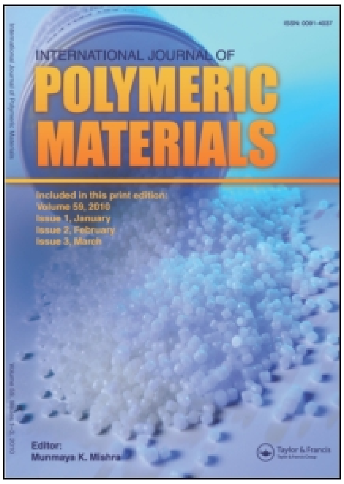

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Investigation of Morphology and Sorption-Diffusion Characteristics of Segmented Polyetherurethanes

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Sorption and diffusion of water into a number of segmented polyetherurethanes were studied. It has been demonstrated that the heat of sorption in the temperature range of 25°–55° equals approximately zero. The activation energy of the diffusion process is approximately 10 kcal/mole. The influences of synthesis and film formation conditions, ratios of flexible/rigid blocks, nature of the flexible block and heat-treatment on the degree of microphase separation were studied. The control of supermolecular structure of samples was performed using X-ray diffraction method, DSC, IR-spectroscopy and isotropic H → D exchange.

KEY WORDS Segmented polyetherurethanes, morphology, sorption, diffusion.

INTRODUCTION

At present, segmented polyetherurethanes (SPU) are widely applied as constructional materials as well as materials for designing artificial organs and tissues, particularly in heart-vascular surgery.[1,2] They excel over rubbers because of their mechanical properties, and their high hemocompatibility makes them superior to other polymer materials.

The unique combination of visco-elastic and thromboresistant characteristics is explained by domain structure of polymers.[3]

Segmented polyurethanes are compounds that consist of alternating flexible olygoether (or olygodiene) and rigid polyurethane fragments. Unlike flexible fragments, rigid ones provide strong intramolecular interaction in the chain, the total effect being similar to linking chains by chemical bonds.

As a result of the thermodynamic incompatibility of soft and rigid fragments of SPU, a microheterogeneous structure (with different degree of completeness) is formed, which is characterized by the presence of domains of rigid blocks distributed in an elastic polyester matrix.

The application of flexible and rigid segments of different chemical natures, sizes and variations in quantitative ratio produces materials with different degrees of microphase separation. And, as a consequence of this, provides the difference in physico-chemical parameters of the material that define many of the exploitational characteristics of SPU-based materials.

It is interesting to clarify the interconnection of diffusional and morphological characteristics of polymer matrix for "SPU-water" systems, because water is the dominant component of blood and contacts SPU articles very often. The mechanism and the rate of sorptional processes of other blood components will depend, in many aspects, on the rate of water penetration into matrix as well as their solubility.

There are many studies devoted to the SPU supermolecular structure and the influence rigid block content has on it.[4–13] Such methods as diffraction X-ray structural analysis,[8,9] PMR,[10] electron microscopy,[11] mechanical relaxation[12] and differential calorimetry (DSC)[13] were applied.

In the present work the method of isotopic H → D exchange, as well as the X-ray diffraction method, DSC and IR-spectroscopy were used to investigate SPU supermolecular structure. Previously the H → D exchange method was successfully used for studying aliphatic[14–16] and aromatic[17] polyamides.

While there exists significant data on the influence of rigid block content on the degree of microphase separation, there is very little data on this influence on sorptional-diffusional characteristics. The aim of this study was to determine the role of SPU supermolecular structure on water sorption in polymers with different content of rigid block.

The investigation of SPU structural heterogeneity by the method of isotope H → D exchange is based on the fact that the deuterating agent, penetrating into accessible regions of polymer matrix, participates in the reaction of isotope exchange with a mobile hydrogen atom in urethane group.

Because the rate constant of the exchange reaction in accessible regions of polymer matrix is several orders higher than that of the inaccessible (crystal) regions, kinetic limiting of the H → D exchange reaction rate is observed when all the accessible functional groups have reacted. The ratio of such groups to all functional groups of that type existing in the polymer is called accessibility (f).

In the case of equilibrial bimolecular reaction of the following type

$$\sim\!-R_1H + R_2OD = R_1D + R_2OH \qquad (1)$$

which runs without structural change of polymer the accessibility depends on the nature and activity of the deuterating agent and deuteration temperature.[18,19] Deuteration proceeding in the excess of deuterating agent allows to move the reaction equilibrium (1) to the right and to deuterate fully all the functional groups, accessible under these conditions. Accordingly, it follows that supermolecular structure of polymer can be characterized with the help of the accessibility definition. With high levels of polymer order it also reflects polymer crystallinity. In general the former is not equivalent to the latter, because it refers to "polymer-deuterating agent" system and depends on nature of deuterating agent.

Heavy water was used as the deuterating agent in the present work. It has been successfully applied by the authors earlier for studying the structure of polyamides.

EXPERIMENTAL

SPU of Hemotan-T and Vitur-T trade marks were selected as objects for investigation. Vitur-T (samples 1–3) was synthesized using polytetramethyleneoxide (PTMO) with terminal hydroxyl group content of 3.21 mass % (olygomer has been dried in vacuum until water content becomes below 0.03 mass %); 4,4′-diphenylmethane-diisocyanate (MDI) of "Bayer" Company and 1,4-butandiol (BD) with water content not higher than 0.05%. For Hemotan-T synthesis (samples 4–21) another simple ether (SE) has been used instead of PTMO. The reaction has been carried out in melt (sample 1)[20] or by polycondensation in solution in DMCO and DMAA medium.[21,22]

SPU were synthesized according to four schemes. In the first, a flexible SPU block was synthesized in the first stage by obtaining a prepolymer on the basis of MDI and polyester. A stoichiometric amount of BD was introduced into the reaction system at the second stage.

In the second scheme, a rigid SPU block was synthesized at the first stage by obtaining a prepolymer on the basis of MDI and BD. A stoichiometric amount of polyester was introduced into the system at the second stage.

The third scheme represented a combination of the first two: two prepolymers were synthesized first and then mixed in the second stage.

And, finally, the fourth variant of the synthesis was the introduction of stoichiometric amounts of all the components into the system simultaneously.†

Moreover, two other models were synthesized. One of them represented a polymer on the basis of MDI and PE (model 1), and the second one included a rigid block based on MDI and BD (model 2).

Film samples were formed by pouring the polymer solutions in DMAA on a glass plate and drying it in vacuum at $1 \cdot 10^{-2}$ mm m.c. until a constant weight was reached. The residual content of solvent did not exceed $5 \cdot 10^{-3}\%$.

Some characteristics of studied SPU are shown in Table I.

Film deuteration ($l < 300$ μm) was performed using D_2O for 0.25–48 hours depending on experimental temperature and sample thickness. After deuteration the films were vacuumed for 1–2 hours at $1 \cdot 10^{-2}$ mm m.c. pressure, and their IR-spectra recorded (Figure 1).

IR-spectra of initial and deuterated films were recorded by "Perkin-Elmer" spectrometer (model 1600 FTIR). The number of scannings for deuterated films was 10 (duration 40 sec.); the number of scannings for initial films was at least 250. The application of IR-spectrometer with Fourier-transformation allowed us to perform quick record of spectra and avoid errors caused by the reverse exchange.

Concentration of accessible NH-groups and f value were calculated, knowing the extinction coefficient of absorption band of ND-groups (ε_{ND}).[23] The value of ε_{ND}^{2490} equals 8 m^2/mole for polyetherurethanes, which contain structural group of [$CH_2OCONHPh$] type. In a number of cases isotopic film exchange was performed in water solutions of D_2O, because the intensity of 2490 cm^{-1} band at deuteration

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†The last series differed from the previous one in that the rigid block content (urethane group concentration) was varied in samples as well as synthesis conditions. Block content was designated by the change of initial component ratio.

TABLE I

Properties of SPU as dependence of chemical structure[1] and scheme of synthesis[2]

N	Methodof synthesis	ω_r, (C_{OCONH}) mol/l	Viscosity dl/g	Rupture stress MPa	Rupture elongation %
1^3	4	0,46(2,9)	0,9	–	–
2	4	0,46(2,9)	0,9	–	–
3	I	0,46(2,9)	0,9	–	–
4	I	0,29(I,9)	I,0	I4,0	I200
5	I	0,38(2,5)	0,8	I0,0	I400
6*	model I	0,I9(I,0)	0,9	I2,0	900
7*	2	0,36(2,4)	0,9	I8,0	800
8*	2	0,42(2,7)	I,0	32,0	850
9	2	0,43(2,8)	0,8	20,0	–
I0	2	0,45(2,9)	0,6	–	–
II*	2	0,50(3,2)	0,8	16,2	–
I2	2	0,52(3,4)	0,8	20,0	–
13*	2	0,70(4,5)	I,I	32,0	750
14*	2	0,82(4,5)	I,0	49,0	200
15*	model 2	I,00(6,5)	I,0	5I,0	50
I6	3	0,30(2,0)	0,9	5,0	300
I7	3	0,35(2,23)	–	–	–
I8	3	0,40(2,6)	I,0	32,0	750
I9	4	0,29(I,9)	0,5	–	–
20	4	0,42(2.7)	–	–	–
2I	4	0,55(3,6)	0,9	–	–

^{I}1) Then will be used concentration of urethane groups

^{2}2) (*) -s for DMSO as solvent

3) Reaction in melt.

in pure D_2O for thick films could be very high. Optimal optical density was selected by varying D_2O concentration in water solution.

It has been shown by special experiments, that the depth of isotopic exchange is proportional to molar part of heavy water (at $C_{D_2O} < 30\%$).

Sorption-diffusional measurements were performed using a McBain balance at 25°, the quartz spring sensitivity was 0.778 mg/mm. Coefficient of water diffusion into SPU (D) was determined by interval method and was calculated by the equation[24]

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \exp\left(\frac{\pi^2 Dt}{l^2}\right) \tag{1}$$

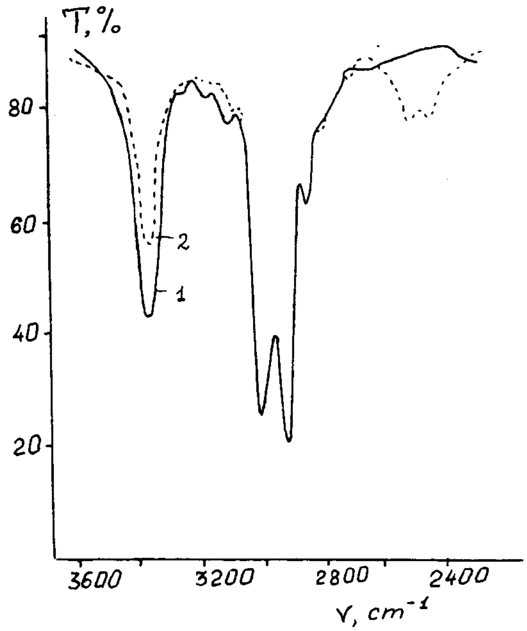

FIGURE 1 IR-spectrum original (1) and after H → D exchange (2) of Vitur-T films.

where M_t and M_∞ are the film weights at a time t and at conditions of sorptional equilibrium respectively.

Sample thermograms were recorded by differential scanning calorimeter of DSC-2M trade mark in the temperature range of 100–200° for samples of 45 mg weight, at constant heating rate of 16 grad/min.

Wide-angle X-ray scatterings (WAXS) were obtained using a URS-2 device by photographic method at CuK_α radiation, in a camera with $R = 200$ mm. Small-angle X-ray scatterings (SAXS) were also obtained by photographic method, using a Kratki collimator, reduced to point collimation because of sizes and placement of the sample, at $R = 325$ mm, and a diffractometer, equipped by line coordinate detector (exposition time is 200 s, SAXS recording interval in angle range of 2θ varies from 0.2 to 3.4°, sample thickness is about 0.4 mm). The approach to analysis of diffractograms was the same as in Reference 25.

Heat-treatment of initial Vitur-T films was performed by heating them in drying box up to 90, 165 and 190° with the following abrupt freezing in liquid nitrogen.

RESULTS AND DISCUSSION

At the first stage of the work we compared results of supermolecular structure investigations of polymers, obtained by three methods—X-ray, DSC and isotope exchange, on the example of Vitur-T trade mark SPU.

It is known from literature that SPU has regions without regularity besides the ones with alternating rigid and flexible blocks. When alternating period d_m changes by 20–30% of its value (by means of varying of rigid or soft block length), the corresponding supermolecule structure does not lead to formation of discrete small-angle scattering.[26] Thus, there are two varieties in SPU of irregular structure from the SAXS point of view: volumes homogeneous for X-ray irradiation and the ones heterogeneous because of irregularly alternating domains. They create background, which decreases monotonically with increasing angle from the initial irradiation beam.

Figure 2 shows small angle X-ray diagrams and distribution curves of domain radii by sizes for films investigated. It is seen from Figure 2a that they have X-ray diagrams of similar character. According to the distribution curves (Figure 2b) domains with ~30 Å radius are predominant in SPU. The comparison of d_m values

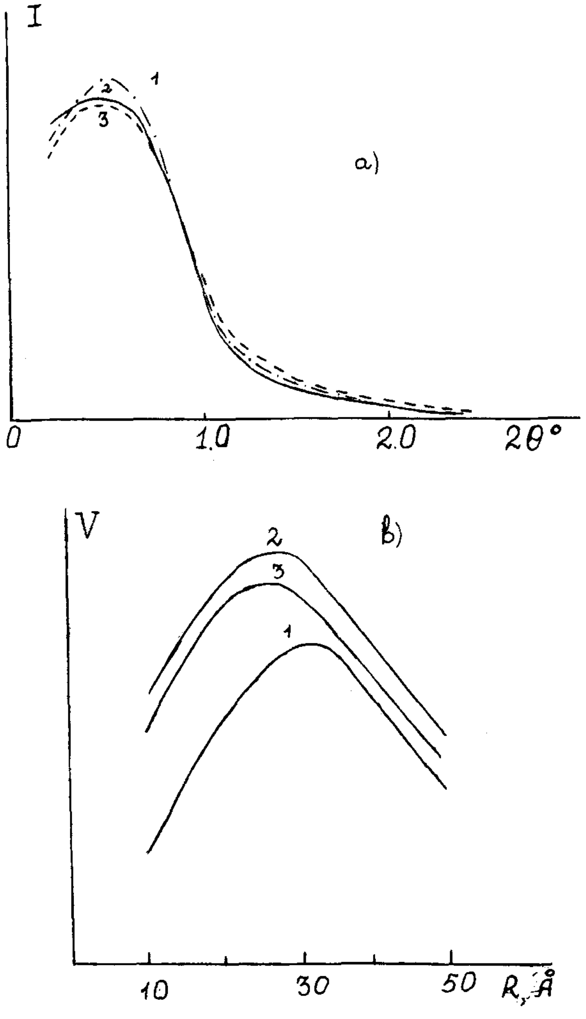

FIGURE 2 SAXS difractograms (a) and distribution curves for domene sizes (b); number of series for "Vitur-T" films: 1(1); 2(2); 3(3); on Figure 2b curves displaced arbitrary along axis *y*.

TABLE II

The dependence of f on conditions of synthesis and ratios DMAA:TGF

N film	f		
	Ratio DMAA:TGF		
	I:0	I:I	3:7
I	0,29	-	0,33
I3	0,36	0,38	0,37
8	0,60	0,53	0,56
5	0,54	-	-
I8	0,57	-	-
IO	0,53	-	-
4	0,79	-	-
I6	0,72	-	-

Moreover it is seen that the minimal and maximal quantity of water is sorbed by Hemotan-T films are found with C_{OCONH} concentrations of 4.5 and 6.5 mole/l, respectively. This means that there is no direct correlation between the urethane group concentrations and water sorption.

These data differ from results of both the paper,[34] in which the increase of water absorption has been observed with urethane group concentration decrease, and the paper,[35] in which it is pointed that this dependence goes through a maximum.

This difference in the results reflect different effects of urethane group concentration on supermolecular polymer structure. To answer this it is necessary to calculate the solubility data taking into account the polymer matrix accessibility for water molecules.‡

Sorption isotherms obtained in this way are shown in Figure 9. The dependence of water sorption (at all medium humidities) on urethane group concentration is clearly seen, namely the higher the C_{OCONH} the higher the water absorption.

The comparison of water sorption isotherms for Hemotan-T ($f = 0.6$) and Virtur-T ($f = 0.3$) at C_{OCONH} close to 2.9 mole/l shows that taking into account differences in accessibilities of sorption isotherms leads to similar trends.

The difference in accessibilities also can explain the differences in sorption iso-

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‡Water absorption for LPU was fully taken for rigid blocks, because this one for SPU is much higher than in flexible olygomer block (less than 0.2%[36]).

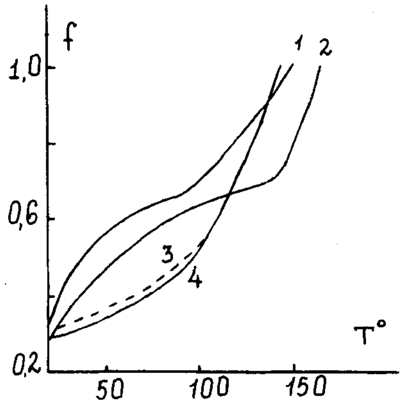

FIGURE 4 The dependence of f on temperature for Vitur-T films before (1, 3, 4) and after (2) heat-treatment; 1-(1, 2); 2-(3); 3-(4).

As it is shown by data of DSC (Figure 3), in a dry polymer the degradation begins at 155°, and at a much lower temperature for the investigated polymer-water systems. This correlates with the information on the dependence of polymer T_{melt} on water content in a matrix, as discussed in Reference 27.

According to data obtained by H → D isotope exchange method, films 2 and 3 differ by neither f values at room temperature, nor character of their dependence on temperature (Figure 4), but do differ from the film 1 (curves 1, 2).

As it is known, temperature increase leads to the development of SPU domain structure and hardening stabilizes this change.[28] The heating of film 1 to 165° followed by hardening moves the point of the beginning of the right slope towards higher temperatures. This reflects the fact that at preliminary heat-treatment non-stable and small paracrystals are melting, but large rigid domains still exist and may increase their size at higher temperature. That is why the beginning of the right curve $f(T)$ of the preliminarily heat-treated sample is moved to the right.

Figure 5 compares SAXS and curves of domain distribution by sizes for the initial film 3 with the samples, affected by heat-treatment at 90° and 190° with the following hardening. It is seen from the figure that temperature processing at 90° leads to the increase of dispersion intensity at small angles (Figure 5a). This means that material heterogeneity and the development of domain structure is increased. Figure 5b shows that the part of large domains more stable for degradation increases slightly upon heat-treatment at 90°C. This correlates with the results of isotope H → D exchange (Figure 4, curves 1, 2). Heat-treatment of the sample 3 at 190° noticeably changed the picture of small-angle X-ray scattering. Curves of domain distribution by sizes (Figure 5b) show that the most common radius here is smaller than in the initial sample and in the one heat-treated at 90°. Obviously, this is the result of melting at temperature 190° of the sample and the subsequent formation of new domain structure during the hardening process.

Two haloes at WAXS, 4.5 and 8.0 Å—reflect dense Van-der-Waals packing of macromolecule in the investigated material. Porod logarythmic curves,[29] of this sample, show that its structure in the colloid size range has the same layer-lamellar character as the initial sample.

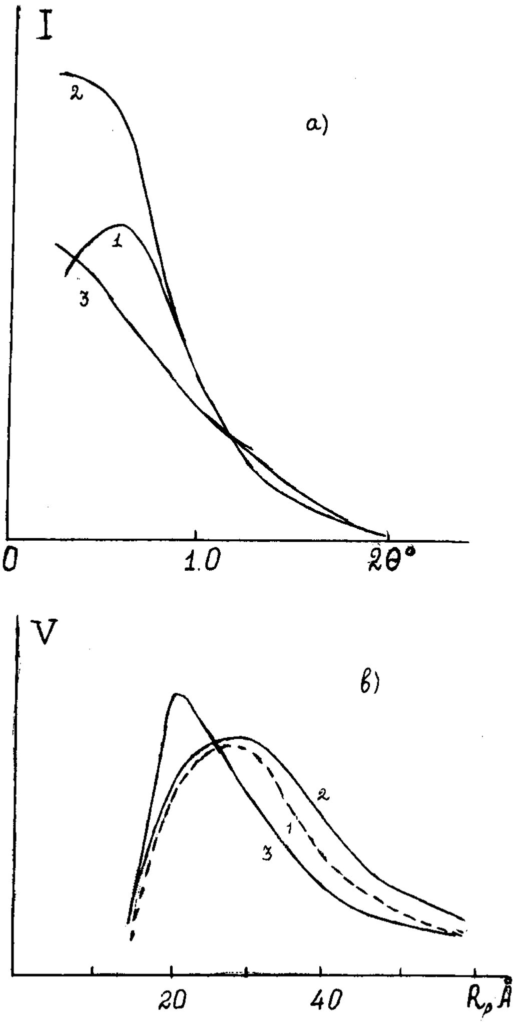

FIGURE 5 SAXS difractograms (a) and distribution curves for domene sizes (b) are for film 3; original (1) and quenched after heating at 90° (2), 190 (3).

The authors of Reference 30, who investigate the domain structure of SPU, regard the thermomechanics, X-ray structural analysis, and DSC as the most informative methods. We believe that isotope H → D exchange method should be added to this set. First, by studying the change of deuteration depth with temperature we can estimate the quantity of spheres inaccessible for D_2O, in this case SPU domains. Second, the form of $f(T)$ curves reflects the differences in structure of regions outside the rigid blocks. Thus, it is seen from data shown in Figure 4 that stable rigid-chain domains are contained in the polymer matrices varying from 65% for Vitur-T (sample 1) to 45% for samples 2 and 3. The advantage of isotope H → D exchange method before X-ray diffraction method makes it possible to determine separately the part of weakly regulated and stable rigid-chain formations.

Furthermore the isotope H → D exchange method was used for the investigation of supermolecular structure Hemotan-T sample that contained different amounts of rigid block. Investigations of that kind represented both the scientific interest as well as technological value because the analysis of the results of sorption-diffusion measurements elucidate the role of rigid blocks in the supermolecular structure of these systems.

Figure 6 shows values of *f* at 25° for the films with different φ_l synthesized according to method 2. It is seen that *f* values depend on φ_l (C_{OCONH}) in a complex way: it has clear minimum in the region $\varphi_l = 0.7$ with $f = 0.37$. Maximal *f* value was observed for SPU film synthesized on the basis of MDI and PE (model 1), whose matrix was fully accessible for water molecules. The data obtained correlate with the results of spectral measurements.

Figure 7 shows IR-spectra of this film and film 4 with $C_{OCONH} = 1.0$ and 1.9 mole/l, respectively. It is seen from the figure that the first film, unlike the second, has no absorption band at 1703 cm^{-1}. According to the literature,[31,32] there are two types of hydrogen bonds in SPU that are formed by NH-group of urethane fragment: 1) between NH group and urethane bond carbonyl; 2) between NH group and C—O—C group of flexible block. As microphase separation increases the first type of interaction becomes predominant. As a result of this, the intensity of 1703 cm^{-1} band (linked carbonyl groups) increases, and that of 1733 cm^{-1} (free carbonyl groups) decreases.

It should be mentioned that some authors use absorption bands 1703 and 1733 cm^{-1} for quantitative estimation of the degree of microphase separation. We be-

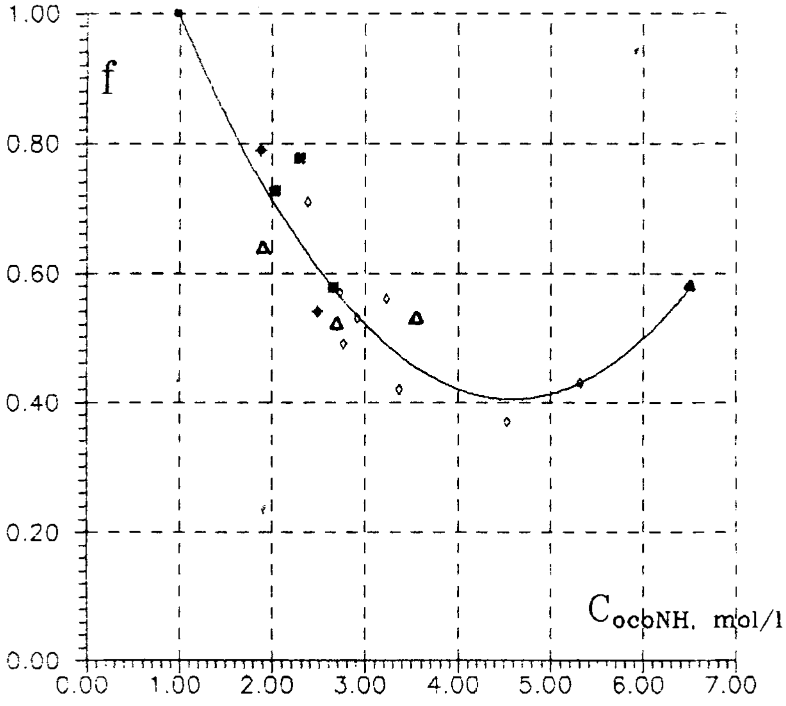

FIGURE 6 The influence of synthesis and ratios of flexible-rigid block on *f*; model 1 (□), model 2 (▲) and condition of synthesis 1 (+); 2 (◇); 3 (■); 4 (△).

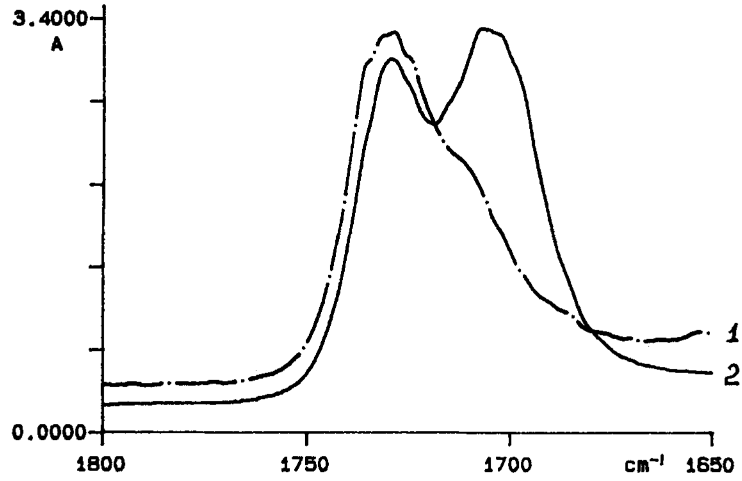

FIGURE 7 IR-spectrum original films 6 (1) and 4 (2).

lieve that this is not well-founded. In fact, IR-spectrum of sample 15 (rigid block) has no 1733 cm^{-1} band. However, as the results of isotope H → D exchange show, this does not mean the degree of supermolecular structure order has been reached.

In parallel with the study of f as C_{OCONH} we also performed investigation of the influence of Hemotan-T synthesis conditions and film formation conditions on the accessibility of, and, consequently, on water sorption. The results of this work show that neither SPU production conditions nor varying of solvent ratio DMAA:TGF lead to noticeable differences in f values (Table II, Figure 6).

For a better comparison of supermolecular structure of the investigated samples we studied the dependence of accessibility on temperature of five samples from this series. As shown above, this dependence allows us to obtain additional information on the relative amounts of weakly regulated and stable rigid-chain forms in the polymer volume. The data in Figure 8 show that the characteristics of this dependence for films 5 and 18 having a low content of rigid blocks differs from that of films in which the content of rigid blocks is high (films 13 and 14). For the films 13 and 14 the presence of a plateau is characteristic, namely a part at which f does not change much with temperature. Films 5 and 18 exhibit no such plateaus. However, their $f(T)$ shows two sections differing in their accessibility dependence on temperature. This indicates the presence of stable rigid-chain formations. The fraction of these rigid-chain formations changes in the range from 5–15% (for films 5, 18) to 35–45% (for films 13, 14). We also observed, as reported in paper,[33] the increase of T_{melt} of stable rigid-chain formations with the increase of rigid block fragment. The film 13 in comparison with the film 14 has a narrower distribution of domains sizes.

Let us now consider the sorption-diffusion characteristics of SPU-water systems. The data on water solubility in Hemotan-T and Vitur-T samples with concentration of urethane groups from 1.0 to 6.5 mole/l at several medium humidity levels are shown in Table III. It follows from these data that a film from Vitur-T series sorbs about one half as much water as a Hemotan-T film with a similar concentration of C_{OCONH}.

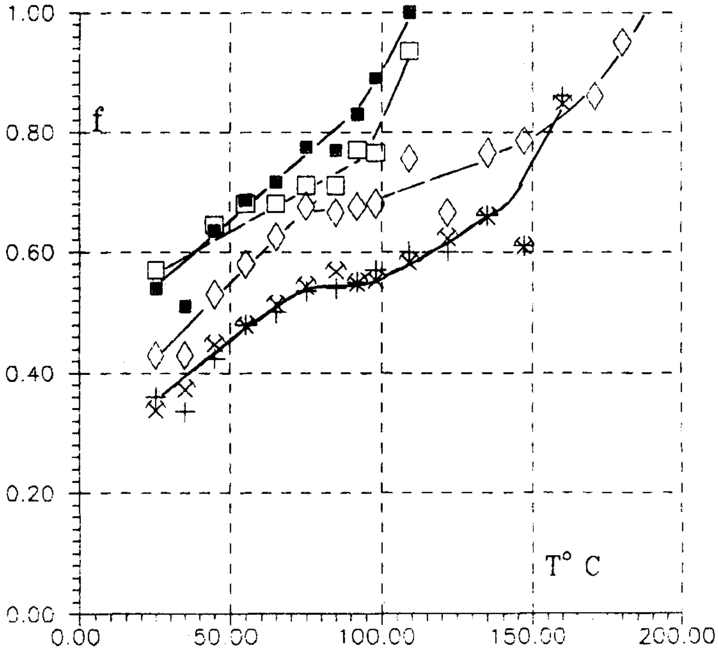

FIGURE 8 The dependence of the accessibility on temperature for films 14 (◇), 13 (+, ⚒), 18 (□) and 5 (■); the symbol (+) and (⚒) for film obtained in DMAA and DMAA:TGF (7:3), respectively.

TABLE III

The dependence of water solubility in SPU on humidity

N film	C_{OCONH} mole/l	Solubility, g/I00g Humidity,% 25	 50	 80
I	2,9	0,20	0,56	I,I
6	I,0	0,32	0,9	I,9
7	2,4	0,42	I,0	2,0
8	2,7	0,40	0,95	I,8
I3	4,5	0,36	0,8	I,5
I4	5,3	0,50	I,0	2,0
I5	6,5	0,75	I,55	2,8

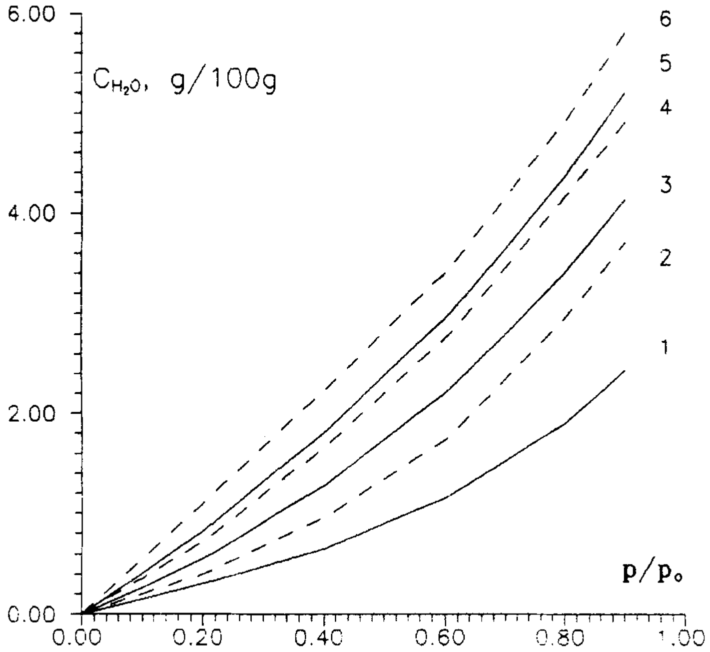

FIGURE 9 Sorption isotherms of water by films of Hemotan-T: 6(1), 7(2), 8(3), 13(4), 14(5), 15(6).

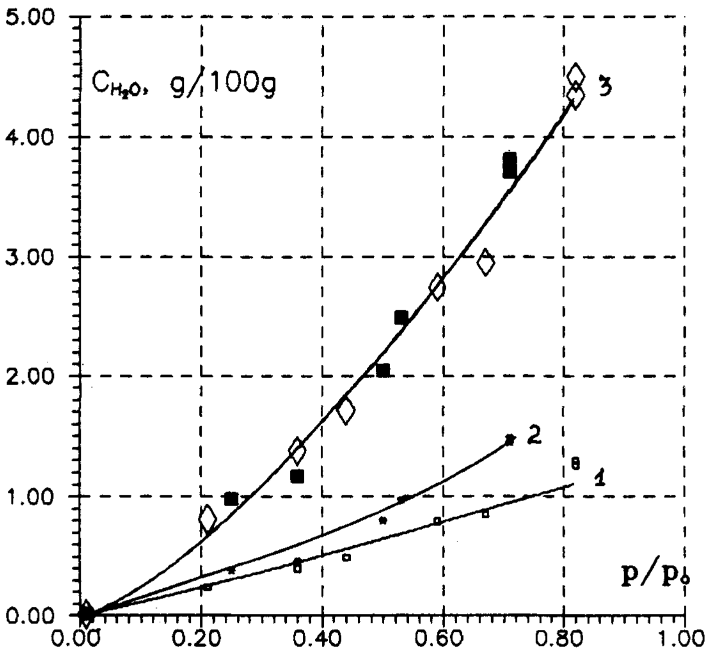

FIGURE 10 The solubility of water in heat-treated (1) and original (2) film 1 before (1, 2) and after (3) taking into account *f*.

therms of hardened and initial sample 1. Indeed, after taking into account *f* values, the water solubility in both samples becomes similar (Figure 10).

It should be mentioned that the method of group contributions suggested by Van-Krevelen[37] could not be used for a quantitative description of water sorption of SPU, because in dependence on microsurroundings of urethane group in polymer chain the number of water molecules sorbed at equilibrium changes. For example, at medium humidity of 80% 1.2 mole of water is sorbed per urethane group in the film 6, while in the film 15 it is only 0.5 mole.

The attempt to treat experimental data according to Flory-Huggins theory was also unsuccessful. According to this theory at $\bar{V}_2 >> \bar{V}_1$ the change of sorbate chemical potential in the system ($\Delta\mu$) is expressed by the equation

$$\Delta\mu/RT = \ln(p/p_0) = \ln(1 - \varphi_2) + \varphi_2 + \chi\varphi_2^2 \tag{2}$$

where, φ_2 is volume ratio of the polymer; $\bar{V}_1$ and $\bar{V}_2$ is partial molar volumes of sorbate and polymer; χ is Flory-Huggins dimensionless parameter.

It can be shown by the example of film 1 that with the help of Equation (2) one cannot describe the sorption isotherm. Indeed, the value of parameter χ (Table IV) is a function of water concentration in polymer matrix.

To describe the characteristics of the sorption isotherms we also used equations that follow the theory of polymolecular adsorption.[38]

$$\frac{p/p_o}{a(1 - p/p_0)} = \frac{1}{Ca_m} + \frac{C + a_m}{Ca_m} \cdot p/p_0 \tag{3}$$

$$a = \frac{a_m Cp/p_0}{1 - p/p_0} \cdot \frac{1 - (n + 1)(p/p_0)^n + n(p/p_0)^{n+1}}{1 + (C - 1)(p/p_0) - C(p/p_0)^{n+1}} \tag{4}$$

where a is the sorbed substance quantity; a_m is the substance concentration in continuous monolayer; C is a constant, related to the sorption of heat; and n is the number of sorptional layers.

In Equation (3) (BET equation) linearity is observed just at the initial part of sorption isotherms up to p/p_0 values of approximately 0.35 (film 6) to 0.45 (film 15).

According to the paper[39] deviation of sorption isotherms from linearity can be explained by completing the monomolecular layer formation. Further increase of

TABLE IV

The dependence of Flory-Huggins parameter on p/p_0 for film 1

p/p_0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8
χ	2.43	2.39	2.31	2.30	2.26	2.21	2.16	2.09

water content in polymer matrix is accompanied by its swelling and weakening of hydrogen bonds caused by incrased separation of urethane groups. As a result, the hydration of new active centers and water cluster formation becomes possible.

The linear relationship between urethane group concentration and a_m values of Hemotan-T films (Figure 11) is presented for comparison. The calculation shows that 0.15 of water molecules are sorbed by one urethane group. On the whole, the shape of the curve seems to indicate that we are dealing either with the presence of a number of active centers concentrated in flexible blocks or with poor water solubility in these blocks.

Equation (4) differs from BET equation in that the attempt has been made to take into account the role of elastic forces, appearing at swelling and preventing water sorption in a solid. The possible formation of sorption layers is limited by a finite number n. At $n \rightarrow \infty$ Equation (4) is reduced to Equation (3). Changed BET equation describes experimental data on the entire range of investigated relative vapor pressures (Figure 12). Thermodynamic and steric factors limit the possibility of the formation of sorption layers from 5 to 7 in dependence on the nature of SPU. The values of C constant change are in the range from 2.05 to 2.45.

Since both the n and C values change from one SPU to another is random the validity of process description by Equation (4) is confirmed.

However, the above mentioned shortcomings should not prevent the application of Equation (4) for predicting SPU water sorption with sufficient accuracy for the entire range of p/p_0. This can be performed using: 1) the dependence of a_m on concentration found for urethane groups and 2) average values of $n = 6$ and $C = 2.25$.

The next figure (Figure 13) shows the data on water sorption dependence on

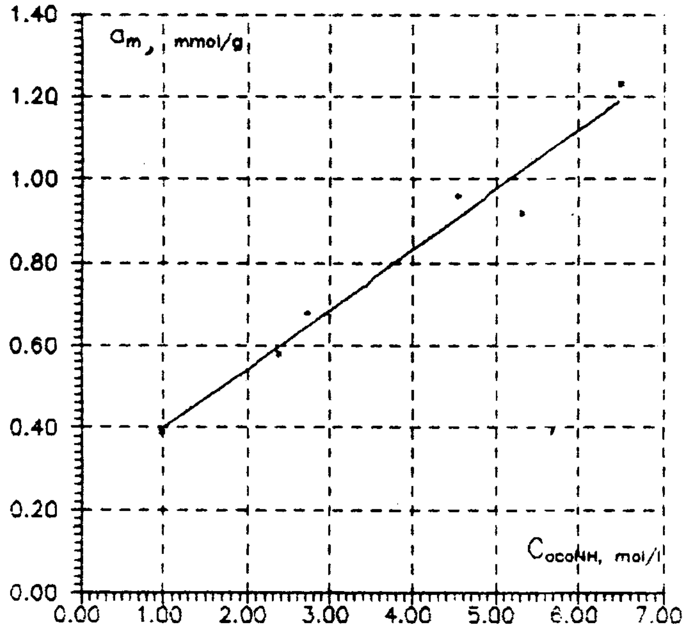

FIGURE 11 The dependence of a_M on the concentration of C_{OCONH} in the polymer.

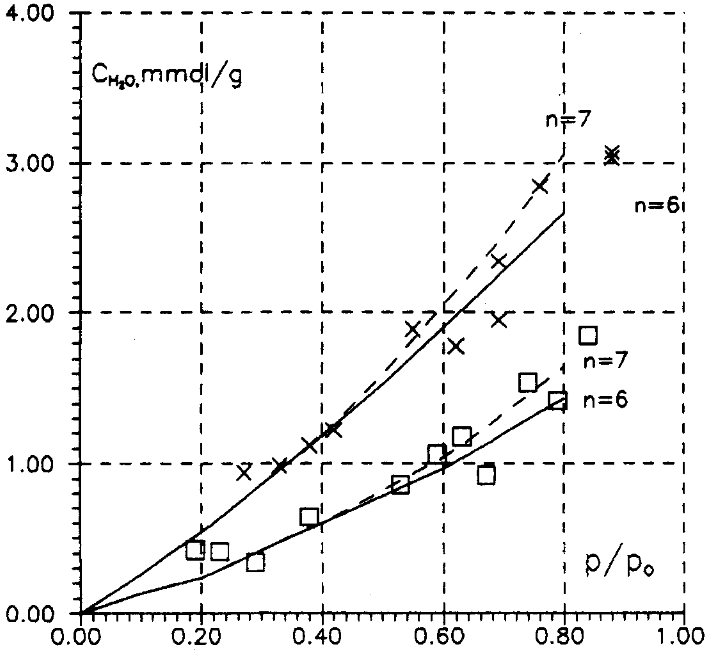

FIGURE 12 Experimental data and calculated curves for water sorption by films 15 (□) and 7 (×). The curves were calculated using Equation 4.

sorption temperature. As seen from these results, the sorption heat in the investigated temperature range (25–55°) is close to zero, which correlates with the data from the paper.[40]

Interesting results have been obtained during the study of water influence on diffusion coefficient *D* value (Figure 14). It is best seen with films having C_{OCONH} = 1.0 mole/l, where *D* decreases with decreasing water content in the concentration range investigated.

As rigid block content increases this dependence becomes weaker and disappears at films with rigid blocks only. Moreover, C_{OCONH} value influences sufficiently the absolute *D* value leading to its decrease with the rigid content increase in SPU.

Most likely the characteristics of diffusion coefficient dependence on concentration is related to two competing processes in the matrix, which change *D* in opposite ways: plastification and cluster formation. At low urethane group content (low φ_g) the second process prevails. As C_{OCONH} increases, processes begin to compensate each other, and *D* dependence on concentration disappears.

It was interesting to perform the comparison of water diffusion coefficients in investigated polymers in conditions under which we could neglect the above mentioned processes. In this regard, the extrapolation of *D* values to $C_{H_2O} = 0$ was made.

These data show that values of zero diffusion coefficients D_0 depend on urethane group concentration. When the concentration of the urethane group in the investigated range increases the coefficient decreases by more than 1.5 degrees.

Let us consider that the breaking of urethane groups as a result of the interaction of these groups with water molecules as a bimolecular reaction

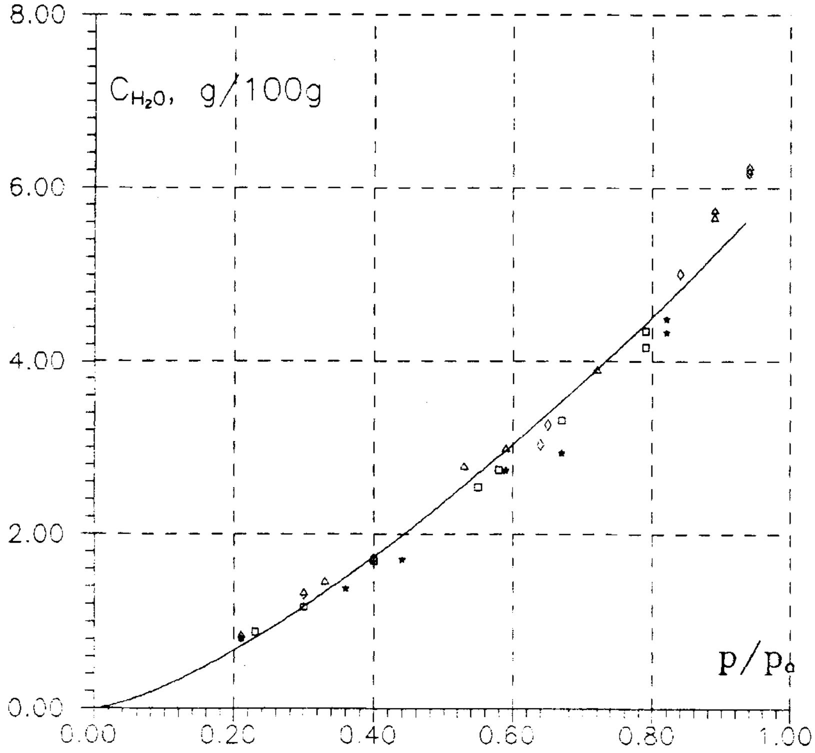

FIGURE 13 The dependence of the solubility of water in the film 1 by temperature: 25 (★), 35 (△), 45 (◇), 55 (□).

$$\underset{(A)}{\sim OCONH\sim} + \underset{(B)}{H_2O} = \underset{(AB)}{[OCONH \cdot H_2O]} \qquad \text{(II)}$$

And a description of sorptional process by Langmuir law (even if at the initial stage) diffusion coefficient should change with concentration of active centers A according to the law[41,42]

$$D = \frac{D_0\lambda}{K(1 - \lambda B)} \qquad (5)$$

where λ = the reciprocal of the active center concentration:

$$D_0 = D_i\lambda/K \qquad (6)$$

D_i = const − diffusion coefficient of solved molecules; K = the equilibrium constant.

It follows from Equations 5 and 6, that D_0 value should change inversely to urethane group concentration. However, this was not observed.

Another possible variant which we analyzed was that Fick's diffusion process was accompanied by quick proceeding of bimolecular reaction according to the

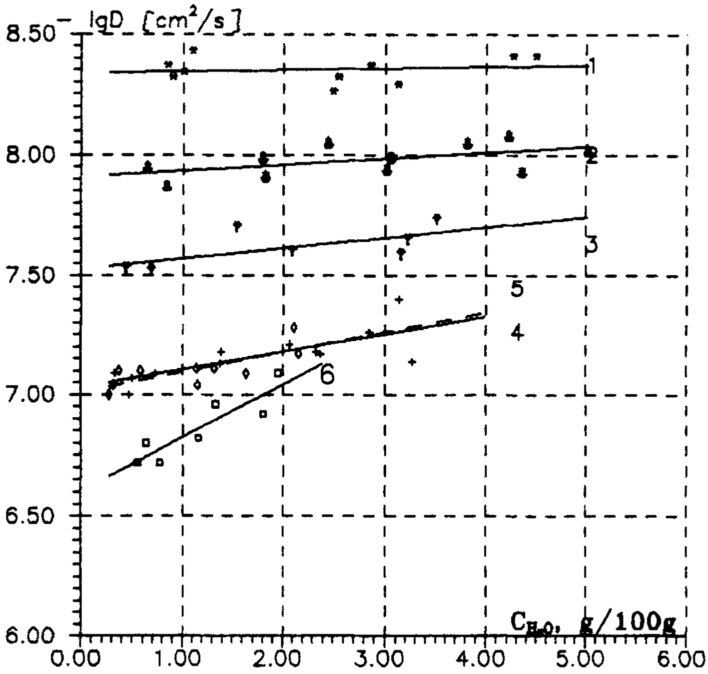

FIGURE 14 Concentration dependence of log D for films: 15(1), 14(2), 13(3), 8(5), 7(4) and 6(6).

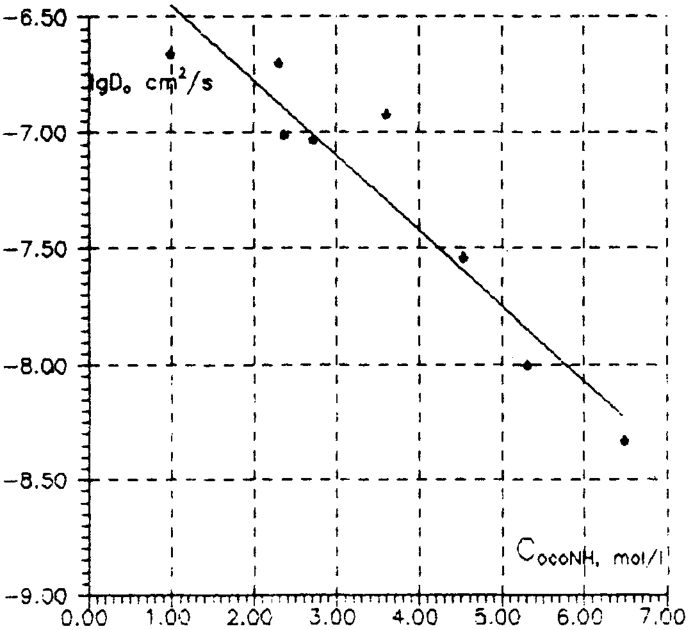

FIGURE 15 The dependence of log $D_{C=O}$ on C_{OCONH} in SPU.

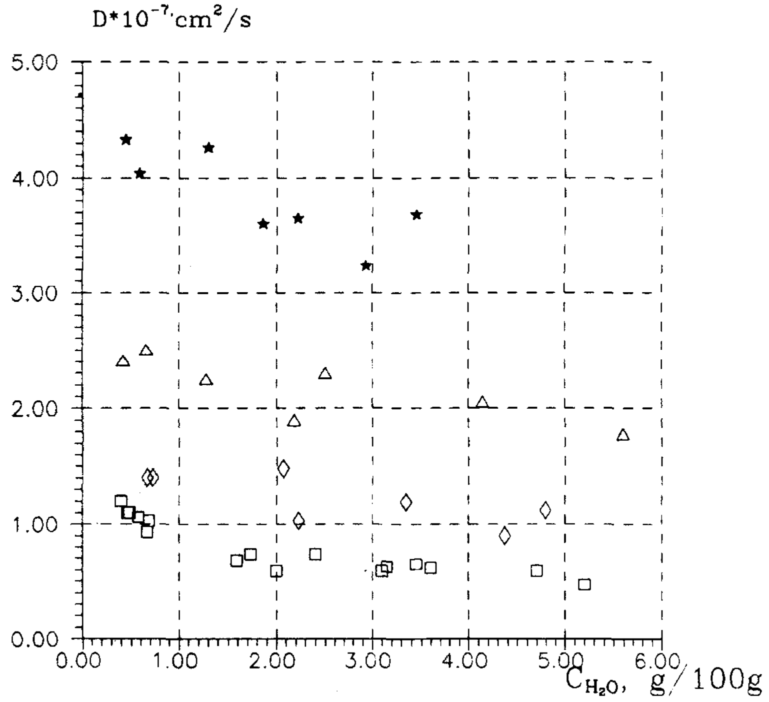

FIGURE 16 Concentration dependence of D for the film 1 by temperature: 25 (□), 35 (◇), 45 (△), 55 (★).

scheme mentioned above. It could be shown that if the rate of equilibrium setting is much higher than the diffusion rate, then the equation

$$\frac{\partial B}{\partial t} = D\frac{\partial^2 B}{\partial^2 x} - \frac{\partial AB}{\partial t} \tag{7}$$

at the condition $A \cong A^0 >> B$ acquires the following view

$$\frac{\partial B}{\partial t} = D^*_{\text{eff}}\frac{\partial^2 B}{\partial x^2} \tag{8}$$

where

$$D_{\text{eff}} = D/(1 + K_r A^0) \tag{9}$$

For this it is necessary to differentiate the expression

$$K_r = AB/(A^0 B) \tag{10}$$

and the obtained one

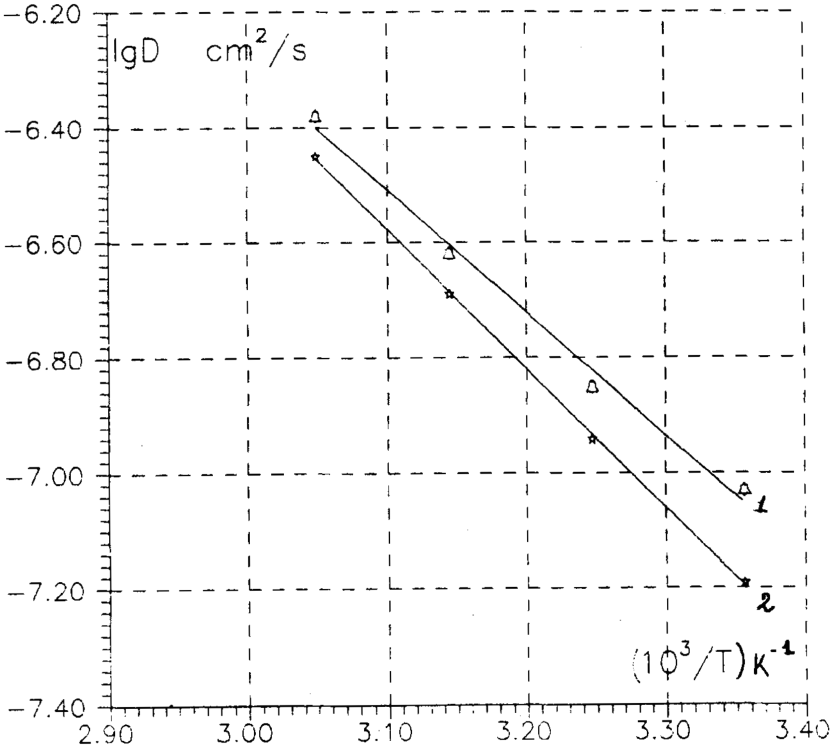

FIGURE 17 Arrhenius plots of D of film 1 by C_{H_2O}: 0,5 (1) and 3,0 (2) mole/l.

$$\frac{\partial AB}{\partial t} = K_r A^0 \cdot \frac{\partial B}{\partial t} \tag{11}$$

should be substituted into Equation (7).

However, the experimental data do not follow Equation (9), i.e. interaction is more complicated.

Finally we should point out an empirical relationship between lg D_0 and urethane group concentration with correlation coefficient of 0.99 (Figure 15). Extrapolation of this dependence to zero urethane group concentration intersects the ordinate axis at lg D_0 in soft block (-6.28). The figure also shows the coefficient of water diffusion into SPU, taken from the paper.[40] This SPU has the same chemical composition of rigid block as the SPUs of the present study. The flexible one, however, differs slightly in its structure. It is seen that this value correlates quite well with that found using this relationship. But additional data are necessary for more definite conclusions on the role of flexible blocks.

It can be concluded that the sorption-diffusion process proceeding in SPU at any humidities of the medium is determined by the quantity of accessible urethane groups. This quantity in turn, depends on the degree of microphase separation in the polymer. Moreover, it was shown that the rigid block content and the nature of the flexible block have a minimal influence on the sorption characteristics. The conditions of synthesis and the conditions of film formation are even less important.

The last stage of the work was the study of the diffusion process proceeding in SPU at different temperatures using the sample 1. Figure 16 shows results of the investigations, performed in the temperature range of 25–55°. The character of D dependence on water concentration in the polymer matrix does not change with the temperature: the higher the C_{H_2O}, the lower the D values, i.e. there is no sufficient change in the influence of two competitive processes on the diffusion. Activation energy of diffusion process E_a was found using Arrhenius equation. It was found practically independent on water concentration in polymer (Figure 17), and it equals approximately 10 kcal/mole. This differs considerably from the results reported in Reference 40, where E_a values change in the range from 5.5 to 11.0 kcal/mole in dependence on C_{H_2O}.

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