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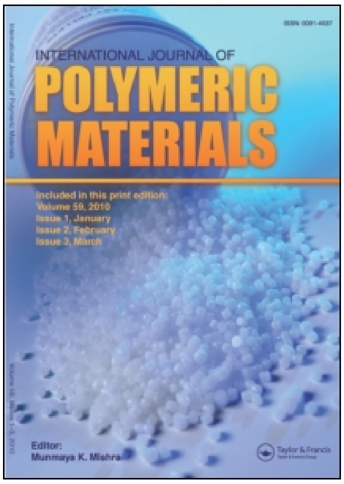

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Structure-Forming Role of Surfactants in Formation of Polymers Network

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Structure-Forming Role of Surfactants in Formation of Polymers Network

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The structure forming action of surface active substances in the process of formation of polyurethanes and polyepoxides is investigated.

KEY WORDS Polyurethanes, polyepoxides, networks structure, surfactants

INTRODUCTION

Surfactants (SAS) dissolved in heterochain oligomers, as a rule, change the system properties in the interface as those introduced into the low-molecular organic solvents.[1,2] The indifference to oligomer solvent and chemical interacting are the peculiarities of SAS introduced to reactive oligomers.[1,3] As is shown in Reference 3 in the latter case one can succeed to achieve stable improvement of a number of properties, including the adhesion strength. In the former case the dependence of these properties is of extremal character. While the oligomer is consumed and transformed and the molecular mass of the formed product grew, the medium polarity and SAS solubility in the reaction mixture change[3] and this may result in the change of its role as the structure-forming agent.[4] In the light of the above-stated the authors have undertaken the investigation of structure-forming action of surface active substances in the process of formation of polyurethanes and polyepoxides.

EXPERIMENTAL RESULTS AND THEIR DISCUSSION

Dimethyl siloxane and alkylene glycol block copolymer KEP-2 was used as an effective SAS with its surface activity even in very low concentrations. The reaction

TABLE I

Values of rate constants in the reaction of space-network polyurethanes formation of PPG-100, TDI-TMP in presence of different amount of KEP-2 at 80°C

Surfactant Conventration C_{KEP-2}, %	$K_1 \cdot 10^2 (\frac{1}{mol \cdot NCO \cdot min})$	$K_1 \cdot 10^2 (\frac{1}{mol \cdot NCO \cdot min})$
0	1.45	1.0
0.02	1.80	1.40
0.03	1.52	1.06
0.05	1.80	1.41
0.11	2.04	2.00
0.15	1.07	1.10
0.2	2.06	1.45

kinetics has been studied in the system 2,4-toluylenediisocyanate, polyoxypropelene glycol with M_n = 1000, trimethylol propane with different content of KEP-2 (0.02%–0.2%) at 353 K.[5] The observed reaction rate constants of urethane formation on the first and the second sections of anamorphoses of the kinetic curves (Table I) have been calculated from the data of calorimetric measurements according to the second order equation. As is evident, the KEP-2 presence accelerates the reaction. Two concentrations of SAS (0.03% and 0.15%) are the exception. The observed acceleration becomes more noticeable in the region of high degrees of the reaction comoletion (above 60% of isocyanate groups transformation). Since SAS are active structure-forming agents it is supposed that the observed accelerating action of SAS is connected with just this their capacity. That is why the further study deals with the effect of KEP-2 on the structural parameters of polyurethane reaction mixture in the experiment on estimating viscosity and light diffusion during hardening. As is evident from the curve of viscosity growth with the rise of the reaction depth (Figure 1), the process of gel formation begins the later, the higher is the amount of the introduced SAS. Such a character of KEP-2 effect in the hardening systems seems to be connected both with the SAS behaviour peculiarities on the interfaces and the formation mechanism of network structures according to the polycondensation mechanism. As is shown for the one-stage method of polyurethane production,[6] microparticles of the cross-linked polymer appear in the reaction medium when the reaction is completed by 55%. As soon as the other phase appears, the molecules of SAS can sorb on the already formed surface of microheterogeneities as on the interface. The adsorption layer of SAS prevents from formation of hydrogen bonds and from the other forms of physical interaction of these particles with the rest of the medium. It also promotes chemical interaction of the formed microgels. This manifests in the decrease of viscosity values and in the delay of the process of viscosity sharp growth respectively.

Light diffusion method was used to determine the amount and character of

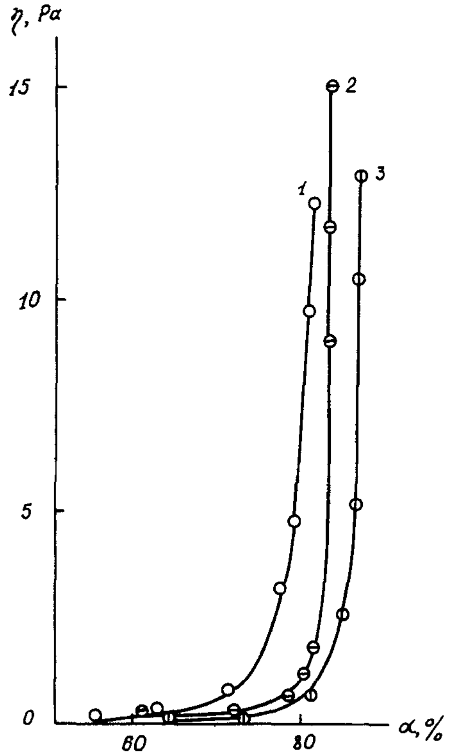


FIGURE 1 Curve of viscosity variations in the process of hardening of TDI-based system: 1—(KEP-2) = 0; 2—(KEP-2) - 0.1%; 3—(KEP-2) = 0.2%.

changes in microheterogeneities under hardening of the polyurethane reaction mixture.[2] A general view of the dependence curves to 85% of transformation has no distinctions from the other processes of formation of spatially cross-linked polymers studied by this method.[7,8] Therefore, the observed picture, due to the viscosity change in the course of the reaction, may be interpreted as follows. Before the considerable growth of viscosity in the presence of SAS there is the formation of the larger scattering particles than without SAS. The particles size grows with the amount of KEP-2 in the system. Hence, one can suppose that there is the estimation of the value of "scattering nuclei," which are the polymer regions with density different from the rest of the mass and which carry on their surface the thicker layer of SAS the higher is its amount introduced to the reaction mixture. As a result the reaction rate increases and more extended regions with the other density in the reaction mass are formed (Figure 2). The viscosity curves and light diffusion ones being compared it becomes evident that the beginning of the sharp viscosity growth corresponds to the region of reaching maximum and following decrease of the formations sizes. Thus, the redistribution of SAS between the reaction mass surface and the volume takes place under the network polyurethane formation, which must result in the impoverishment by SAS of the surface layer in the reaction-mass-air interface. The estimation of surface tension during the

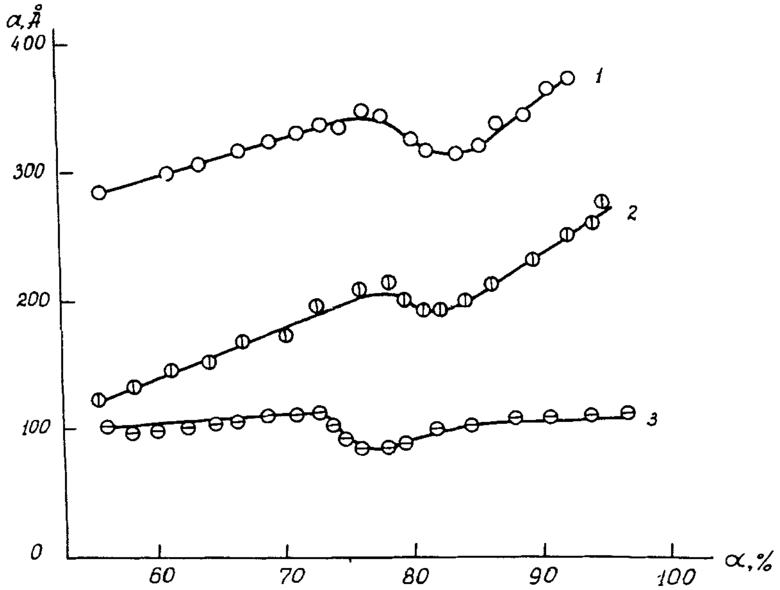


FIGURE 2 Dependence of sizes of microheterogeneities formed during hardening of TDI-based system on the degree of reagents transformation: (KEP-2) = (1); 0.1 (2) and 0.2% (3).

reaction of polyurethanes hardening in presence of 0.1% KEP-2 has shown 35% growth of the surface tension in the gel formation region.

Thus, the hardening of toluylene diisocyanate-based polyurethane system in the presence of microquantities of KEP-2 possessing surface-active properties, occurs at all stages of the process under the conditions different from the ordinary hardening mixture—trimethylol propane-diisocyanate-oligoglycol. These differences become apparent under the kinetic and structural study of the process of hardening. The final product is a polymer with the very weak, against the initial specimen, adhesion (hardening temperature 353 K).

The increase of urethane-formation reaction rate constants in the presence of KEP-2 (Table I) may be connected with the decrease of the reaction mass viscosity due to the weakening of intermolecular interactions and the increase of the reacting molecules mobility. But in such a case the availability of SAS considerations cannot be explained when the effect of its presence is not practically realised in the system. It may be supposed that the essential structural rearrangements possible due to the bi-feelic molecular structure of oligoglycol occur in the system under these concentrations of SAS. Thus, it proves necessary to define thermodynamic functions of the surface layers. The correct mathematical approach to this definition is possible in the simple system, binary ones, for example.

Of all the reagents of the reaction mixture under study polyoxypropelene glycol possesses the highest chemical affinity for KEP-2 and defines the distribution of the latter in the reaction system. And so, the model system oligoglycol—KEP-2 has been studied to find out the structure-forming effect of SAS. Concentration dependence of the surface tension γ for the concentration range of SAS from 0 to 0.3% has been analysed and the isotherms typical of the SAS solutions, have been

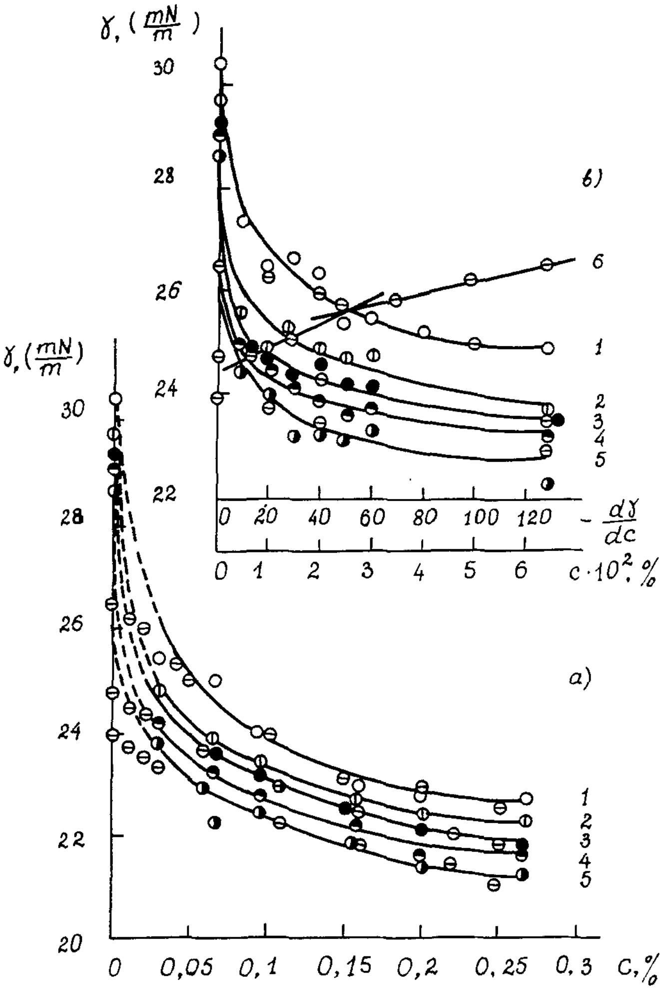


FIGURE 3 Dependence of surface tension of binary system PPG-1000-KEP-2 on concentration at different temperatures (a, b): (1) 333 K; (2) 338; (3) 343; (4) 348; (5) 353 K; (c, 6) dependence of a derivative ($\alpha\gamma/\alpha C$) on the surface tension in the system PPG-1000—KEP-2; (x-estimated values of γ (curves 1, 3, 5)).

obtained (Figure 3). In this connection there was an attempt to describe them using the equation suggested for the binary solutions of SAS.[9]

$$\gamma = (\gamma_1 - \gamma_2)e^{-bc} + \gamma_2 \tag{1}$$

where γ—surface tension of the solution containing SAS, γ_1—surface tension of the solvent, γ_2—surface tension of SAS, c—SAS concentration, b—coefficient of proportionality, with dimension of inverse concentration. ($1/b$-concentration of such a solution for which the adsorption value by Gibbs reaches maximum).

A comparison of experimental and estimated curves (Figure 3) prove that this *a* *b*

FIGURE 4 Electron-microscopic structure of the surface layers PPG-1000 (a), binary mixture PPG-1000—0.03% KEP-2 (b).

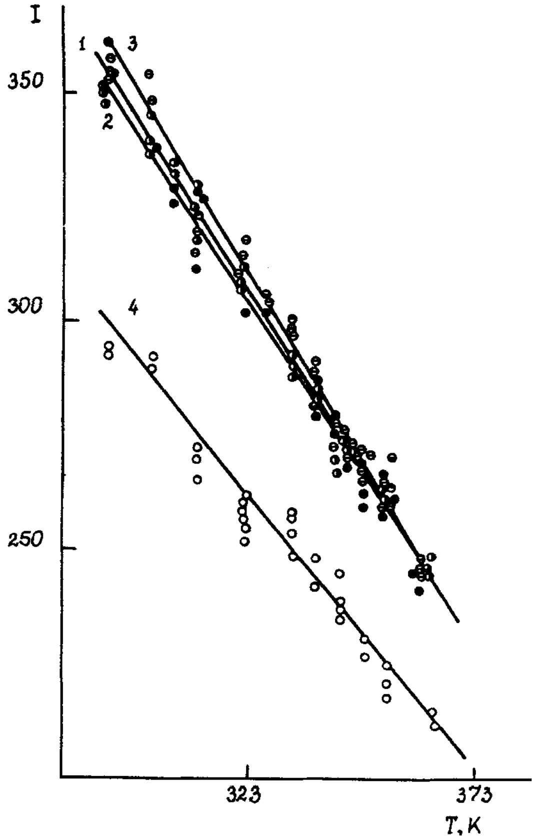


FIGURE 5 Dependence of integral intensity of proton signals on temperature in the system PPG-1000—KEP-2 with KEP-2 content: 0 (1); 0.1 (2); 0.15 (3); 0.03% (4).

equation satisfactorily describes experimental data only when KEP-2 concentrations exceed 0.03%. A sharp change of the SAS surface activity under the mentioned concentration is the cause of divergence between the estimated and experimental data. One can suppose a layer of SAS molecules rolled-up in a form of plane discs into the helix-like shape.[10] Such a possibility was considered under the equation and thus, the estimated values of the surface tension are lower than the experimental ones (Figure 3). Reorientation of SAS molecules in the adsorption layer can lead to drawing oligoether molecules into this process. This is indirectly confirmed by the sharp change of morphology of the binary mixture surface layer (Figure 4a and b) and may be reaffirmed by the data of NMR study (Figure 5).[11] Different amounts of KEP-2 being introduced, the chemical shifts of proton signals do not change, while the integral intensity regularly decreases with the rise of the measured temperature. As is evident from Figure 5 the considerable decrease of integral intensity (~20%) in the temperature range under study is observed only for one SAS concentration—0.03%. Such a decrease of integral intensity may be evidence for the limitation of mobility[12] of oligoether molecules to such an extent that a share of protons does not make its contribution to the NMR signal. The experiment result indicates the changes of volume properties in the binary mixture under effect of SAS.

All the data adduced evidence that the complex character of structure formation in the KEP-2 solutions in oligoglycol is under doubt. So it was of great interest to estimate thermodynamic functions of the surface layers of different composition. For the binary system being considered it becomes possible to make thermodynamic calculations for the mixtures of different concentrations at different temperatures (Figures 6 and 7). These calculations were by the equation which connects the surface pressure with the change in entropy and enthalpy of the surface layers[13]

$$\Delta H_s = \Pi + T\frac{d\Pi}{dT} \tag{2}$$

where ΔH_s—change of the surface layer enthalpy, Π—surface pressure, $(d\Pi/dT)$—change of the surface layer entropy.

As is evident from Figures 6 and 7, two concentrations of SAS (0.03% and 0.15%) are distinguished by their characteristics. The independence of ΔS_s of temperature is characteristic of the first one (Figure 7) and, this evidences for the existence of the structure which is not amenable to the effect of thermal factor, basing on the data of the NMR method within rather wide temperature range. Thus, the behavior of 0.03% solution of KEP-2 in oligoglycol may be interpreted as reorientation of SAS molecules in the surface layer, the glycol molecules being drawn in and this results in the formation of stable ordered combined structure (Figure 4b).

As is evident from isotherms of the surface tension (Figure 3), beginning from KEP-2 concentration equal to 0.25%, the increase of SAS content does not decrease the surface tension of the system, i.e., this concentration corresponds to the critical one.

The CMC (0.15% KEP-2) is not achieved yet, the extremum in the change of

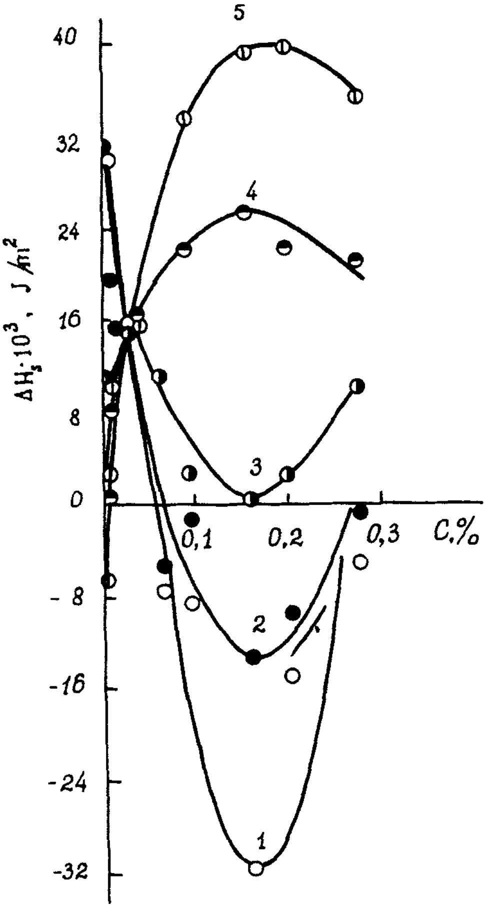


FIGURE 6 Dependence of change of surface enthalpy on concentration of KEP-2 at different temperatures in the system PPG-1000—KEP-2: (1) – 335; (2) – 338; (3) – 343; (4) 348; (5) 351 K.

thermodynamical function of the SAS surface layer (Figures 6 and 7) entropy, in particular, is observed in the system. This testifies to structural changes in the adsorption layer[10] and may be explained using the modern views on the process of micellae formation. Micellae formation like adsorption is of not only energetic but also of entropic nature[14] that is shown under thermodynamic study of water solutions of proteins.[15] Besides, micellae formation is characterized by the region of concentrations but is not a critical point.[16] Based on the calculation of parameter b in equation (1) one can draw a conclusion that the position of extremum on the concentration dependences of ΔS_s and ΔH_s (0.15%) approximately corresponds to concentration of KEP-2 under which the Gibbs adsorption reaches maximum.[9] Thus, it may be considered that already under KEP-2 concentration 0.15%, the process resulting on micellae formation begins in the system studied. Depending on the system temperature it is characterised either by the maximum energy and the highest degree of randomness or by the highest packing density and minimum energy (Figures 6 and 7). Under these conditions change of a sign of thermodynamic

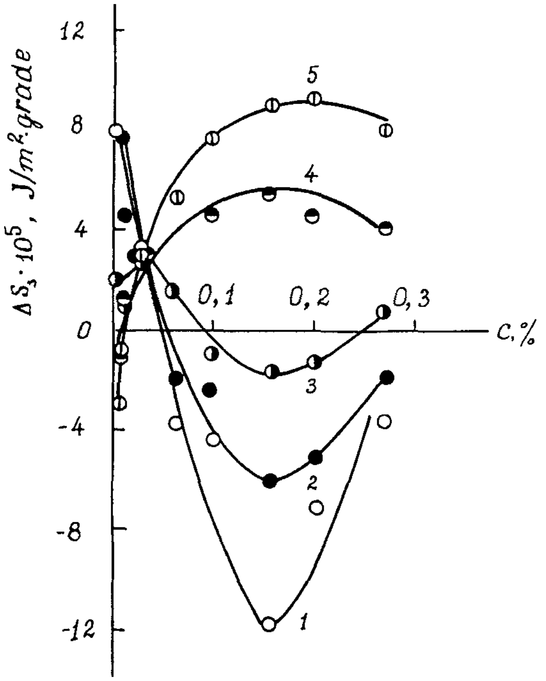


FIGURE 7 Dependence of change of surface enthalpy on concentration of KEP-2 at different temperatures in the system PPG-1000—KEP-2; (1) −335; (2) −338; (3) −343; (4) 348; (5) 351 K.

functions may be connected with the change in the packing density[10] and conformation of molecules taking part in the construction of micellae.[14]

Thus the KEP-2-polyoxypropylene glycol mixture being analyzed, it is established that there are two specific concentrations of SAS. The state of the surface layer of 0.03% solution is characterised by the highest stability and reflects the behaviour of separate molecules. The extremal values of thermodynamic functions describing the beginning of the micellae formation in the adsorption layer, i.e., the cooperative behaviour of KEP-2 molecules are characteristic of the second concentration. The results of the given study permit a conclusion that the interface role being increased in the reaction of polyurethanes formation one should expect changes of their kinetic parameters. As soon as KEP-2 belongs to strong SAS, the effect of surface (adsorption) layer in the investigated systems spreads at a considerable distance from the interface. The interface thickness in the range of the studied SAS concentration calculated proceeding from the data of Reference 16 is $\sim 1.3 \times 10^{-6}$.

In the results of kinetic studies being compared with these conclusions we see exactly when the transition state of SAS adsorption layer is observed, its availability in the reaction system does not affect formal kinetics of polyurethane formation. The reaction acceleration is achieved when introducing KEP-2 into the system in quantities different from 0.03% and 0.15%. It is shown that there is a relation between the effect of SAS on the formation kinetics of polyurethane networks and the structure of SAS layers in oligoglycol which are basic for obtaining these polymers.

Hence one can suppose that two concentration regions with the expressed effect on the polymer formation processes in the systems with possible specific interaction of SAS with reagents must exist for nonionogenic SAS. These concentration regions correspond to the arrangement of lyophobic groups in the interface plane and perpendicularly to it.

Proceeding to the study of the role of KEP-2 adsorption layers under polyepoxides formation we used the conclusions on the important role of thermodynamic function in the characterizing surface layers of SAS and their relations with the process of formation of chemical and physical structure of polyurethanes. That is why we have begun from the thermodynamic study of the binary model system PhGE—KEP-2. We have studied the effect of temperature (283–313 K) and concentration of SAS (0.001–0.1%, within the limits up to CMC) on the surface tension of this SAS solutions in PhGE, and thus, on the surface pressure calculated from Reference 13. It is evident from curves 2 and 3 (Figure 8), for the extreme temperatures that the most changes in the surface pressure are observed at lower temperature and in the region of SAS concentration to 0.01%. At higher concentration of the surface-active addition the increase of its amount insignificantly affects the growth of the surface pressure. The information on the values of surface pressure at each of the studied temperatures for each concentration permitted calculating by Π the value of surface entropy (ΔS_s) and enthalpy (ΔH_s) characterizing thermodynamics of formation of SAS adsorption layers under the corresponding conditions.[9] Concentration dependences ΔS_s and ΔH_s evidence for the extremal character of the change of thermodynamic functions in the temperature range of 288–313 K (Figure 9, curves 5–12) and for their approximation to the minimum constant value at 283–288 K (Figure 9, curves 1–4). Temperature lowering leads to the expansion of maximum and its shift towards high concentration (from 0.01 to 0.075%). The decrease of both the thermodynamic functions to minimum values evidences for formation of the most ordered structure of the adsorption layer. Due to the notion for SAS based on polydimethylsiloxane, the monolayer being com-

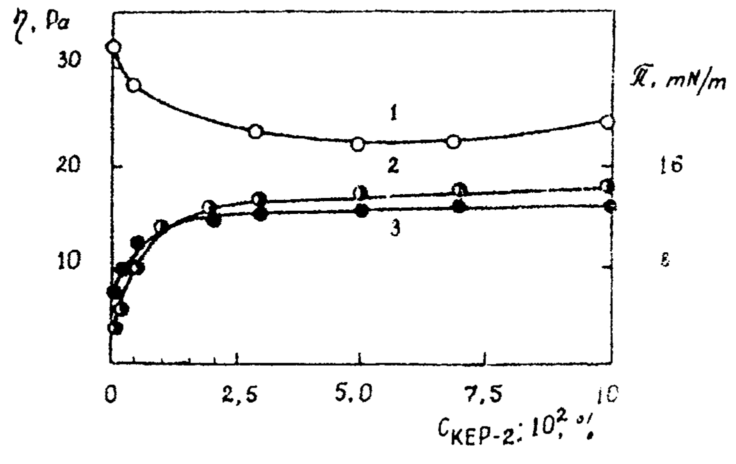


FIGURE 8 Dependence of dynamic viscosity of resin ED-20 at 298 K (1) and surface pressure of SAS solution in PhGE at 283 K (2) and 308 K (3) on KEP-2 concentration.

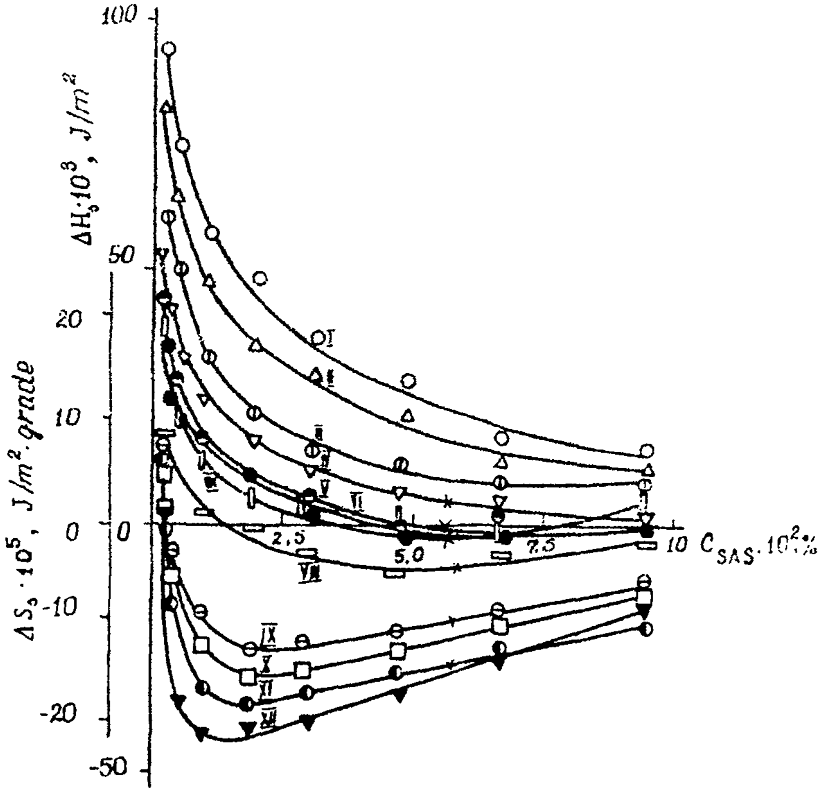


FIGURE 9 Dependence on KEP-2 concentration of thermodynamic function ΔS (IV, V, VII, VIII, IX, XI), and ΔH_s (I-III, VII, X, XII) of adsorption layers of SAS solutions in PhGE at 283 K (I, IX), 288 K (II, V), 293 K (II, VI).

pressed there occurs the rearrangement in its structure from molecules rolled-up in a form of plane discs[10] through the compaction of these two-dimensional formations to the following change of the molecules conformation into the helix-like shape. The transition of the values of function ΔS_s to the region of negative values this fact. Certain analogy being drawn between the compaction of the siloxane SAS layer under the effect of compression stress[10] and change of its structure with the increase of the number of SAS molecules in it due to the concentration rise of the latter, let us consider the obtained results. Proceeding from the change of thermodynamic functions Figure 9, one can draw a conclusion that the functions ΔS_s and ΔH_s in the region of negative values describe the process of packing coiled molecules to maximum ordered state (the region of extremum). Gradual disordering of the adsorption layer proceeds under the further SAS concentration increase[10] and this is accompanied by the increase of ΔS_s and ΔH_s values (Figure 9, curves 5–12). Thus, it follows from the conducted thermodynamic study that the concentration dependence of thermodynamic functions permits determining C_{SAS} values which promotion of the surface layer with the closest packing of molecules. These concentrations are in the region of the values deliberately below the critical ones and depend on temperature. (The stated results belong to the model system phenyl glycidyl ether—SAS).

The results obtained based on thermodynamic characteristics of the SAS surface layers in phenyl glycidyl ether may be referred to the binary system resin ED-20—SAS. Figure 8, curve 1, represents the dependence of this resin viscosity on the concentration of the introduced SAS. As it follows from the figure, the dependence η on the amount of surface-active addition is characterised by the decrease of viscosity with minimum value at 0.05% which is in good agreement with the position of the extremum on the concentration dependence of ΔS_s and ΔH_s (Figure 9, curves 7 and 8). It follows from a set of the presented data that SAS being introduced into ED-2, the resin viscosity becomes lower, and it is the lower the more close SAS molecules packings are in the adsorption layer. So far as it is volume viscosity which is characterized here, so we shall deal with the effect of two interfaces: solution-air and surface, determined by microheterogenetic structure of epoxide oligomer itself.[19]

The process of gel formation under formation of aminoepoxide begins very quickly and it should be expected that to change the properties of polyepoxide hardened in the presence of different amounts of SAS one must observe the dependences with the extremum of the addition concentration obtained from the analysis of thermodynamic functions of surface layers. Figure 10 represents the data on the concentration dependence of such characteristics of hardened polyepoxide as equilibrium swelling (curve 1) and breaking load under normal separation (curve 2). As is evident from the figure these curves are in good agreement, and the position of the maximum of strength and closeness of polyepoxide cross-link corresponds to the concentration 0.05% for SAS. Therefore, the existence of closely packed SAS layers in the hardening system promotes the formation of network polyepoxide with more closely cross-linked structure and higher adhesion characteristics. It also follows from Figure 10 that in the concentration region of 0.003% of SAS the presence of surface-active addition results in formation of a polymer with defect structure and low strength, respectively. Nonmonotonous dependences of adhesion strength of polyepoxides on SAS concentration were obtained before.[1] The decrease of adhesion strength of low concentrations of SAS was explained by the decrease of the surface tension of solid glue and ther-

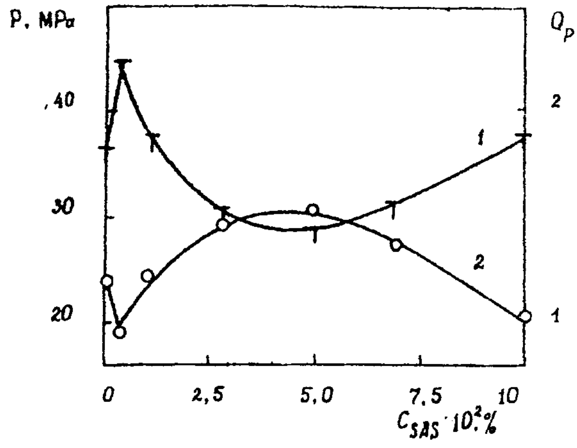


FIGURE 10 Dependence of equilibrium swelling Q_p in acetone (1) and force under break away (2) of polyepoxide samples depending on quality of the introduced KEP-2.

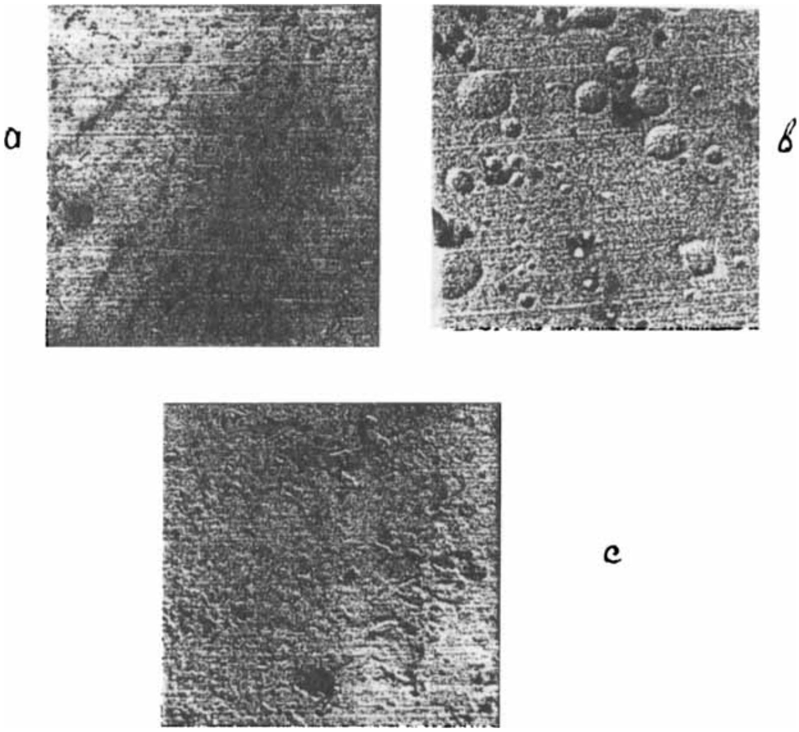


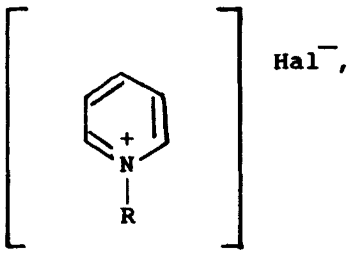
FIGURE 11 Microstructure of polyepoxides. Mass share of KEP-2 (5) in polymer: *a*—0; *b*—0.003%; *c*—0.05 × 20000.

modynamic work of adhesion, respectively. But the reason for such a decrease of characteristics at low concentration of SAS remains obscure.

In this connection we have studied morphologic structure of the surface of polyepoxides formed in presence of SAS additions. Microphotographs from Figure 11 show that network polymer without additions is characterized by the structure of globular type with the size of formations from 50 to 900 nm(a). Separate supermolecular formations are grouped into folded structures from 50 to 100 nm in width. The study has shown that the introduction of SAS promotes a decrease of average sizes of globular formations in polyepoxides. At concentrations of SAS of 0.05% (Figure 11c) the structure of a polymer is characterised by strictly bounded formations with a diameter ~50–80 nm, which are grouped into structures of irregular shape with the extension maximum ~250 nm. As is evident from Figure 11b, the introduction of 0.03% of SAS into the polymer promotes the formation of microstructure with characteristic globular formations of irregular shape and low package density which correlates with the found changes in the polymer properties (Figure 10). Hence, one can draw a conclusion that the structure of polyepoxide formed in the presence of the studied SAS depends both on the concentration of SAS molecules in the adsorption layers (this determines conformation) and their package density.

Thus, block copolymer based on dimethyl syloxane and alkylene glycols being used as surface active addition show that there is a relation between the structure of the epoxide system in liquid state and that in hardened state. This permits one to regulate the properties of polyepoxides using thermodynamic characteristic of these SAS solutions in epoxide monofunctional compound. Besides, it is found that the introduction of SAS of the epoxide series to polyepoxides rather differently affects the parameters of the polymer structure depending on the arrangement of lyophobic group of KEP-2 in a monolayer in respect to the interface: parallel or perpendicular to it.

The use of quarternary ammonium salts[20] as SAS for polyepoxides is of interest. As is shown (Reference p. 310) these additions increase the rate and extent of transformation of the epoxide groups in the boundary layer. The concentration (extremal) dependence of polyepoxides properties typical of nonreactive SAS is observed under such conditions. But further study of such systems has shown that the term nonreactive SAS may be applied to quaternary amount salts in the system containing epoxide compounds with reserve. When using salts of the type of



where *R* is ethyl, octyl (in octyl pyridinium bromide, OcPyBr) heptyl (in heptyl pyridinium chloride, HepPyCl) bensone, Hal-Cl-Br. It is found that these salts being dissolved in the epoxide compounds, colouring with a characteristic band at 404 nm (Figure 12) and the consumption of the epoxide groups are observed (Figure 13). To more completely study the behaviour of a number of halogenides of pyridinium *N*-arylates and *N*-alkykates we have studied their interaction with PhGE as the model compound and compared with the binary system pyridine—PhGE (Figure 13).[21] As is evident from the fragment of electron spectrum given in Figure 12 (curve 3) the same band as in the case of OcPyBr introduction to epoxy com-

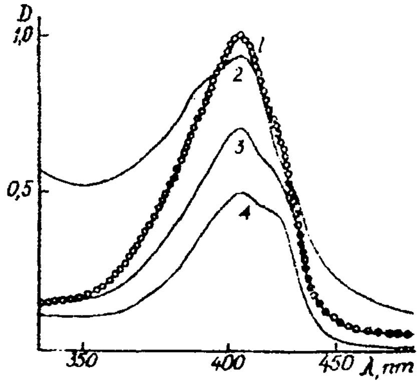


FIGURE 12 Fragments of absorption spectra in the visible region of solution in ethanol of the following systems: 10% OcPyBr (1) and 3% BenPyCl (2) in ED-20, 5% OcPyBr (4) and 1% pyridine (3) in PhGE.

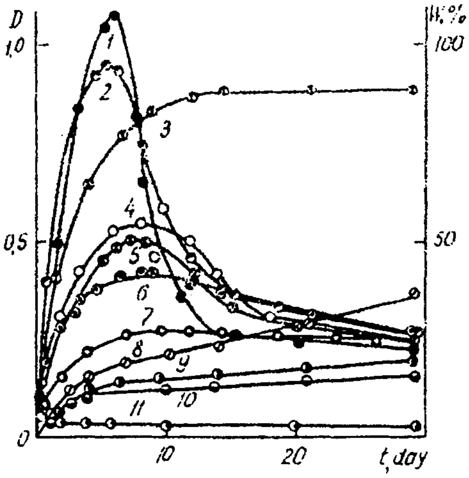


FIGURE 13 Kinetics of change of intensity for optical band with maximum at 404 nm (1-7, 11) and content of epoxide groups (8-10) for solutions in PhGE (of 1% pyridine (5, 10) with addition of absolutized ethanol (10-fold surplus of pyridinium salt) (2) and (11), respectively; 10% EthPyBr or OcPyBr (3), 10% HepPyCl or BenPyCl (6-9). (7, 9—when using 90% solution of salt in water). Spectra are taken for alcohol solutions of concentration of 6.0 × 10^{-2} (1-5, 11) and 6.0 × 10^{-3} l/mol (6, 7) by PhGE.

pound appears in the system pyridene—PhGE (Figure 12, curves 1 and 4). Proceeding from the stated experimental results and ionic nature of the mechanism of polymerization process of the epoxide compounds under the effect of tertiary amines, the appearance of a complex band with maximum at 404 nm may be referred to as the formation of the intermediate complex of epoxy compounds with the introduced additions which then leads to the opening of the epoxide cycle or the most active centre of ionic polymerization.

Kinetics of accumulation of the compound characterized by the band at 404 nm (Figure 13, curves 4 and 6) evidences for the existence of dependence between the amount of pyridinium halogenides introduces to epoxy compounds and the concentration of the formed product: the addition amount being increased, maximum achievable intensity of the absorption band in the visible region grows. But the character of curves describing the accumulation and consumption of spectrally active particles is different for bromides and chlorides (Figure 13, curves 3 and 6). It follows from the data of Figure 13 that the character of changes of the band with maximum at 404 nm (Figure 13, curves 4-6) is connected with the consumption of the epoxide groups (Figure 13, curves 8-10). For example, the reaction rate constants for the system containing 10 and 1% of HepPyCl compose 9.2 × 10^{-6} and 4.2 × 10^{-6} l/mol·min respectively. The interaction of growth of viscosity and intensity in the observed band is found in the reaction with participation of ED-20.

As it is stated above the introduction of the protodonor additions in case of tertiary amines considerably accelerates their interaction with epoxides 22-24 which is also demonstrated by the data from Figure 13 (curve 1). As it is evident from

Figure 13 (curve 2) pyridinium quaternary salts being used by the process of formation of spectrally active particles is accelerated by nucleophylic reagent. At the same time the presence of protonodonor in the solutions of pyridinium halogenides can both completely inhibit the appearance of the initiated particles (Figure 13, curve 11), and lead to its considerable deceleration (Figure 13, curve 7). The latter is accompanied by the two-fold decrease of the rate constant of exhaustion of epoxy groups (Figure 13, curve 9, K^2—4.7×10^{-6} l/(mol·min). Hence, one can suppose that the opening of the epoxide cycle under the effect of pyridine and pyridinium halogenides proceeds due to the different addition of these substances. As a result, different finite products—cross-linked and of linear or branched structure are formed.

The method of electron microscopy in the ultraviolet region by the band characterizing the aromatic ring—250–260 nm was also used to analyze the reaction between epoxy compounds and pyridine or its derivatives. Both aromatic and aliphatic monoepoxides were taken for the study. Change in the intensity of the studied band during the reaction may be unambiguously interpreted as butylglycidyl ether being used. It follows from Figure 14 (curves 3–5) that the number of aromatic molecules decreases in the course of pyridine or HepPyCl interaction with epoxy compound. With the availability of the other aromatic structure being excluded in these systems, the observed decrease of the band within the region of 250–260 nm

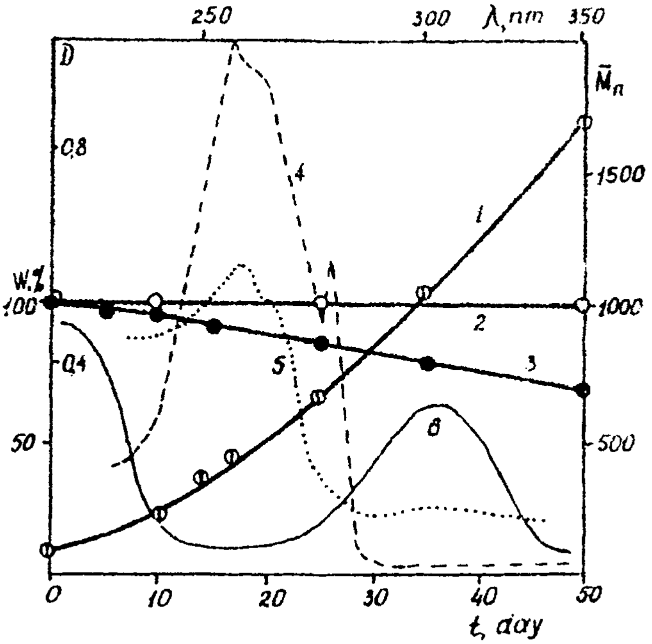


FIGURE 14 Dependence of the average-number molecular mass of reaction products of PhGE with pyridine (1) and intensity of the band with maximum at 255 nm in the system PhGE—2,6-lutidine (2) and pyridine—Butyglycidyl either (3) on the time reaction processing. UV-spectra of solutions: in 90% water solution of HepPyCl in BytGE immediately after the preparation (4), the month later (5), N-methyl-pyridone (6).

should be related to the consumption of pyridine heterocycles or its quaternary salt.

As the reaction proceeds there appears a band in the region of 300–310 nm. But the use of heterocyclic amine not always results in such a change of UV-spectrum of its mixture with epoxy-compound. For instance, in the case of 2,6-dimethypyridine the consumption of aromatic molecules under interaction with PhGE is not observed (Figure 14, curve 2). It should be noted that the reaction of 2,6-dimethylpyridine with PhGE is characterized by the appearance and accumulation of substances producing two bands in the visible spectrum (at 408 and 505 nm), and by a decrease of the number of epoxide groups.

Thus, when comparing the variation peculiarities of the band with a maximum at 255 nm in the reaction with unsubstituted and substituted in both α-positions pyridine, one can conclude that the reaction proceeds with participation of the cycle CH-groups near the heteroatom. To specify the mechanism of reactions proceeding under interaction of epoxy compounds with heterocyclic tertiary amines and their derivatives the IR and NMR—spectroscopic analyses have been conducted.

When studying the reaction between epoxy- and pyridins-containing compounds by the PMR-spectroscopy it is shown that the areas of signals in the region of values σ 8.57–6.88 ppm and 9.70–8.50 ppm, which characterize the protons of aromatic ring of pyridine and HepPyCl, respectively, decrease ~1.5 times quicker than the common limitation of mobility due to the growth of the reaction mixture viscosity observed in the system. The measure of protons consumption from the reactive group is the ratio of integral intensity (II) of proton signals of the both hetero cycles to II of protons of the aliphatic radical HepPyCl or OCH$_2$ in glycidyl groups their decrease being connected only with immobi-

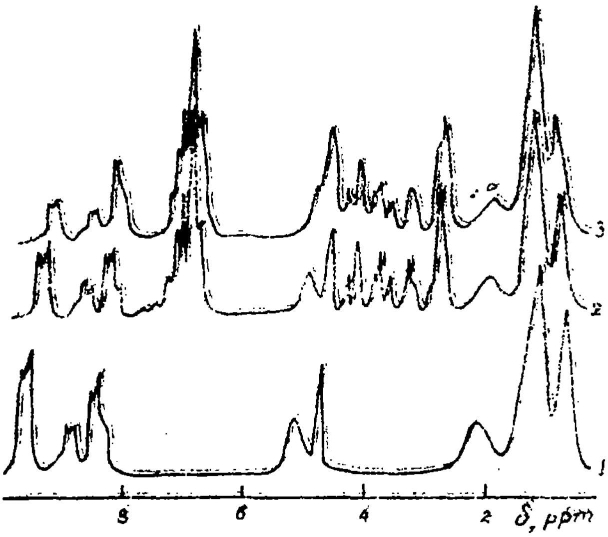
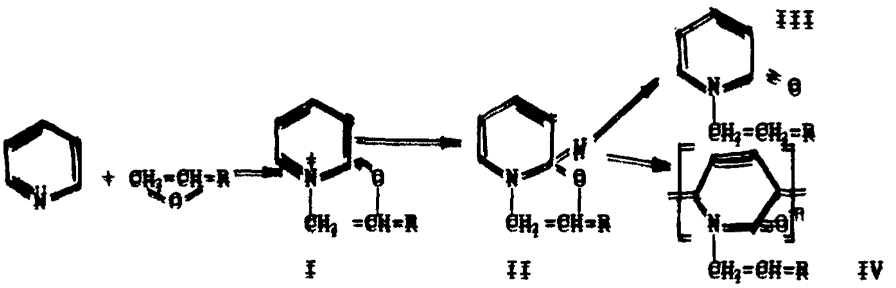


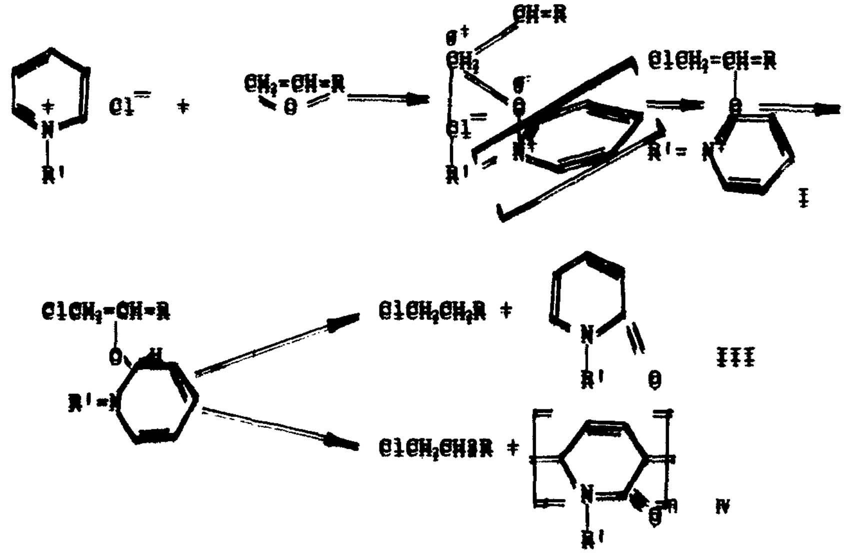
FIGURE 15 NMR-spectra of 90% solution of HepPyCl in D$_2$O (1), mixture of 90% solution of HepPyCl in D$_2$O with PhGE immediately after mixing (2) and 30 days later (3).

lization of the corresponding protons. Such a processing of the NMR spectra permits one to observe the proportional consumption of the pyridinium and epoxide cycles in the reaction of pyridine and its salt with epoxy compounds. There is time-limit for the method because of rapid and essential growth of viscosity in the course of the reaction. To broaden the possibilities of such a study we have used the ability of proton-donor reagent to inhibit reactions of quaternary chlorides with epoxy compounds. Use of 90% solution of heptylpyridinium chloride in D_2O permitted, firstly, obtaining the spectrum of the system salt-phenyglycidyl immediately after mixing, and, secondly inhibiting the viscosity growth in the system during the reaction. Thus, it was found that HepPyCl dissolution in the epoxy compound evokes a momentary interaction: all the signals of protons of quaternary cation shift towards the strong field. The 0.27; 0.20 and 0.24 ppm shift of the ring protons in the α-, β-, γ-positions, respectively, as well as the 0.25; 0.20; 0.10 and 0.0 ppm shift of protons of heptyl radical bound with nitrogen atom as it moves away from the latter (Figure 15, curves 1, 2). These results show that, like the case with pyridine,[25] chemical interaction of reagent is preceded by the stage of complexation or association due to electrostatical forces. The latter is rather probable, as the great dipole moment of ionic pairs, which are quaternary salts, evokes their strong interaction with polar molecules.[26] It should be noted here, that the tertiary amine complexation with epoxy compound is effective for the following oligomerization only in the presence of proton donors.[25] In our experiments the appearance of colors in the system pyridine-epoxide is also observed 3–5 hours later depending on the ratio of reagents. When using quaternary salts, the accummulation of substances characterised by the band with maximum at 404 nm begins immediately after mixing the reagents (Figure 13), and this evidences that the pyridinium introduction to the quaternary salt system without coreagents is sufficient for physical interaction with both oxygen and hydrogen atoms of the epoxide cycle.

Different change of II signals in α-, β-, and γ-positions of aromatic heterocycle has distinctly manifested due to the interaction inhibition (Figure 15). It follows from Figure 15 that in the NMR-spectrum of heptylpyridinium cation there is a considerable decrease of the signal 9.43 ppm (curves 2 and 3), characterizing the protons of aromatic heterocycle.[27] Hence, the total decrease of II of a signal of pyridinium cycle protons is mainly determined by the consumption of α-protons, and, the observed decrease in the number of aromatic molecules is connected not with the rupture of heterocycles but with the change of their structure. Besides, under the study of BytGE interaction with pyridine by the NMR-method it is found that in the region δ 6.2–5.7 ppm there appears a weak signal the position of which is characteristic of β-proton and α-pyridones.[28] This is confirmed by the taken NMR-spectrum of *N*-methyl-α-pyridone. The results of the study in the reaction of epoxide compounds with pyridine or its quaternary salt by the methods of electron and NMR-spectroscopy permit us to represent the scheme of their interaction as follows[29]:



(I)



(II)

A probability of such a reaction mechanism is in good agreement with the data of IR-spectral study. It has shown that a simple ester bond of symmetric structure (Figure 16, curve 6) is not practically formed for 20 days in the system PhGE—pyridine and PhGE—HePyCl. One can observe the exhaustion of epoxide groups (Figure 16, curves 10 and 11) and aromatic heterocycles (Figure 14, curves 1–3), the appearance and growth of the bands at 1640, 1660 and 1700 cm^{-1} (Figure 16, curves 1, 2, 4) which characterize nonconjugated double bonds and carbonyl groups, respectively.[27] Besides, the molecular mass of the reaction products grows at early stages of the reaction (Figure 14, curve 1) which is the result of the growth of oligomer molecules (product IV) due to the opening of double bonds of 3,5-dienes (product II). Thus, the bands which appear in IR-spectrum may be related to the valent variations of nonconjugated double bond in oligomer and of carbonyl group of pyridone and oligomer product. The band characteristic of the carbonyl groups[27] of pyridones (Figure 14, curve 6) also appears in the electron spectrum at 300–310 nm (Figure 14, curve 5). After 20 days of interaction (Figure 16, curves 7 and 8) a small band appears at 1100 cm^{-1}: a possibility of reaction leading to the band formation is probably determined by the decrease of mobility of the formed alox-

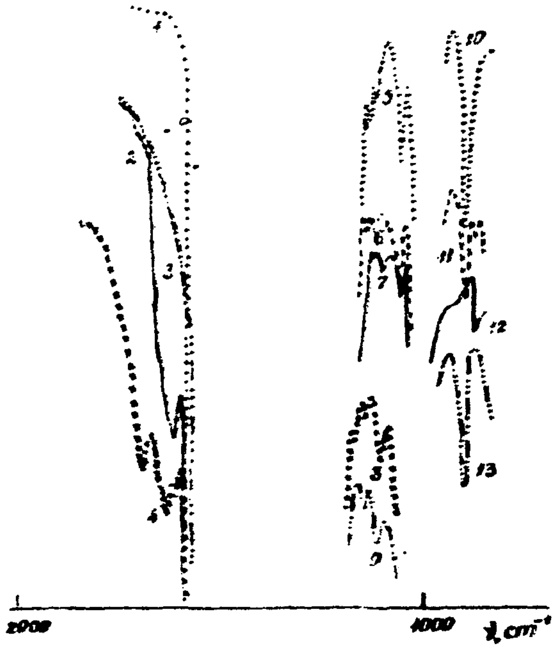


FIGURE 16 IR-spectra of reaction mixture PhGE-pyridine immediately after preparation (1, 5, 10), 15 days later (96, 11), 21 days later (2, 7, 12), the reaction mixture PhGE-HepPyCl 27 days after preparation (3, 9, 13).

uanion because of the intensive growth of the reaction mixture viscosity. 2,6-dimethylpyridine and PhGE being used as reagents, no new bands appear either in the region of 300 nm or in the IR-spectrum in the region of 1600–1700 cm^{-1} (Figure 16, curve 9), though the appearance and accumulation in the system bonds C—O—C are observed, i.e., only the epoxide compound oligomers are formed in this case. Such a behaviour is in good agreement with the results of the creation of epoxide compounds with 2-oxyethylpyridine.[30]

CONCLUSION

Thus, the conducted study permits a conclusion that at room temperature pyridine and its quaternary haloid salt form oligomers when reacting with epoxides by several mechanisms. As the initial stages of the reaction (15–20 days) one can mainly observe the formation of heterocyclic 3,5-dienes their oligomerization resulting in formation of a chain of heterocycles containing one nonconjugated double bond. As it is demonstrated this reaction is a result of the attack by alkoxyanion of α-hydrogens of aromatic heterocycles; *n*-substituted pyridone is formed as a by-product. Parallel homooligomerization of the epoxide compounds by the anion mechanism typical of the systems epoxide-tertiary amine proceeds at the following stages of the interaction.

In what case may such a scheme of interaction of quaternary ammonium salt with the epoxide compound in presence of the primary or secondary amines be realized? The reaction proceeding by this mechanism is possible when amine, proton-donor reagent are exhausted and when there are no essential amounts of water. Thus, depending on the state of the quaternary salt introduced to the reaction epoxide system (in front of crystalline salt or water solution) it can operate as the reactive or inert surface-active addition.

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