the other hand, the polymerisation of the polyester frequently takes place under conditions where the polyurethane network has been partly or fully formed, i.e. the polyester network is formed in the presence of the hardened second network, which is believed[33] to be in the solid state. Thus, when the IPN is created, there exists a "solvent effect" in the formation of the polyurethane network and a "solid effect" in the formation of the polyester network, which can influence the mechanism of the reactions occurring.

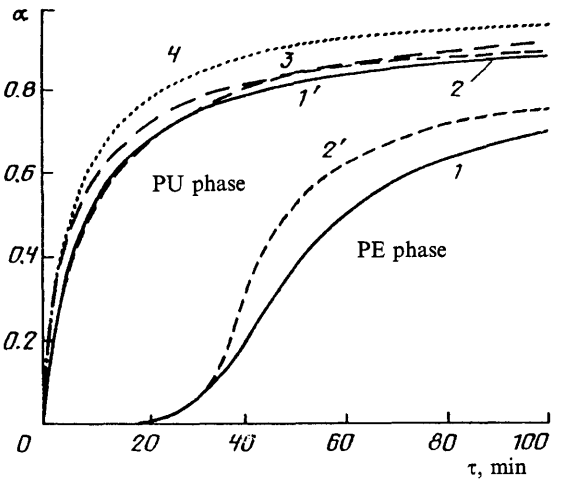


Figure 7. Time variation of the degree of conversion for different PU/PE in the case of consecutively formed IPN at T = 60 °C: *1–4*, for polyurethane; (*1′*, and *2′*) for polyester; *1*, PU/PE = 50/50; *2*, PU/PE = 30/70; *3*, PU/PE = 30/70; *4*, PU/PE = 50/50 (wt.%) [NCO/OH stoichiometric proportions (curves *1* and *2*)].[33]

Within the framework of formal kinetics, the authors obtained an equation for the overall rate of reaction in three possible versions: styrene–styrene, styrene–PE, PE–PE. The rate of reaction of the styrene monomer, the rate of conversion of the C=C bonds in the unsaturated polyester, and the rate of conversion of all the double bonds can be expressed thus:

$$-dc_S/d\tau = k_{SS}\cdot c_S\cdot c_S + k_{ES}c_E\cdot c_S,$$

$$-dc_E/d\tau = k_{SE}c_S\cdot c_E + k_{EE}\cdot c_E\cdot c_E,$$

$$-dc/d\tau = -(dc_S/d\tau + dc_E/d\tau) = k_{SS}\cdot c_S\cdot c_S + k_{ES}c_E\cdot c_S + k_{SE}c_S\cdot c_E + k_{EE}\cdot c_E c_{E'},$$

where S represents styrene, E represents the C=C bonds in the unsaturated polyester, S˙ and E˙ are the radicals in styrene and the polyester, c is the concentration, and k the rate constant. The rates of reaction can be determined experimentally from IR spectra.

Since the structure of the network in the polyester phase depends on the copolymerisation mechanism, information about the dependence of the degree of conversion of the polyester in the polyester phase is very important. Fig. 8 illustrates such dependences. If it is assumed that the contribution of the rate of the PE–PE

reactions to the overall rate is insignificant, then the rate of reaction of the styrene monomer can be expressed as follows relative to the rate of reaction of the C=C bonds in the polyester:

$$\frac{dc_S}{dc_E} = 1 + r_S \frac{c_S}{c_E}, \quad r_S = k_{SS}/k_{SE}.$$

If the copolymerisation takes place under azeotropic conditions, i.e.

$$c_E/c_S = 1 - r_S ,$$

then

$$\frac{dc_S}{dc_E} = \frac{c_S}{c_E} , \qquad \text{(curve 1)}$$

while for the alternative copolymerisation we have

$$\frac{dc_S}{dc_E} = 1 . \qquad \text{(curve 2)}$$

Experimental data for IPN show (Fig. 8, curve 3) that the PE–PE reaction in the polyurethane network is more favourable at low conversions than the styrene–PE and styrene–styrene reactions. This is probably associated with the fact that the polyurethane phase can intensify the intermolecular reactions of the polyester molecules. On the other hand, at high conversions the styrene–styrene reaction is more favourable than the reaction involving the C=C bonds in the polyester.

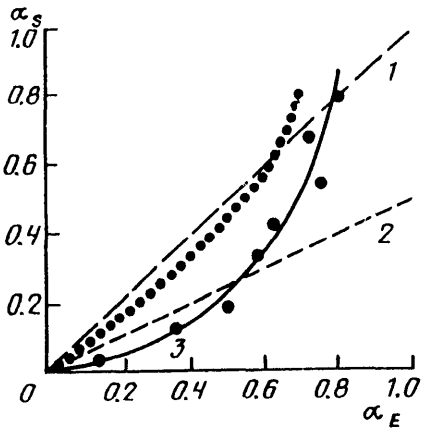


Figure 8. Dependence of the degree of conversion of styrene on the degree of conversion of C–C bonds for the PU–PE reaction in the IPN at T = 60 °C calculated theoretically for copolymerisation under azeotropic conditions (curve 1) and for alternating copolymerisation (curve 2) and determined experimentally for the 30/70 (wt.%) composition.[33]

The authors[33] concluded that the kinetics of the urethane formation reaction in bulk differ from the kinetics of the reaction in solution. However, if the IPN is created, the "solvent effect" operates in the formation of the polyurethane network and the "solid effect" operates in the formation of the polyester network, the two effects altering the mechanisms of both reactions. However, as regards the formation of the polyurethane in the presence of the polyester component, the authors do not take into account the "solvent effect" in their explanation of the increase in the rate of urethane formation with increase in the content of the polyester component in the IPN.

Fully grafted, half-grafted, and non-grafted IPN have been obtained[34] for three unsaturated polyesters and a polyurethane. The kinetics of the formation of the IPN as well as the rheological and morphological properties of the IPN obtained were investigated by differential scanning calorimetry, electron microscopy, and dynamic mechanical spectroscopy. The polyurethane component was obtained from diphenylmethane diisocyanate (MDI) and polycaprolactonetriol. The polyester component was obtained from the unsaturated polyester in the presence of styrene. The unsaturated polyester was synthesised from maleic anhydride and propylene glycol. The industrial non-block polyester contained terminal OH and COOH groups, the synthesised polyester contained only COOH groups, and the third type of unsaturated polyester was blocked using phenyl isocyanate.

Consequently fully grafted IPN were obtained on the basis of the industrial polyester, since there is a possibility of the interaction of the terminal OH and COOH groups with the NCO groups of the diisocyanate. Half-grafted IPN were obtained from the synthesised polyester as a result of the reaction of the COOH and NCO groups, while the blocked polyesters yielded non-grafted IPN.

Studies on such complex systems have shown that a better phase compatibility is characteristic of the fully grafted IPN, in contrast to the grafted and non-grafted IPN. It is manifested in the temperature variations by a broad peak in the range between 60° and 120 °C. The half-grafted IPN have three distinct peaks at 38°, 74°, and 120 °C, while the non-grafted IPN exhibit a high and broad peak at 50 °C and a shoulder at 99 °C. As the chemical interaction between the phases intensifies, the modulus of shear G' increases under these conditions. Thus the authors concluded that the interaction between the two phases plays an important role in decreasing the spreading of the phase separation between the polyurethane and polyester networks and also affects the kinetics of the formation of the IPN itself.

The relation between the kinetics of the formation of the two unlike three-dimensional structures in the IPN was also investigated for polyurethane–polyester acrylate.[35] The rate of hardening of polyurethane was determined by the ratio of the tri(hydroxymethyl)-propane–tolylene diisocyanate adduct and the oligoglycol, while the rate of hardening of polyester acrylate (PEA) was specified by the concentration of the initiator AIBN (0.01% for series I, 0.5% for series II, and 3.0% for series III). The kinetics of the formation of the IPN were investigated by the DTIR method. Figs. 9 and 10 illustrate the kinetic curves for the hardening of the polyurethane and PEA networks separately and in the blend. Judging from the slopes of these curves, the rates of cross-linking of unlike networks in the IPN, obtained by the single-stage method, are not independent.

Special experiments showed that the mutual influence is not associated with the chemical interaction between the networks. The authors determined the rate of hardening $\partial\alpha/\partial\tau$ of polyurethane or PEA at each point on the curve from the dependence of $\partial\alpha/\partial\tau$ on the composition of the IPN for different contents of the initiator at fixed time intervals elapsed since the beginning of the reactions. It was shown that the rate of urethane formation in the IPN depends, especially in the initial stages, on the concentration of the oligoester

acrylate and on the rate of its hardening. In the presence of small amounts of additives, the PEA network retards the cross-linking of the polyurethane. The oligoester acrylate inhibits the cross-linking in the series I specimens, where it is hardened at a lower rate than the individual polyurethane. In the series II specimens, the oligoester acrylate hardening at a higher rate inhibits the cross-linking of the matrix network less effectively. In series III, the retardation of the urethane formation reaction is observed over a wide range of compositions.

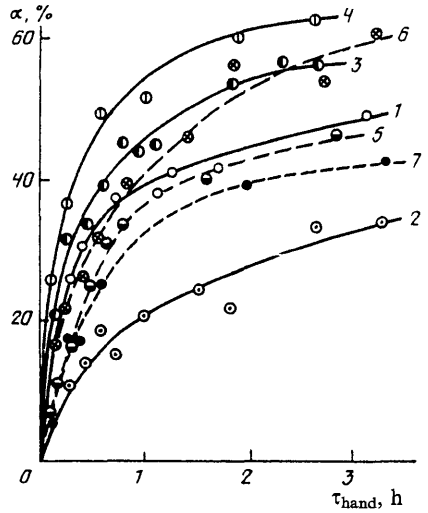


Figure 9. Kinetic curves for the hardening of pure polyurethane (curve *1*) and the polyurethane in the IPN for different PEA contents (wt.%): *2*, 0.5; *3*, *6*, and *7*, 2; *4*, 20; *5*, 0.3; curves *1*–*4* refer to series I, curves *5* and *6* to series II, and curve *7* to series III;[35] τ_{hard} = hardening time.

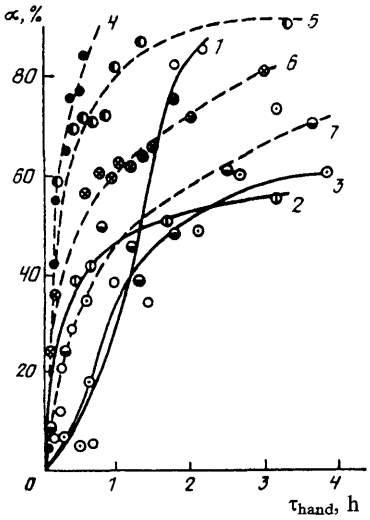


Figure 10. Kinetic curves for the hardening of pure PEA (curves *1* and *4*) and the PEA in the IPN for different PU contents (wt.%): *2*, and *6*, 30; *3*, and *7*, 50; *5*, 10; curves *1*–*3* refer to series I and curves *4*–*7* to series II.[35]

In the range of average compositions, the oligoester acrylate (OEA) accelerates the cross-linking of the polyurethane already in the initial stages of the reaction and the effect depends on the rate of hardening of the OEA. The rate of formation of PEA in the IPN is determined in its turn both by the initiator concentration and by the content of polyurethane. In the series I IPN, the polyurethane hardening at a higher rate initiates the cross-linking of the OEA in the experimental range of compositions. On the other hand, in series II, where the rate of its hardening is lower than that of the OEA, it behaves as an inhibitor of this process.

As the reaction mixture is hardened, the chemical composition and the system of intermolecular interactions continuously change. At a certain degree of conversion, the growing networks become thermodynamically incompatible. Following the onset of microphase separation, the influence of the PEA network on the hardening of the polyurethane should weaken. Indeed, the rate of hardening of the adduct in the IPN approaches the rate of hardening of the pure polyurethane as the reaction develops. After a time, microregions of the "rigid block" type arise in the segregated polyurethane phase, which is indicated by the appearance in the spectrum of bands due to the self-associated urethane groups at 1710 to 1720 cm^{-1}.

On the basis of the results, the authors conclude that, for the simultaneously formed IPN, the rates of hardening of unlike networks are related via the microphase separation process. In IPN with small amounts of the second network, the time of the onset of microphase separation increases sharply and the hardening of the IPN having this composition is characterised by a low degree of segregation of the components and by diffuse phase boundaries.

It is of interest to investigate the kinetics of the formation of simultaneously produced IPN based on polyurethane and polystyrene (PS) by IR spectroscopy.[36] The effects of temperature, of the concentrations of the catalyst, the initiator, and the cross-linking agent for polystyrene, and of the PU/PS ratio on the rates of the formation reactions of polyurethane and polystyrene were investigated. The kinetic results for the urethane formation reaction obtained spectroscopically agree with data obtained by chemical titration. It was shown that, with increase in the ratio PU/PS, the rate of formation of polyurethane increases and the rate of formation of polystyrene diminishes. The variation of the concentration of the catalyst (OcSn) affects the rate of formation of polyurethane but not the rate of formation of polystyrene in simultaneous reactions. The radical polymerisation reaction behaves similarly.

The authors observed that the rate of urethane formation and the rate of the radical polymerisation of styrene are higher for the pure systems than in the IPN. The results obtained for the polymerisation of styrene are surprising, since the catalyst and initiator concentrations in the polyurethane–polystyrene system investigated were chosen in such a way that the rate of formation of polyurethane should be much higher than the rate of formation of the polystyrene. Consequently the polystyrene in the IPN is formed when the degree of conversion of the polyurethane reaches 40–60%, depending on the conditions in the formation of the IPN, and the viscosity of the medium is high. The rate of termination of radical polymerisation is known to diminish sharply with increase in the viscosity of the medium and the rate of formation of polystyrene in the IPN after autoacceleration should therefore be higher than the rate for the pure polystyrene, which was not observed in the above study.

One should also note that the authors[36] do not attempt to explain the influence of the catalyst of initiator, when they are varied, on the formation of polystyrene or polyurethane. However, it has been shown[35,37] that these two processes are so interrelated that a change in the rate of urethane formation is reflected in the rate of formation of polystyrene in the IPN.

A more detailed study of the kinetics of the formation of IPN and semi-IPN confirmed the close relation with microphase separation.[37] It was shown that the rates of formation of the two three-dimensional structures via different mechanisms (polyaddition and radical polymerisation) in the IPN and the formation of the network and linear polymers in the semi-IPN are interrelated: a change in the formation of one of the networks affects significantly the rate of hardening of the second network or the linear polymer. In addition, two processes are superimposed under these conditions: the physical microphase separation process is superimposed on the chemical IPN formation processes.

Table 2. Composition and parameters of the microphase separation in the semi-IPN based on polyurethane and PBMA.[37]

PU/PBMA, wt.%	$I \times 10^2$, M	$K \times 10^3$, % s^{-1}	τ_{MPS}, min	α_{MPS}	
				PU	PBMA
75/25	0.74	0.7	70	0.57	0.034
75/25	0.48	0.83	65	0.50	0.040
75/25	2.96	2.66	55	0.38	0.062
75/25	5.40	3.80	45	0.36	0.080
75/25	10.80	6.60	35	0.21	0.091
65/35	5.40	2.20	65	0.37	0.110
85/15	5.40	5.50	60	0.45	0.28

Notation: I is the initiator concentration and K the rate constant for polymerisation to PBMA before autoacceleration.

The objects of study were semi-IPN and IPN. The semi-IPN was obtained by the method involving the formation of the network polyurethane from polyoxypropylene glycol with a molecular weight of 2000 and an adduct [the product of the interaction of tri(hydroxymethyl)propane with tolylene diisocyanate in proportions of 3 : 1] in the presence of butyl methacrylate (BMA), in which the radical polymerisation initiator (AIBN) had been dissolved beforehand. The catalyst concentration for the urethane formation reaction was constant in all the experiments and equal to 1.4×10^{-4} M. The kinetics of the formation of polyurethane and poly(butyl methacrylate), individually and as part of the composition of the semi-IPN, were investigated at 60 °C using a DAK-1-1A differential calorimeter. The onset of the MPS during the reaction was determined simultaneously for the same systems and under the same kinetic conditions by the method of turbidity points using an FPS-3 photocalorimeter. The composition of the semi-IPN obtained and the time of the onset of the MPS are given in Table 2. Assuming the additivity of the contributions of the heats of formation of each component of the semi-IPN to the overall heat evolution in the reaction, the heat evolution area corresponding to the formation of PBMA in the semi-IPN and the degree of conversion into the PBMA in the half-IPN were determined. The area under the heat evolution curve corresponding to urethane formation was calculated from the degree of conversion obtained by an independent method (back titration of the NCO groups).[38] The kinetic curves for the formation of polyurethane and PBMA in the half-IPN thus obtained for the ratios 75/25 wt.%) in the presence of different initiator concentrations (Fig. 11) show that, for simultaneously occurring reactions, the rate of formation of the polyurethane diminishes with increase in the initiator concentration as does the rate of formation of PBMA compared with the rate of formation of the individual polyurethane network. Evidently the retardation of the polyurethane network formation reaction in the semi-IPN formed can be attributed to the increase in the viscosity of the PBMA reaction system. The rate of polyurethane formation is lower, the higher the rate of formation of PBMA (Fig. 11). Polymerisation to give PBMA takes place in a matrix consisting of a mixture of the polyurethane formed at the given instant and the components from which it is synthesised, i.e. the polymerisation reaction takes place, as it were, in a "dilute" system, as a result of which the initial rate of formation of PBMA is diminished compared with the pure polymer. However, subsequently the rate of formation of PBMA in the semi-IPN becomes higher than for the pure PBMA, which is clearly seen from the variation of the reduced rates of formation of the initial PBMA and the PBMA in the IPN (Fig. 12). This increase in rate may be associated with the overall increase in the viscosity of the reaction system.[17] During the formation of the semi-IPN, the viscosity increases so much that it leads to a sharp decrease in the termination constant (K_t) relative to the propagation constant (K_p) and hence to an increase in the ratio K_p/K_t and in the rate of chain propagation V_p in accordance with Eqn. (1).[17]

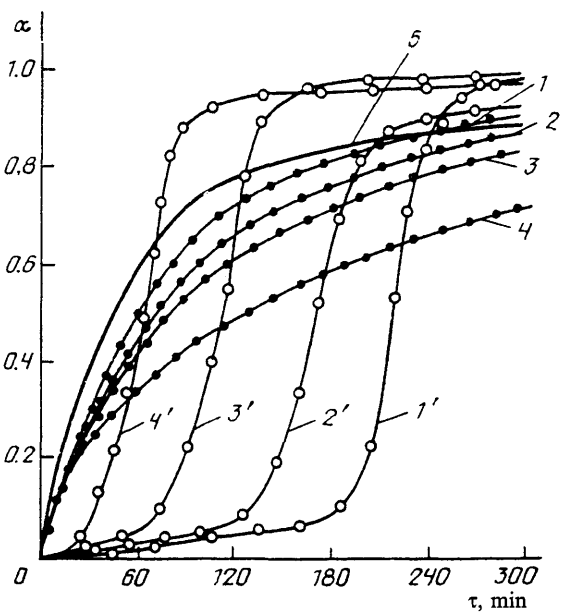


Figure 11. Kinetics of the formation of polyurethane (curves *1–4*) and PBMA (curves *1′–4′*) in the semi-IPN with the composition PU/PBMA = 75/25 for different initiator concentrations $I \times 10^2$(M): *1*, 0.74; *2*, 1.48; *3*, 2.96; *4*, 10.8; *5*, polyurethane.[37]

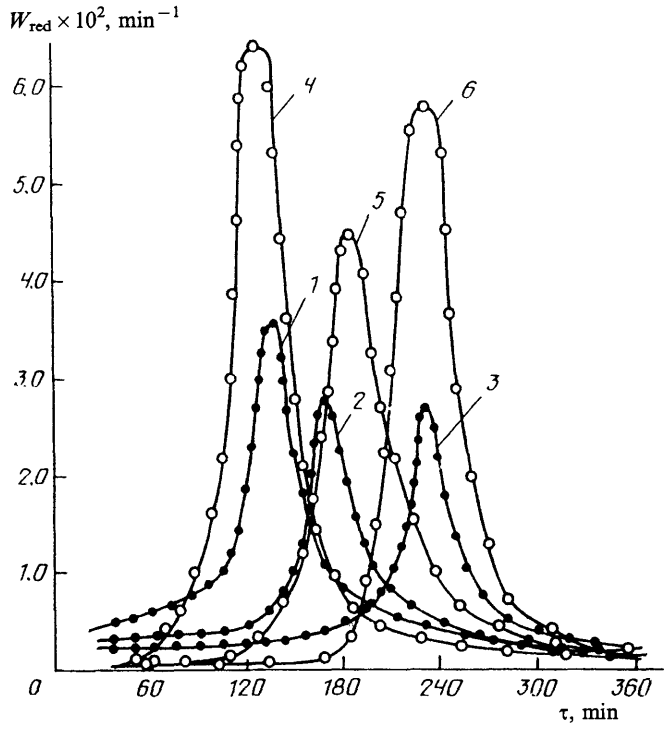


Figure 12. Time variation of the reduced rate of polymerisation (W_{red}) of butyl methacrylate at different molar initiator concentrations $I \times 10^2$ for the pure methacrylate (curves *1*–*3*) and the methacrylate in the semi-IPN with the composition 75/25 (curves *4*–*6*): *1*, and *4*, 2.96 M; *2*, and *5*, 1.48 M; *3*, and *6*, 0.74 M.[37]

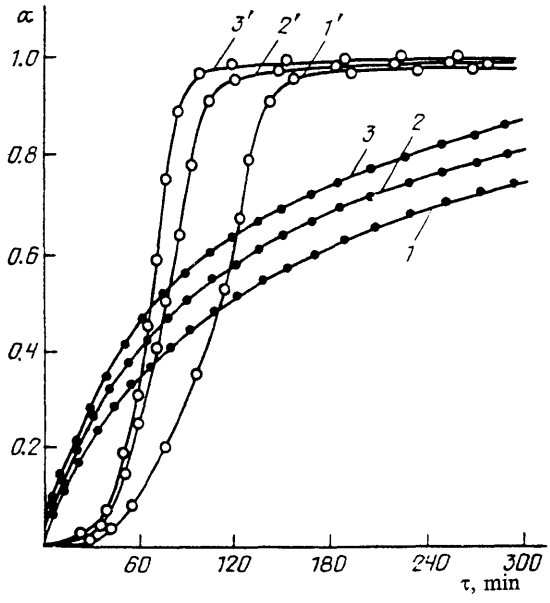


Figure 13. Kinetics of the formation of polyurethane (curves *1*–*3*) and PBMA (curves *1′*–*2′*) in the semi-IPN for $I = 5.4 \times 10^{-2}$ M and different component ratios (wt.%): *1*, and *1′*, 65/35; *2*, and *2′*, 75/25; *3*, and *3′*, 85/15.[37]

Fig. 13 presents kinetic curves for polyurethane and poly(butyl methacrylate) in different proportions in the blend at constant initiator and catalyst concentrations. The calculated reduced rates (W_{red}) for PBMA in the blend show that the rate of formation of PBMA increases in the sequence 65/35 < 75/25 < 85/15 compared with the initial rate, which is associated with the increase in the viscosity of the system. In the experiment with the 85/15 (wt.%) ratio, the viscosity was higher than in the experiment with the 65/35 (wt.%) ratio. Hence K_t diminished and K_p and V_p increased. As can be seen from Fig. 13, the rate of formation of polyurethane under these conditions in the blend diminishes in the sequence 85/15 > 75/25 > 65/35 compared with initial rate.[37]

If one adopts the concept already formulated and assumes the existence of a relation between the kinetics of the formation of the IPN and the microphase separation processes, then it is evident that there exists a distinct relation between the kinetics of the formation of the IPN and its structural characteristics. Such a relation has been established for semi-interpenetrating networks based on cross-linked polyurethane and PBMA formed in a polyurethane network matrix by the radical polymerisation of the monomer.[39]

Table 3 presents some data concerning the conditions in the formation of networks and their structural characteristics determined from low angle X-ray scattering data.[40] The polyurethane formation reaction in the given system begins before and terminates after the butyl methacrylate polymerisation reaction. As can be seen from the data in Table 3, with increase in the initiator concentration and hence in the overall rate of reaction, the heterogeneity distance l_s and the extent of the transition layer also increase. These data can be interpreted as follows. The increase in the rate of formation of PBMA leads to a faster onset of the thermodynamic incompatibility of the components of the interpenetrating network considered (we neglected here the differences between the molecular weights of the PBMA associated with the differences in the rate of initiation). There is then a rapid increase in the viscosity of the reaction system. Against the background of the simultaneous formation of the polyurethane network, these factors retard the microseparation process as a consequence of both the increase in viscosity and the fixation of the microphase separation regions arising on formation of the polyurethane network. The larger dimensions of the inhomogeneity regions and the greater extent of the transition layer are "quenched" as a result.

Table 3. Composition of the semi-IPN based on polyurethane and PBMA and their structural parameters.[39]

No. of specimen	PU/PBMA	$I \times 10^2$, M	Method of synthesis of the IPN	l_s, Å	E^2, (Å)^2
1	75/25	0.74	simultaneous	68	38
2	75/25	5.4	" "	70	27
3	75/25	10.8	" "	75	60
4	85/15	5.4	" "	65	37
5	65/35	5.4	" "	81	61
6	75/25	5.4	stage I–photopolymerisation, stage II–thermopolymerisation	66	21
7	75/25	5.4	stage I–thermopolymerisation at 25 °C, stage II–photo-polymerisation	72	65

Notation: l_s is the heterogeneity parameter and E^2 the thickness of the transition layer.

Indeed it is known[41] that, on spinodal separation, the boundary between the microphase regions in the initial stages is diffuse, but subsequently the differences between the compositions of these regions and the boundary become more distinct. Judging from the experimental data for the structure of the IPN, the observed structural parameters are consistent with this finding. The sooner is the structure of the IPN fixed as a consequence of the inhibition of the microphase separation process, the greater are the microheterogeneity distances and the thickness of the transition layer. Indeed, for the same rate of initiation but for a different PU/PBMA ratio [85/15 and 65/35 (wt.%)] in those cases where the content of PBMA is higher, separation is evidently slower, the transition layer is more extensive, and the heterogeneity distance is longer. We also observed a difference between the structural characteristics of consecutively formed IPN, based on the same components, under the conditions of the polymerisation of butyl methacrylate in the matrix of a polyurethane network formed previously.

Thus one may claim that there exists a relation between the structure of the hardened IPN and the kinetics of the formation of the constituent networks, the latter determining the possibility of the occurrence of the microphase separation process. However, since, apart from the factors which we have examined, the microphase separation is influenced also by others (including the change in the thermodynamic compatibility as a function of the composition and the degree of conversion which we did not take into account), a more detailed treatment of the above data does not appear desirable.

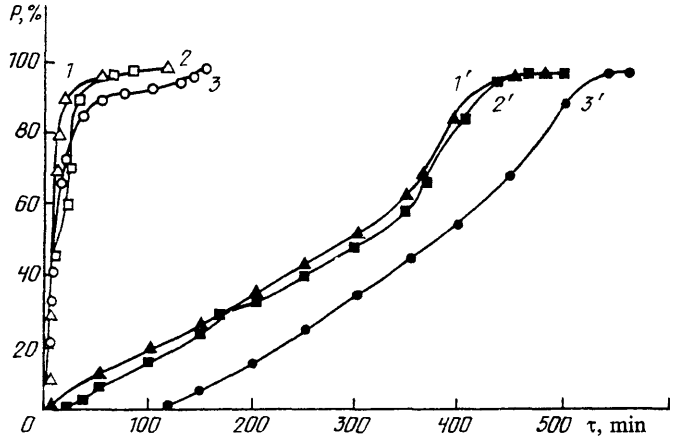


Figure 14. Time variation of the degree of conversion (P) in the formation of the semi-IPN with the composition PU/PS = 30/70 (wt.%) for different polyurethane formation times before the onset of the radical polymerisation of styrene: *1*, and *1′*, 5 min; *2*, and *2′*, 15 min; *3*, and *3′*, 2 h; *1*–*3*, polyurethane; *1′*–*3′*, polystyrene.[42]

The kinetics of the formation of polyurethane and polystryene as part of the composition of a semi-IPN as well as the influence of different kinetic conditions in the formation of the half-IPN on the phase separation in the system have been investigated[42] by FTIR spectroscopy. In order to obtain the half-IPN with the composition PU/PS = 30/70 (wt.%), a mixture of the initial components was maintained at room temperature for different times τ (5 min, 15 min, and 2h) and then the temperature was raised to 70 °C and the mixture was polymerised until the complete disappearance of double bonds. Fig. 14 presents kinetic curves for the formation of polyurethane and polystyrene. Evidently, for times of 5 and 15 min, the polyurethane network and polystyrene are formed simultaneously but at different rates, whereas for τ = 2 h polystyrene is formed in the fully polymerised polyurethane network. The different kinetic conditions in the formation of polyurethane influenced the phase separation in the system, which is clearly seen from the time variation of the transmittance (T, %) (Fig. 15). The system loses transparency on simultaneous formation of polyurethane and polystyrene (τ = 5 min) when the degree of conversion into polystyrene is about 2%. When the semi-IPN is obained consecutively (τ = 2 h), the system remains transparent, but for τ = 15 min a tendency towards a decrease in transmittance (T, %) is observed at later stages in the formation of the half-IPN.

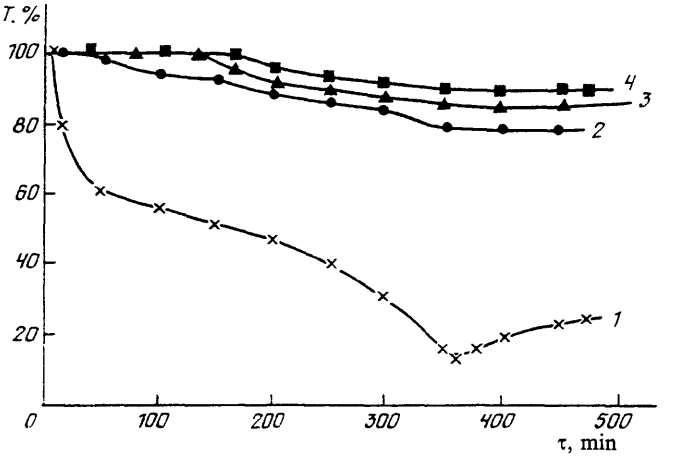


Figure 15. Transmittance (T) curves for the semi-IPN with the composition PU/PS = 30/70 (wt.%) at 70 °c for different polyurethane formation times before the radical polymerisation of styrene: *1*, 5 min; *2*, 15 min; *3*, 2 h; *4*, 6 h.[42]

The introduction of polymerised polystyrene and polyurethane in an amount of 0.5–1% in the first minute induces phase separation in the reaction system. The authors also showed that, with increase in M_n for polystyrene, phase separation is manifested sooner and becomes explicit (Fig. 16). Thus the authors conclude that, when the reaction mixture is separated before the onset of gel formation in polyurethane, the half-IPN are turbid. If separation takes place after gel formation, then transparent IPN are produced, i.e., using certain kinetic parameters it is possible to obtain materials with a wide range of properties.

In order to investigate further the influence of the kinetics of the formation of IPN on the microphase separation, a study was made of IPN based on two networks: polyurethane and a loosely cross-linked butyl methacrylate in the presence of triethylene glycol dimethacrylate (TGM-3).[43] The composition of the IPN and the concentrations of the cross-linking agent (TGM-3), the initiator, and the catalyst are presented in Table 4. The kinetics of the formation

of the IPN were investigated by the calorimetric method described above. The kinetic curves for the initial polyurethane and PBMA and the copolymer with the cross-linking agent TGM-3 having different contents of the latter are presented in Fig. 17. Fig. 17 shows that the initial section on the kinetic curves for the radical polymerisation of butyl methacrylate and the butyl methacrylate–TGM-3 copolymer remains unchanged, so that the introduction of a small amount of the cross-linking agent (up to 0.15 M) does not affect the initial rate of polymerisation of butyl methacrylate but does influence the degree of conversion (α_a) at which autoacceleration begins. With increase in the concentration of TGM-3, the degree of conversion falls, but, after the attainment of a definite value of α_a, the rate of formation of the copolymer increases with increase in the amount of cross-linking agent. This is usually explained by the decrease in the rate of the chain termination reaction when the rate of initiation and the rate of chain propagation are altered slightly. Kinetic curves for polyurethane and PBMA have been obtained by the method described for simultaneously produced IPN with the compositions 75/25 and 65/35 (wt.%) (Fig. 18) in the presence of different concentrations of the initiator and cross-linking agent (Table 4). The experimental data show[43] that the rate of formation of the butyl methacrylate–TGM-3 copolymer in the IPN diminishes in the initial stage owing to the dilution by the components of the polyurethane network but subsequently increases compared with the initial value and the degree of conversion at the onset of the autoacceleration (α_a) diminishes under these conditions. It has been observed that the rate of polymerisation of the copolymer in the IPN changes after the start of autoacceleration with increase in the initiator concentration (Fig. 18, curves *2* and *3*) and a slight decrease in the degree of conversion after the onset of autoacceleration is observed. Under these conditions, the rate of urethane formation also diminishes slightly (curves *1*–*3*). The change in the rate of formation of the loosely cross-linked PBMA in the IPN owing to the variation of the initiator and cross-linking agent concentrations is manifested more markedly on the kinetic curves for the formation of polyurethane in the IPN for the component ratio 65/35 (wt.%) (Fig. 19).

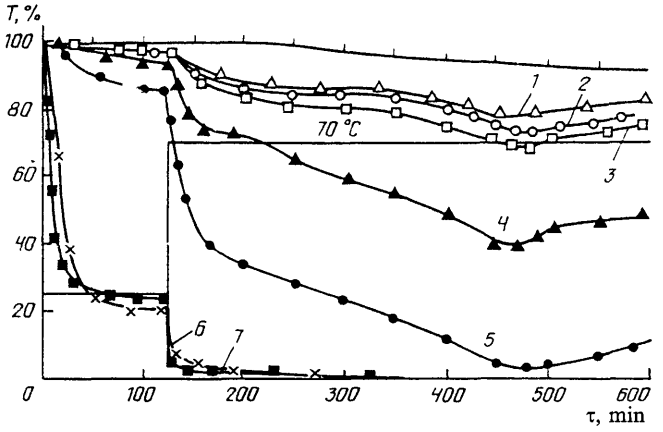


Figure 16. Transmittance (*T*) curves for the semi-IPN with the composition PU/PS = 30/70 (wt.%) at 70 °C with 0.5% polystyrene having different molecular weights M_n: *1*, 2000; *2*, 4900; 3, 22 000; *4*, 27 000; *5*, 40 300; *6*, 52 000; *7*, 105 000.[42]

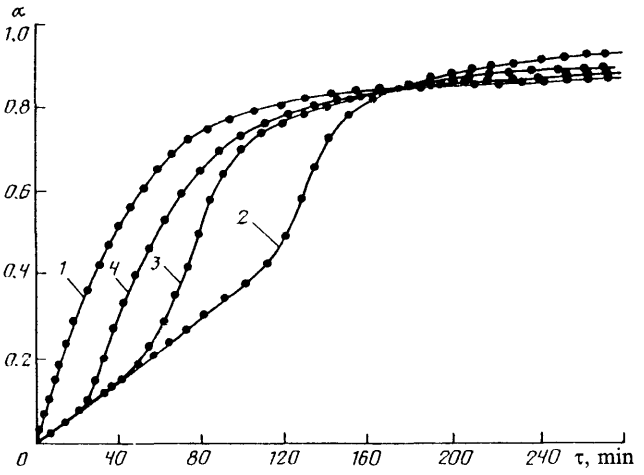


Figure 17. Kinetics of the formation of polyurethane (curve *1*) and PBMA (curve *2*) and of the copolymerisation of butyl methacrylate with triethylene glycol dimethacrylate: *2*, $I = 2.96 \times 10^{-2}$ M; *3*, PBMA + TGM-3; $I = 2.96 \times 10^{-2}$ M, [TGM-3] = 0.031 M; *4*, PBMA + TGM-3, $I = 2.96 \times 10^{-2}$ M, [TGM-3] = 0.156 M.[43]

Table 4. Physicochemical parameters of the IPN based on polyurethane and PBMA.[43]

PU/PBMA (wt.%)	$I \times 10^2$, M	[TGM]*, M	τ_{MPS}, min	α_{MPS}	
				PU	PBMA
75/25	2.96	0.031	60	0.51	0.045
75/25	2.96	0.156	56	0.47	0.050
75/25	5.40	0.031	57	0.44	0.200
65/35	2.96	0.031	60	0.47	0.030
65/35	2.96	0.156	56	0.42	0.050
65/35	5.40	0.031	38	0.28	0.070
50/50	2.96	0.156	70	0.37	0.040

*[TGM] is the concentration of the cross-linking agent.

The calculated reduced rates (W_{red}) for PBMA in the blend for different component ratios show that the rate of formation of PBMA increases in the sequence 50/50 < 65/35 < 75/25 (wt.%). Under these conditions, the dependence of the maximum reduced rate on the PU/PBMA ratio is linear (Fig. 20) and is correlated with data obtained for the semi-IPN. The explanations are similar: with increase in the viscosity of the system, the termination constant diminishes and the chain propagation constant increases with the corresponding increase also in the rate of formation of the copolymer in conformity with Eqn. (1) presented above. The rate of formation of polyurethane diminishes in the sequence 75/25 > 65/35 > 50/50 (wt.%).

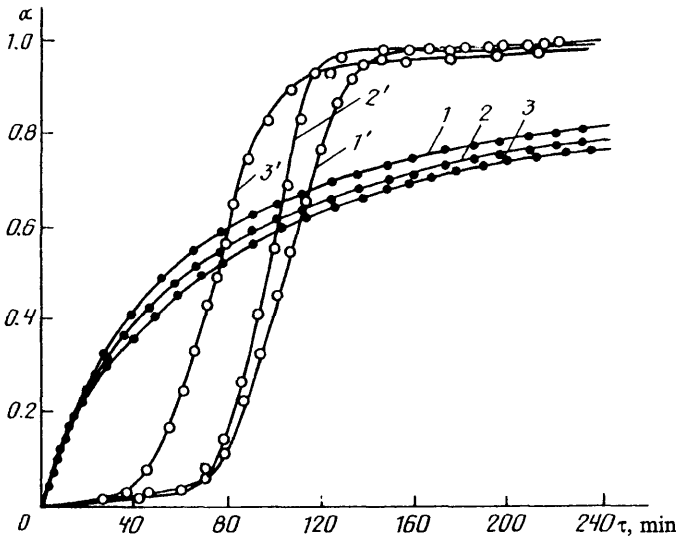


Figure 18. Kinetics of the formation of polyurethane (curves *1*–*3*) and of the cross-linked PBMA (curves *1'*–*3'*) in the IPN for PU/PBMA = 75/25 (wt.%) and different TGM-3 and initator concentrations: *1*, and *1'*, $I = 2.96 \times 10^{-2}$ M, [TGM-3] = 0.031 M; *2*, and *2'*, $I = 2.96 \times 10^{-2}$ M, [TGM-3] = 0.156 M; *3*, and *3'*, $I = 5.4 \times 10^{-2}$ M, [TGM-3] = 0.031 M.[43]

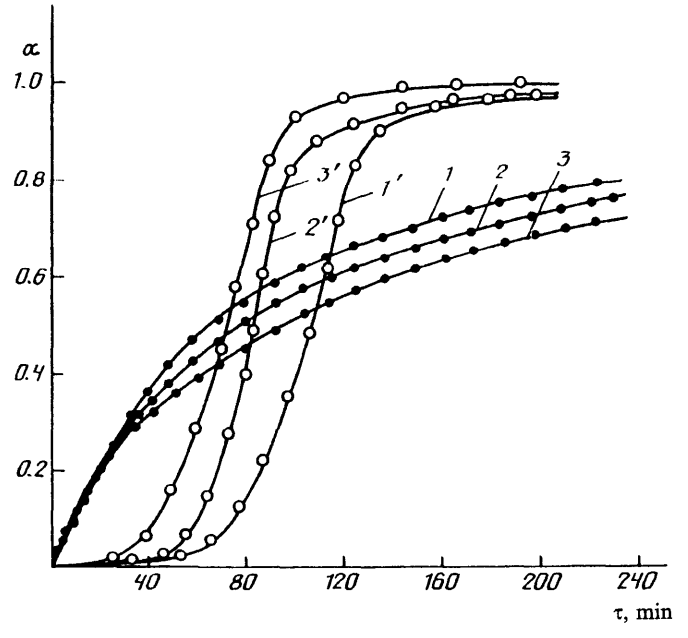


Figure 19. Kinetics of the formation of polyurethane (curves *1*–*3*) and of the cross-linked PBMA (curves *1'*–*3'*) in the IPN for the ratio PU/PBMA = 65/35 (wt.%) and different TGM-3 and initiator concentrations: *1*, and *1'*, $I = 2.96 \times 10^{-2}$ M, [TGM-3] = 0.031 M; *2*, and *2'*, $I = 2.96 \times 10^{-2}$ M, [TGM-3] = 0.156 M; *3*, and *3'*, $I = 5.4 \times 10^{-2}$ M, [TGM-3] = 0.031 M.[43]

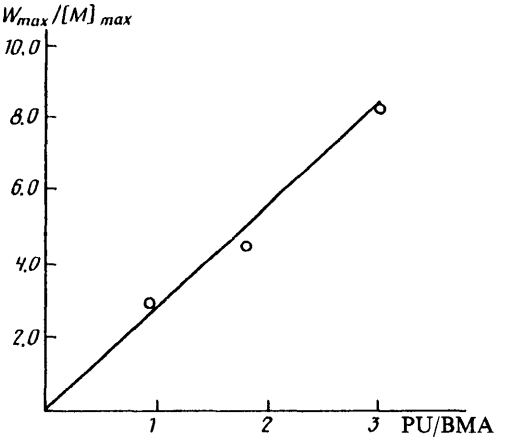


Figure 20. Dependence of the maximum reduced rate of polymerisation of butyl methacrylate in the presence of TGM-3 in the IPN on the component ratio.[43]

Analysis of the data obtained on the kinetics of the formation of polyurethane and PBMA in the case of the simultaneously produced semi-IPN and IPN leads to the conclusion that the introduction of the cross-linking agent for the second polymer network accelerates the formation of the second network, which is reflected directly in the kinetics of the formation of the first network. This is manifested more strikingly with increase in the amount of the second network. The features of the kinetics of the formation of the two networks remain unchanged as the component ratio PU/PBMA varies both in the IPN and in the semi-IPN.

We shall now consider the influence of microphase separation in semi-IPN and IPN and the kinetics of the reactions in the given system. The onset of the MPS was determined simultaneously for the same systems and under the same kinetic conditions in the course of the reaction by the method of turbidity points on an FPS-3 photocalorimeter.[37,43] Tables 2 and 3 present data characterising the microphase separation occurring during the formation of the semi-IPN and the IPN. Analysis of the data presented shows that the time to the onset of the MPS diminishes almost linearly with increase in the concentration of the initiator of the polymerisation of PBMA in the semi-IPN. Calculation of the rate of reaction of PBMA along the initial section (up to the onset of autoacceleration) shows that there is also a linear relation between this quantity and the time of the onset of the MPS. It follows from Table 2 that, for a constant initial composition of the system, the degree of conversion into the polyurethane diminishes at the instant of phase separation with increase in the rate of polymerisation, while the degree of conversion of PBMA increases. The weight fractions of the components in the phase separation were determined from the initial system composition for different rates of polymerisation.[37] Evidently the fraction of polyurethane then falls while that of PBMA increases, which is associated with the influence of the initiator concentration, examined above, on the ratio of the reaction rates. Compatibility is known to be determined not only by the component ratio but also by the ratio of the molecular weights. Evidently the amount of polymer formed at the instant of phase separation, and not the molecular weight, plays a decisive role in the appearance of

incompatibility. We may note that the weight fraction of polyurethane in the semi-IPN at the instant of phase separation is significantly greater than its value in the initial system (of the order of 0.9), which also suggests that the accumulation of PBMA is the decisive factor in the PMS. The higher the rate of polymerisation leading to PBMA, the higher the degree of conversion into PBMA at the phase separation point, and the lower the fraction of polyurethane for which separation begins, while the time up to the onset of the MPS in the system diminishes.

The onset of the MPS depends also on the ratio of the polyurethane and PBMA components in the semi-IPN. For the component ratio 85/15 (wt.%), the degree of conversion up to the onset of MPS is indeed higher for both components than for the ratio 75/25 wt.%, while in the case of the ratios 65/35 and 75/25 wt.%) the degrees of conversion are similar. At the same time the weight fraction of the polyurethane at which MPS begins proved to be smallest for the 65/35 ratio and greatest for the 85/15 (wt.%) ratio. Account must be taken of the fact that the rate of MPS in a highly viscous medium is clearly lower than the rates of the reactions and may therefore lag in time behind the degree of conversion at which this would have occurred under equilibrium conditions uncomplicated by the reaction occurring in the previous period.

The study of the influence of microphase separation on the kinetics of the formation of IPN showed that, for a constant composition of the components, the degree of conversion into polyurethane at the instant of phase separation falls with increase in the rate of formation of PBMA and the degree of conversion into PBMA increases, the influence of the initiator concentration being more marked compared with that of the cross-linking agent. Such behaviour can be traced for two component compositions — 75/25 and 65/35 (wt.%). The time up to the onset of MPS in the system diminishes sharply only for the component ratio 65/35 (wt/%) with increase in the initiator concentration to 5.4×10^{-2} M. When the component ratio is altered at constant initiator and cross-linking agent concentrations, the time of the onset of MPS increases to 70 min and the degree of conversion into polyurethane diminishes from 0.49 to 0.37 and that into PBMA varies in the range 0.04 – 0.05.[43]

Consequently, an increase in the rate of polymerisation, which increases the degree of conversion into PBMA, reduces the time before the onset of phase separation. However, the most significant conclusion arising from the analysis of the rates of reaction and the times of the onset of MPS is as follows. As can be seen from the kinetic data, both before the onset of MPS and afterwards, the nature of the kinetic curves remains unchanged, i.e. the MPS is not reflected in the rates of the continuing reactions. This means that, in the region becoming segregated, the MPS alters the composition to one close to the average composition of the system, i.e. in each segregated phase the ratio of the reacted and unreacted components is approximately the same. This situation can occur only in the case of a microphase separation which proceeds via the spinodal mechanism and is in its initial stage. Evidently, the microheterogeneous system, arising as a result of the formation of the network, is then chemically "quenched",[44] which prevents further phase separation after the attainment of a definite degree of conversion. Otherwise the microphase separation would have progressed further and deviations of the rates of reactions from those in the initially separating system should have been observed, and this is not the case up to high degrees of conversion.

Thus one may conclude that the simultaneously occurring chemical formation reactions of polymer molecules constituting the semi-IPN and the IPN and the physical microphase separation processes take place under non-equilibrium conditions.

This makes it possibile to represent in the following way the process leading to the formation of the IPN. When the IPN is synthesised, the initial reaction system consists of a homogeneous mixture of components capable of forming two independent three-dimensional networks in the course of the chemical reactions occurring via different mechanisms. After the attainment of a definite degree of conversion, as a rule before the attainment of the sol – gel transition point, the growing fragments of the constituent networks become incompatible in the system. The condition for this is the attainment by the thermodynamic interaction parameter χ_{23} of the critical value predicted by the theory. The initial phase separation conditions are specified by the conditions for the transition of the parameters χ_{23} from negative (region of compatibility) to positive (region of incompatibility) values or by the conditions under which χ_{23} becomes zero for the given system composition and at the given temperature. In most cases, this takes place in the initial stages of the reaction in the kinetic region. However, phase separation takes place from the very beginning under non-equilibrium conditions, because it occurs simultaneously with the developing chemical reaction, altering the parameter χ_{23} and thus the phase separation conditions. The rate of attainment of the critical value of the parameter χ_{23} is determined by the rates of the two independent reactions, while the phase separation process begins before the completion of gel formation in the constituent networks.

In the initial period of the reaction (low degrees of conversion), the onset of phase separation is determined solely by the rate of reaction, i.e. by the rate of formation of the polymer and the increase in its molecular weight. However, the cross-linking of sections of the growing chains into a continuous network and the rapid increase, as a consequence of gel formation, in the viscosity of the system have an inhibiting effect on the phase separation, which thus becomes possible only in a definite range of conversions and in a time interval which is a function of the rates of the constituent reactions. Since the cross-linking reactions continue in the time interval $\Delta\tau$, the phase separation then proceeds under non-equilibrium conditions, because the composition of the phases and their proportions vary with time in the reaction system. Thus the real situation arising in the formation of the IPN differs significantly from the case of "chemical quenching" examined theoretically by Frisch and Binder, in which it is assumed that the hardening time is much shorter than the relaxation time of the system in the phase separation.[44]

Both processes — the chemical reaction and the phase separation — take place simultaneously. This determines the nature of the structures which develop and are transformed at different stages of the reaction in the phase separation. The structure produced as a result of the reaction is characterised by a periodicity and order typical for structure arising in phase separation via the spinodal decomposition mechanism[45] The kinetics of the phase separation are described approximately in the initial stages by the linear Cahn – Hilliard theory despite the fact that this entails continuous changes in the degree of conversion, i.e. a drift of the system along the phase diagram implying continuous variation of the parameter χ_{23} and of the composition of the phases being separated. Thus yet another fundamental feature of the formation of the structure is established. It consists of a continuous sequence of structures differing in composition not only in the early stages of the phase separation but, according to the theory, also as a

consequence of the chemical reaction.[46] Thus the structure arising during the reaction is a result of a non-equilibrium phase transition of the liquid–liquid type and the final result of this transition is determined by the system composition (the ratio of the networks, the rates of the reactions, and the degree of the non-equilibrium phase separation during the time interval $\Delta\tau$).

It follows from the foregoing that, from the thermodynamic point of view, IPN are non-equilibrium systems. However, phase separation microregions, which can be described as quasi-equilibrium regions, are manifested in them. Indeed, each of the two experimentally observed phases has a glass point different from the glass points of the constituents. Each given phase contains both constituents. We can consider such a phase as a region in which the state of the molecular blending of the components (compatibility), corresponding to the equilibrium conditions preceding the given state of the entire system, has been "frozen". Overall, this is a thermodynamically non-equilibrium two-phase system whose state is determined by the conditions for incomplete microphase separation. However, each phase is in a quasi-equilibrium state. The structure of the IPN is microheterogeneous and molecular blending of the components takes place in the constituent phases.

IV. Conclusion

Analysis of the data presented shows that the principal experimentally demonstrated fact in the formation of IPN is at the present time the influence of the kinetics of the formation of the constituent networks in the IPN on the kinetics of the microphase separation and also the occurrence of the MPS under non-equilibrium conditions in the chemically varying system. However, this postulate has been formulated in a qualitative form.

The previous literature describes no attempts at a formal analysis of the kinetics of the network formation reactions taking into account the factors which influence the kinetics and which were examined above.

Numerous data essential for the understanding of the mechanisms of the formation of IPN are lacking. Thus, in radical three-dimensional polymerisation, the role of the reaction involving chain transfer to the second network, being formed via a non-radical mechanism or already formed (consecutive hardening), was not established. An appropriate study of the kinetics of the formation of the network in the matrix already produced (consecutively formed IPN), which strictly speaking should have preceded the investigation of the kinetics of the simultaneous reactions, was not carried out.

Although the fundamental role of MPS in the kinetics and their mutual influence has been established, the fundamenal problems arising in this connection have still not been studied. These include the following. Despite the fact that the degree of the MPS in the IPN may be estimated quantitatively,[41] it has not been estimated at different degrees of conversion of the systems for which the kinetics have been investigated. It is not clear in which stage and at what degree of conversion the MPS is frozen as a function of the kinetic conditions in the formation of the networks (rate, composition, and temperature). There are no data on the kinetics of the MPS after its onset.

It is also not clear in what way the reaction takes place after the MPS in MPS regions of different composition and how the chemical interaction between the phases is achieved. We have no information about the influence of the constituent networks and the MPS on the conversion at the gel point. Accordingly, and this is very important for the estimation of mechanical properties, the density of the constituent network is unknown under the conditions of the mutual influence of the kinetics of the reactions and the kinetics of the MPS on the formation of the IPN.

From the standpoint of the phase state, three cases of the formation of IPN are possible. The first arises when one network is formed much faster than the other, i.e. it is formed virtually in the liquid phase comprising the components of the second network, which results in a microphase structure with a fairly high degree of segregation. The second case occurs when the formation reactions of both networks are rapid and there is insufficient time for the occurrence of the MPS, whereupon the structure of the system characteristic of the single-phase state is frozen. The third, commonest case obtains when the rates of formation of both networks are comparable. The MPS begins in the course of the reaction and its continuation is inhibited as the network structure is produced. Among the three versions specified above, the formation kinetics as well as the relation with the microphase separation in the IPN have been studied in greatest detail for the third, commonest case, leaving the first two cases without due attention. All this demonstrates how far we are from a true understanding of the mechanism of the formation of IPN.

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