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Physical transitions in polymers plasticized by interacting penetrant

Svetlana I. Semenova[a], Haruhiko Ohya[b,*], Sergei I. Smirnov[a]

[a] *AO "Polimersintez", ul.Frunze 77, Vladimir 600016, Russian Federation*

[b] *Department of Material Science and Chemical Engineering, Yokohama National University, 79-5 Tokiwadai, Hodogayaku, Yokohama 240, Japan*

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Abstract

Plasticization by a penetrant of a polymer with the functional groups, specifically interacting (donor–acceptor type of interactions) with the penetrant is analyzed by using the systems: ammonia which is an electron-donor/aromatic polyamides, where amide group is as an electron-acceptor; sulfur dioxide which is an electron-acceptor/polymers with electron-donor groups.

It is shown that there is the plasticization of polymer by penetrant as the result of the sorption of penetrant molecules on the active functional groups of a polymer. There are four sections (regions) on the concentration dependencies of the diffusion coefficient. The boundaries between them correspond to the transition of the polymer (or rigid phase of block-copolymer) from one glassy state to another (β-transition), from glassy state to rubbery state (α-transition), and from rubbery state to the viscous-flow state.

Essentially, the concentrations of a penetrant on the active functional groups, n, (or the degree of fullness of the effective sorptive capacity of the functional groups, φ), which corresponds to the α- and β- transitions in the polymer, have the ratio: $n_\alpha/n_\beta \cong \varphi_\alpha/\varphi_\beta \approx 4\pm1$. Concentration barriers of the activation, corresponding to the α- and β-transitions also have the same ratio. It seems, that the process of α-relaxation in the polymer includes the intermolecularly correlated displacement of neighboring segments of the same size as in the β-transition, i.e. close to the Kuhn's segment, but it is close to the correlated displacement of 3–5 segments.

Relative concentration activation barriers of the physical transitions depend on the energy of interaction between penetrant and functional group of polymer.

Keywords: Polymer membranes; Gas and vapor permeation; Donor–acceptor interactions; Plasticization; Physical transitions

1. Introduction and background

The investigation of the mass transfer of a penetrant in the polymer with functional groups, which are capable of specific interactions with the penetrant is of vital interest to the researchers of membrane science. The use of specific (for example donor–acceptor) interactions between functional groups of the polymer and the penetrant and also the use of the effect of plasticization of the polymer by penetrant as a result of such interactions allows to obtain polymer membrane with a high permeability and high perms-electivity to the penetrant.

*Corresponding author. Fax: +81-45-339-4012; e-mail: ohya@-chemeng.bsk.ynu.ac.jp.

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The samples of such systems are ammonia as an electron-donor/glassy aromatic polyamides, in which amide group is an electron-acceptor; sulfur dioxide as electron-acceptor/polymers with electron-donor groups (–CO–O–, $-SO_2-$, $-PO_4$, –N<, etc.). It was shown in previous publications [1–17] that there are donor–acceptor interactions between functional groups of polymers and penetrant in that systems. It was also shown [1–3], that the criterion of the energy of reversible interaction of ammonia with amide group is the total positive π-electron charge of amide group Z^{+}_{NC}, $\bar{e}$, calculated by quantum-chemical method. The most probable mechanism of the interaction between ammonia and amide group is bonding of undivided pair of electrons of nitrogen atom of ammonia with low-populated π-orbital of N–C bond of amide group. It was shown that the criterion of the energy of reversible donor–acceptor interactions of sulfur dioxide with electron-donor groups is Gutman's donor number of the group [4]. The donor number characterizes the enthalpy of forming of the donor–acceptor complex.

Donor–acceptor interactions between a penetrant and functional groups of a polymer cause plasticization of the polymer. There are concentration dependencies of mass transfer and mechanical properties of the polymer as a result of the plasticization [1–17].

Concentration dependencies of mass-transfer and mechanical properties of polyamides depend on the number of ammonia molecules per amide group. Concentration dependencies of mass-transfer and mechanical properties of polymers and block-polymers with flexible fragment (oligodien, oligosiloxane, oligoethers) and rigid fragment with electron-donor groups also depend on the number of sulfur dioxide molecules per functional group. The change of mass-transfer and mechanical properties of block-copolymers with the concentration of SO_2 mainly depends on the plasticization of rigid fragments through the interaction between sulfur dioxide and functional group.

A baromechanical method based on the determination of deformation under variable loading of a specimen at various pressures has been proposed to study mechanical properties and physical state of polymers in accordance with the pressure of a sorbed gas or a vapor [6,7,9]. The method allows to reveal physical transitions in polymers that are in sorptional equilibrium with certain atmosphere of gas or vapor. Baromechanical curves are dependences of the modulus of elasticity of the polymer in the media of high sorptive gas (vapor) versus gas pressure $1/E(p)$ or gas concentration in the polymer. They are virtually similar to thermomechanical curves. The difference is: in thermomechanical method mobility of polymer chains changes with temperature, but in baromechanical method, the mobility changes with pressure or with concentration of the high sorptive gas in a polymer. Concentration dependence of the mechanical properties of polymer in gas media allows to correctly determine viscous-flow transition and to estimate α-transition in the polymer.

Fig. 1 presents the common form of the concentration dependences of baromechanical properties and diffusion coefficients of ammonia in aromatic polyamides. For systems SO_2/polymers with electron-donor functional groups, the dependence for diffusion coefficient has the same form, but baromechanical curves sometimes have more complex form [9].

The concentration dependence of integral diffusion coefficient $\ln \bar{D}(n)$ (where n is the number of molecules of sorbed penetrant per one functional group of polymer) can be linearized at some regions of the concentrations. There are four sections in the dependence $\ln \bar{D}(n)$ with different slopes to the concentration' axis:

I – increase of the diffusion coefficient; there is the linear dependence $\ln \bar{D}(n)$ for the region of the concentrations $0 < n < n_\beta$ with the slope γ_1 to the concentration' axis;

II – more intensive increase of the diffusion coefficient; there is the linear dependence $\ln \bar{D}(n)$ for the region of the concentrations $n_\beta < n < n_\alpha$ with the slopes γ_2 to the concentration' axis ($\gamma_2 > \gamma_1$);

III – decreasing of the slope of the increase of $\bar{D}$ with the concentration; there is very weak dependence $\ln \bar{D}(n)$ for the region of the concentration $n_\alpha < n < n_{fl}$ ($\gamma_3 \rightarrow 0$);

IV – abrupt increase of the diffusion coefficient with the transition of the polymer to the viscous-flow state at $n = n_{fl}$.

Comparison of data obtained by baromechanical method, sorption experiment and concentration dependencies of diffusion coefficient allows correctly to determine the concentrations n_α, n_{fl} which correspond to the α- and viscous flow transitions in the

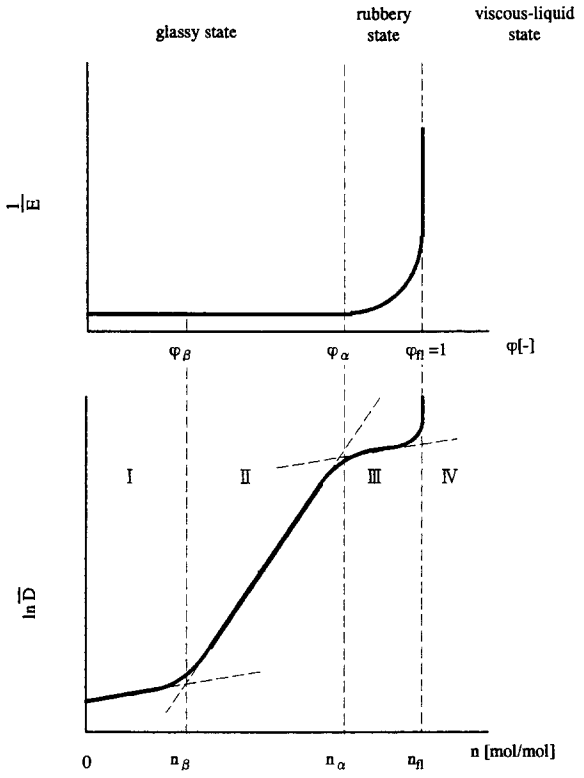


Fig. 1. The common form of the dependences of baromechanical properties of aromatic polyamides and diffusion coefficients of ammonia in them on the ammonia concentration [1].

polymer. The concentration n_β also can be determined from the concentration dependence of diffusion coefficient in the polymer, but the nature of the transition is not clear. In this paper we made an attempt to determine it.

2. Theoretical

2.1. The nature of β-transition in polymers and correspondence between α-and β-transitions

The cooperative movement of fragments of polymer macro-molecules at the temperature close to the glass transition point T_α (α-transition) and at the temperature lower than it (β-transition) are the main relaxation phenomena in polymers [18–20]. The transitions determine such properties of polymers as deformation and diffusion properties.

There are different points of view on the genesis (origin) of the β-transition in polymers. It is referred to the motion of one–two monomer links [19,20], small section of polymer chains [19,21], side-back groups [21,22], or to the motion inside the last one [23], and to the presence of admixtures (water, monomer, etc.) [18,21]. The question on the nature of the potential barriers of β-relaxation is also discussed [20,21,24].

The data appeared which showed that precisely in the region of β-transition (T_β) a rotary-translating displacement sections of the basic chain with side-back groups took place in the location of free volume. It follows from the experiments in low frequency combination scattered light [25], low-angle X-ray and scattered light in polymers [26,27], and also from the analysis of dynamic of hydrogen bonds in deformed polymers [28,29] that there is essential increase of free volume near T_β because of the thermic fluctuation of density and also because of the motion of chain sections with size as some links with rotation on the angles sufficient for the conformation transitions. It was shown in [29,30] that molecular repacking in polymers with change of their properties also took place at the temperature region T_β–T_α [31], and started at T_β [29,30]. The conclusion on the similarity on the molecular motions in liquids and solids, including polymers, in the β-transition was made [32].

Still Eyring found the dependence of the activation energy of viscous-flow of hydrocarbons on the length of their molecules. He established by that the segmental nature of the viscous-flow in polymers [39].

A linear dependence of activation energy of β-transition E_β, on cohesive energy E_{coh} (which corresponds to one mole of monomeric links) has been established for vitrified nonpolymers and glassy polymers by Bershtein et al. [32–38]. If one tentatively regards linear polymers as consisting of quasi-molecules, Kuhn's segment as kinetic units, then according to Bershtein et al., the dependence of the form:

$$E_\beta \approx (0.3 \pm 0.05)E_{coh}S + B$$

proves valid, where E_β is given in kJ per mole of segments, S is the number of elementary links in Kuhn's segment, and term $B \approx 15$ kJ mol^{-1} is a relatively small contribution to the potential barrier of β-transition.

It is noteworthy that the above equality is similar to Eyring's classic relation [39] for activation energy of

the flow of simple liquids:

$$E_{fl} \approx (0.3 \pm 0.05)\Delta H_{evap}$$

where evaporation heat $\Delta H_{evap}=E_{coh}+RT\approx E_{coh}$.

Eyring's relation shows that the potential barrier of molecule's motion in an environment of similar molecules represents a function (about one third) of the total energy of the intermolecular interaction (E_{coh}). The main contribution to potential barrier of β-relaxation in polymers is also made by intermolecular interactions. The difference between Eyring's and Bershtein's relations consists only in the presence of term B, corresponding in value to the barrier of internal rotation in the flexible chain polymer.

The act of β-transition in glasses which consist of simple molecules is rotary translating displacement of a molecule as kinetic unit in the 'hole' [24]. The one in polymers is similar motion of a 'quasimolecule' – the section of polymer chain with size as Kuhn'segment, and kinetic unit in the β-transition in a polymer can't be more than this segment [32,33].

The question about homology of α- and β-transitions is not well investigated. There are papers where homology of α- and β-transitions [20,40–42] and their common nature [43–45] were marked, and there are papers where opposite conclusion was made [21]. For example, Boyer marked the connection between α- and β-transitions [20], because at the frequencies of $\geq 10^7$–10^8 Hz, α-transition reborns to the β-transition.

It seems that α- and β-transition have common genetic, because for polymers, oligomers and even monomers, an approximately equal ratio of activation energies of α-/β-transitions $E_\alpha/E_\beta \approx 4 \pm 1$ was observed [32,33]. Effective activation volumes v_β and v_α corresponding to the β- and α-transitions in polymers are also related as $v_\alpha/v_\beta \approx 4 \pm 1$ [36–38]. According to the author's opinion, the values of E_α correspond to potential barriers of correlated displacement of several neighboring segments and the obtained ratio $E_\alpha/E_\beta \approx v_\alpha/v_\beta \approx 4 \pm 1$ refers to the degree of cooperativity. The large-scale act of α-relaxation includes the intermolecularly correlated displacement of neighboring segments of the same size as in β-relaxation, i.e. close to the Kuhn segment, but it corresponds to the correlated displacement of 3–5 segments.

The correlations of T_α with inter-molecular interaction and the packing coefficient [44] or with rigidity of polymer chain [45] were marked. The dependences of α-transitions on the energy of inter-molecular interactions (energy of cohesion, E_{coh}), thermodynamic rigidity of chains (the number of elementary links in Kuhn's segment, S) and the potential barrier of internal rotation ($B\approx 15$ kJ mol^{-1}) were marked in the papers [32–38,46] written by Bershtein et al. It seems, that the most comprehensive explanation on the nature of β-transition is presented there.

2.2. *Plasticization of polymer by penetrant, specifically interacting with polymer*

Increase of mobility of polymer chains can be realized not only by increase of temperature (as was discussed above), but also by including a plasticizer in a polymer. Particularly, penetrant specifically interacting with polymer can be a plasticizer. Theories of plasticization of polymers by low molecular compounds, can be summarized in the two general ideas [47]:

1. Plasticization of a polymer with polar groups by low molecular compound with polar groups (plasticizer) is realized by the solvation. Every polar group of the polymer strongly bonding with molecules of the plasticizer. In this case, decreasing of the glass transition temperature of polymer should be proportional to the molar fraction of added plasticizer (molar concentrations rule). Bounded molecules screen polar groups of macromolecules and increase the mobility of macromolecules.

2. In the plasticization of nonpolar or low polar polymers, the main role does not belong to the energy of interaction of the polymer and plasticizer (as at the first case), but belongs to the change of the conformations of macromolecular chains of the polymer, which is accompanied by the change of the entropy. In this case, decreasing of the glass transition temperature should be proportional to the volume fraction of the added plasticizer (volume fractions rule) and effectivity of the plasticizer strongly depends on its specific volume.

It is quite clear, that with the presence in the polymer functional groups which are capable of specific interactions with the penetrant the plasticization is realized mainly through the first mechanism and diffusion coefficient should depend on the number of molecules of the dissolved penetrant per functional group of the polymer. It should be possible to watch physical β-, α-, viscous flow transitions in the polymer

with corresponding concentrations n_β, n_α, n_{fl}, the numbers of penetrants molecules per functional group of the polymer. And also, if concentration n_β corresponds to the β-transition in the polymer, it should be some ratio between n_α and n_β and parameters γ_1 and γ_2, similar to α-, β-transitions provoked by increasing temperature.

It was shown that the concentration of penetrant which corresponds to the baromechanical transition to the viscous flow state, n_{fl}, depends on the cohesion energy of sorbing group [17] (see Fig. 2). The different strength of inter- and intra-molecular interactions in the polymers are obstacles for the correct comparison of the concentration dependencies of the polymer, particularly for the comparative analysis of the transition concentrations. It seems, much more correct to introduce the conception of the degree of fullness of the effective sorptive capacity, φ, by assuming that the effective sorptive capacity $\varphi=1$ corresponds to the concentration of gas in the polymer, at which the viscous-flow transition in the polymer determined by baromechanical method takes place (see Fig. 1). Such coordinate would allow to compare polymers with different energy of cohesion.

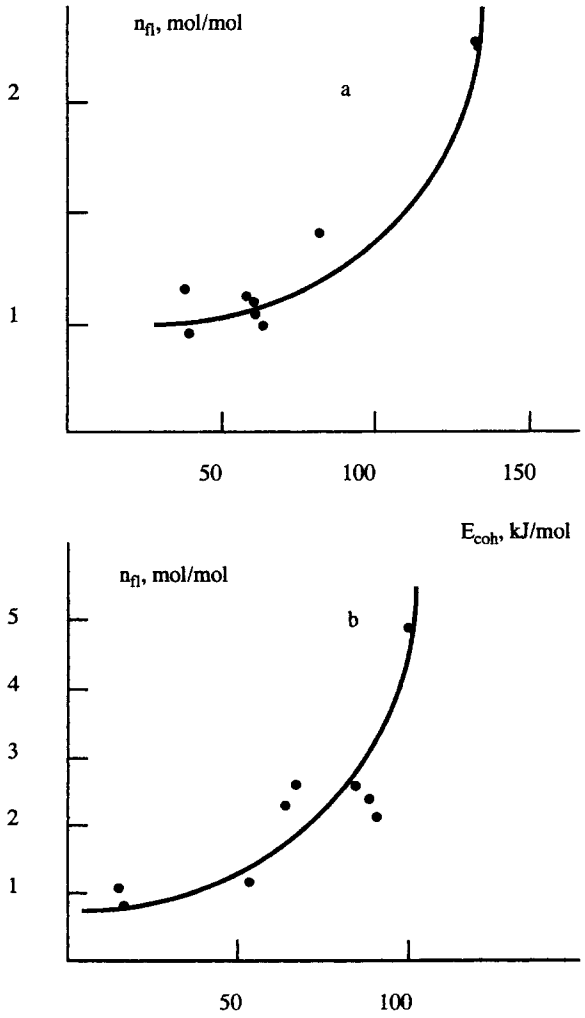


Fig. 2. Dependence of number of molecules of NH_3 (a) and SO_2 (b) per one sorptive group of polymer for the transition polymer to viscous-flow on the cohesion energy of sorptive group [17].

3. Experimental

3.1. Polymers

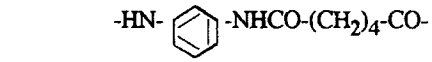
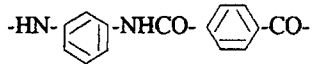
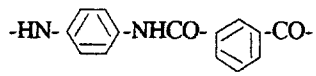
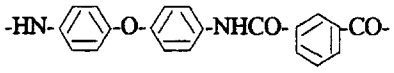
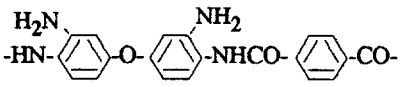
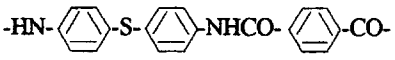
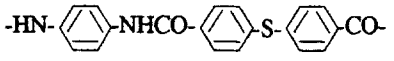
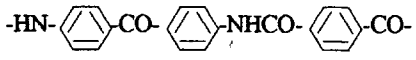
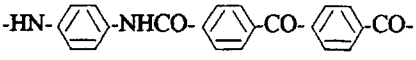
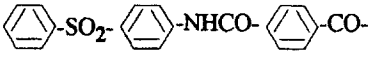
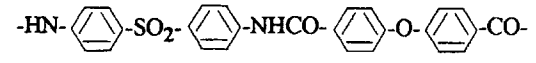
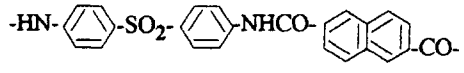
Aromatic polyamides with different isomerism of acid and amine components and with different bridging groups (–O–, –S–, CH_2–, –CO–, $–SO_2–$, $–CF_2–CF_2–$, –N=N–) were investigated. Polymers were synthesized in 'Polimersintez' as ascribed in [48]. Block-copolymers were also investigated: block-copolymer Silar 10 : 100, polyarylate siloxane, where on 10 arylate fragments there are 100 siloxane fragments (the polymer was synthesized in the Institute of synthetic rubber, St. Petersburg), polybutadiensulfone (with 3.2 wt.% S), and also some block-copolymers with electron-donor functional groups in rigid fragments ($–PO_4–$, –CO–O–, –N<, etc.) which were synthezied in 'Polimersintez'.

Monolith films with thickness 30–70 μm were obtained from the solution of a polymer in a suitable solvent. The solution was coated on the glass support by draw plate, and then solvent was evaporated. For example, for aromatic polyamides dimethylacetamide was used as a solvent. After evaporation at 125–130°C for 3 h, films were washed in distilled water at room temperature for 72 h, and dried under vacuum for 24 h. X-ray amorphous films were investigated. For more detail see in [1–17].

3.2. Measurements

Gas permeability coefficients were measured by gas chromatography method, the maximum of relative

Table 1
Parameters γ_1, γ_2 and the boundaries of the physical transitions on the dependencies of $\ln \bar{D}(\varphi)$ for some aromatic polyamides in ammonia (the boundaries of the physical transitions are presented as the degree of fullness of the effective sorptive capacity φ, [–]; $\gamma_{1,2}$ [–])

Polymer structure	φ_β	φ_α	γ_1	γ_2	$\varphi_\alpha/\varphi_\beta$	γ_2/γ_1
	0.30	0.90	1.20	4.80	3.0	4.0
	0.33	0.95	0.70	3.41	2.9	4.8
	0.30	0.88	0.72	3.69	2.9	5.1
	0.30	0.87	0.51	2.44	2.9	4.8
	0.30	0.89	0.78	3.80	3.0	4.9
	0.28	0.83	0.79	3.52	3.0	4.4
	0.29	0.83	0.66	2.77	2.9	4.2
	0.16	0.57	1.30	5.60	3.6	4.3
	0.16	0.58	1.04	5.20	3.6	5.0
	0.14	0.43	1.15	5.20	3.0	4.5
	0.16	0.68	1.92	8.72	4.3	4.5
	0.14	0.67	1.80	9.00	4.7	5.0
	0.16	0.80	1.41	6.85	5.0	4.9
	0.17	0.83	1.12	4.55	4.8	4.1

error of experiment was 10%. Sorptions of gases were measured by Mac Baine method, the maximum of relative error of experiment was 5%. Integral diffusion coefficients were calculated as the ratio between permeability and sorption coefficients.

4. Results and discussion

Table 1 presents parameters γ_1, γ_2 and the boundaries of the physical transitions on the dependencies of $\bar{D}(\varphi)$ for some aromatic polyamides in ammonia. It follows from the data that the ratio $\varphi_\alpha/\varphi_\beta \approx 4 \pm 1$ and $\gamma_2/\gamma_1 \approx 4 \pm 1$ ($n_\alpha/n_\beta \approx 4 \pm 1$ also). Obviously, the boundaries between regions on the concentration dependencies of the diffusion coefficients correspond to the β-, α- and viscous-flow transitions in the polymers. Parameter $\gamma_{1,2}$ can be determined as a relative concentration activation barrier of the increase of the mobility of polymer chains with the increase of the concentration of plasticizer in it. Therefore, γ_1 is the activation barrier to the β-transition and γ_2 is the activation barrier to the α-transition.

If take advantage of the similarity of the reaction of polymers on the increase of a temperature and also on the increase of a plasticizer–penetrant concentration, the conclusion is followed on the similarity of parameters $\gamma(\varphi)$ and energy activation of diffusion $E(T)$. Both parameters characterize the diffusion behavior with change of mobility of polymer chains by plasticizer concentration or by temperature. Therefore, they are determined by such properties as nature and strength of gas–polymer interaction, size and form of penetrant molecules. For example, it is well known that there is the linear dependence of activation energy of diffusion on the square kinetic diameter of a penetrant ϕ^2 [49]. Similarly, there is linear dependence of parameter γ on the ϕ^2 (see Fig. 3).

It was shown in [1] that the electrophility of amide group (total positive π-electron charge of amide group Z^+_{NC}) is the criterion of the energy of reversible interaction of ammonia with amide group. There are linear correlations of parameters $\gamma_{1,2}$ with Z^+_{NC} (see Fig. 4). Therefore, concentration activation barriers depend also on the energy of interaction between polymer and penetrant.

Table 2 presents parameters γ_1, γ_2 and effective sorptive capacity φ for physical transitions for some

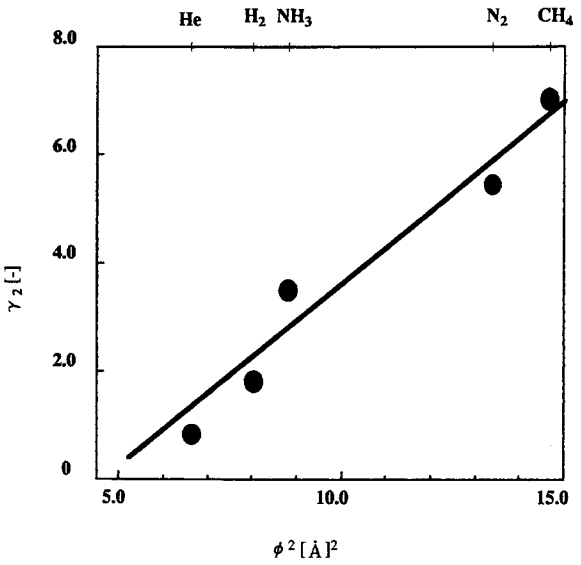


Fig. 3. Dependence of the parameter γ_2, which characterizes the diffusion of some simple gases penetrating together with ammonia through aromatic polyamide phenylone, on the kinetic diameter of the molecules of the gases (T=293 K). (Phenylone is the statistic copolymer of *meta*-phenylene diamine with 50/50 mixture of *tere-*/*iso*-phthaloyl chloride.)

block-copolymers in sulfur dioxide (the transitions take place in rigid fragments of block-copolymers). It follows from the data that the ratio $\varphi_\alpha/\varphi_\beta \approx 4 \pm 1$ and also $\gamma_2/\gamma_1 \approx 4 \pm 1$. Obviously, the boundaries between regions on the concentration dependencies of the diffusion coefficients correspond to the β-, α- and viscous-flow transitions in the polymers. Fig. 5 presents dependence of parameters γ_1, γ_2 on the donor number of functional sorptive group of polymer ND_{SbCl_5}, which is the criterion of the energy of the reversible interactions of sulfur dioxide with functional groups [4]. As for the systems NH_3/ polyamides, there is dependence of the parameters γ on the energy of the reversible interactions of sulfur dioxide with functional groups.

It also seems that the mobility of the active groups in a polymer, energies cohesion of which have a substantial contribution to the total energy cohesion of the polymer, is very important for gas permeability. It was established in the paper [50] that there was plasticization by carbon dioxide of such glassy polymers as polyethersulphone, cellulose acetate, polycarbonate, poly(methyl metacrylate), poly(ethylene

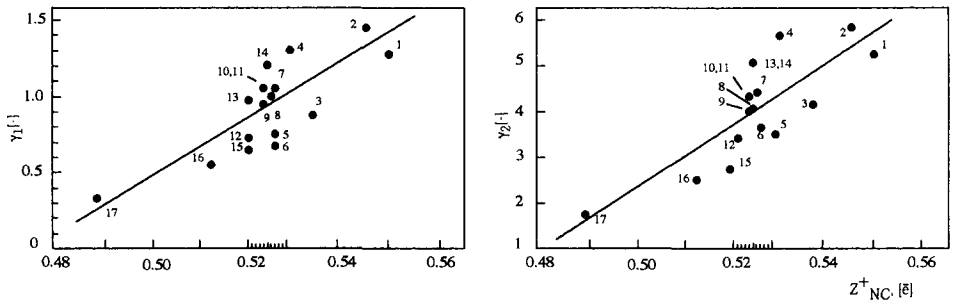


Fig. 4. Dependence of the parameters γ_1, γ_2 on the total positive charge of amide group in aromatic polyamide:

2 -HN-⟨⟩-NHCO-$(CH_2)_4$-CO- ;

4 -HN-⟨⟩-CO-⟨⟩-NHCO-⟨⟩-CO-⟨⟩-CO- ;

6 -HN-⟨⟩-NHCO-⟨⟩-CO- ;

8 -HN-⟨⟩-CO-⟨⟩-NHCO-⟨⟩-CO- ;

10 -HN-⟨⟩-O-⟨⟩-NHCO-⟨⟩-O-⟨⟩-CO- ;

12 -HN-⟨⟩-NHCO-⟨⟩-CO- ;

14 -HN-⟨⟩-CO-⟨⟩-NHCO-⟨⟩-CO- ;

16 -HN-⟨⟩-O-⟨⟩-NHCO-⟨⟩-CO- ;

1 -HN-⟨⟩-NHCO-$(CH_2)_4$-CO- ;

3 -HN-⟨H_2N⟩-O-⟨NH_2⟩-NHCO-⟨⟩-CO- ;

5 -HN-⟨⟩-S-⟨⟩-NHCO-⟨⟩-CO- ;

7 -HN-⟨⟩-CO-⟨⟩-NHCO-⟨⟩-CO- ;

9 -HN-⟨⟩-S-⟨⟩-NHCO-⟨⟩-CO- ;

11 -HN-⟨⟩-NHCO-⟨⟩-O-⟨⟩-CO- ;

13 -HN-⟨⟩-NHCO-⟨⟩-CO-⟨⟩-CO- ;

15 -HN-⟨⟩-NHCO-⟨⟩-S-⟨⟩-CO- ;

17 -HN-$(CH_2)_4$-NHCO-$(CH_2)_6$-CO- ;

Table 2
Parameters γ_1, γ_2 and degree of fullness of the effective sorptive capacity φ for physical transitions for some polymers in sulfur dioxide (BP – block-copolymers)

No.	Polymer	γ_1	γ_2	φ_β	φ_α	γ_2/γ_1	$\varphi_\alpha/\varphi_\beta$
1	BP1	0.40	1.6	0.17	0.53	4.0	3.1
2	BP2	0.26	1.1	0.20	0.60	4.2	3.0
3	Polybutadiene sulfone	0.25	1.0	0.20	0.78	4.0	3.9
4	BP3	0.40	1.9	0.15	0.65	4.7	4.3
5	Polyarylate siloxane	0.36	1.6	0.25	0.95	4.4	3.8
6	BP4	0.50	2.2	0.16	0.68	4.4	4.2
7	BP5	0.50	2.1	0.25	0.80	4.2	3.2
8	Polyvynil acetate	0.38	1.4	0.25	0.80	3.7	3.2
9	Polyarylate butadiene	0.39	1.7	0.28	0.96	4.3	3.4

[a] γ_1, γ_2, φ_β, φ_α [–].

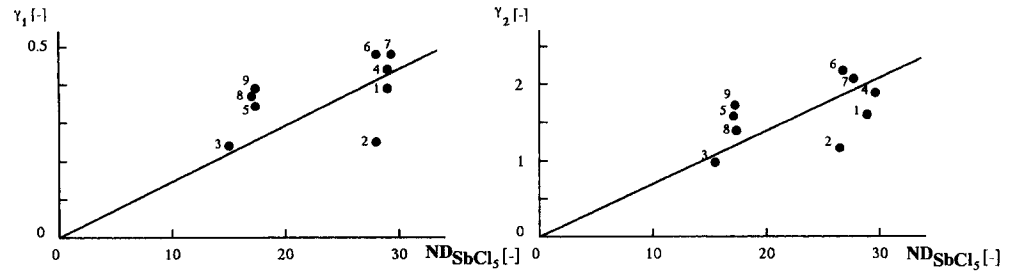


Fig. 5. Dependence of parameters γ_1, γ_2 on the donor number of functional sorptive group of polymer (systems SO_2/ polymers with electron-donor functional groups). The numbers for polymers are the same as in Table 2.

terephthalate) and polyimide Kapton: there were decrease of the glass transition temperatures of the polymers in the medium of CO_2. The plasticization of polymers in that case provoked by the increase of volume of the penetrant dissolved in the polymer (the second type of plasticization as ascribed in Section 2.2). Molecules of CO_2 are capable only for the dipole–dipole interactions with functional groups of the investigated polymers (–SO_2–, –COO, $\begin{matrix}-CO\\-CO\end{matrix}$ > N–) and the interactions CO_2/polymer are quite weak, much weaker than inter- and intramolecular interactions in the polymer. The free volume of the system polymer penetrant changes. There are decrease of permeability with increase of CO_2 pressure for polyethersulphone, polycarbonate, poly(ethylene terephthalate) and polyimide Kapton and dual mode sorption model explains this phenomenon. In these polymers active groups are included in the main chain. But there are increase of gas permeability for cellulose acetate and for poly(methyl metacrylate) with increase of CO_2-pressure. The acetate and the ester groups of these polymers are pendant. There is no chemical bond before and after the groups restricting their motion as exists for segments comprising the main chain. Increase of volume of dissolved penetrant easier provoked increase of mobility of the pendant groups than groups included in the main chain.

5. Conclusion

Mechanical and mass transfer properties of glassy polymers with functional groups specifically interacting (donor–acceptor type of interaction) with penetrant and also of block-copolymers with flexible and rigid fragments, where rigid fragments contain functional groups specifically interacting with penetrant, were investigated.

There is the plasticization of polymers by penetrant because of sorption of penetrant by functional groups.

There are four sections (regions) on the concentration dependencies of the diffusion coefficient. The boundaries between them correspond to the transition of the polymer (or rigid phase of block-copolymer) from one glassy state to another (β-transition), from glassy state to rubbery state (α-transition), and from rubbery state to the viscous-flow state.

The conception of the degree of fullness of the effective sorptive capacity, φ, was introduced with assumption that the effective sorptive capacity φ=1 corresponds to the concentration of gas in the polymer, at which the viscous-flow transition in the polymer (determined by baromechanical method) takes place. Such coordinate would allow the comparison of polymers with different energy of cohesion.

The concentrations of a penetrant on the active functional groups, n, (or degree of fullness of the effective sorptive capacity of the functional groups, φ), which corresponding to the α- and β-transitions in the polymer, have the ratio: $n_\alpha/n_\beta \approx \varphi_\alpha/\varphi_\beta \approx 4 \pm 1$. And relative concentration barriers of the activation, corresponding to the α- and β-transitions also have the same ratio: $\gamma_2/\gamma_1 \approx 4 \pm 1$. It seems, that the process of α-relaxation in the polymer includes the intermolecularly correlated displacement of neighboring segments of the same size as in the β-transition, i.e. close to the Kuhn's segment, but it is close to the correlated displacement of 3–5 segments.

Relative concentration activation barriers of the physical transitions depend on the energy of interaction between penetrant and functional group of polymer.

6. Symbols

B	barrier of internal rotation in the flexible chain polymer ($\approx$15 [kJ mol^{-1}])
E	modulus of elasticity [Pa]
E_{coh}	energy of cohesion [kJ mol^{-1}]
$\bar{D}$	integral diffusion coefficient [m^2 s^{-1}]
ΔH_{evap}	heat of evaporation [kJ mol^{-1}]
ND_{SbCl5}	Gutman's donor number [–]
S	number units in Kuhn's segment [–]
$Z_{NC}{}^{+}$	total positive π-electron's charge of amide group, calculated by quantum chemical method [$\bar{e}$]
n	sorption of gas by one functional sorbing group [mol mol^{-1}]
γ	parameter which characterized concentration dependence of diffusion coefficient (the slope on the dependence $\ln \bar{D}(\varphi)$), relative concentration activation barrier [–]
ϕ	kinetic diameter of a gas molecule [nm]
φ	degree of fullness of the effective sorptive capacity of a functional group, with assuming that the effective sorptive capacity φ=1 corresponds to the gas concentration, at which the viscous-flow transition (determined by baromechanical method) in the polymer takes place [–]

6.1. Subscripts:

α	corresponds to the α-transition
β	corresponds to the β-transition
fl	corresponds to the viscous-flow transition

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