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SUPERCRITICAL CARBON DIOXIDE SWELLING OF POLYHETEROARYLENES SYNTHESIZED IN *N*-METHYLPYRROLIDINONE

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Abstract. Five series of polyheteroarylenes have been investigated with regard to their physical properties before and after swelling with a supercritical carbon dioxide. The study of the dependence of the glass transition temperature and the free volume of polymers on their conformational rigidity showed that the process of swelling in the supercritical carbon dioxide is influenced by the voluminous side groups and by the high boiling solvent *N*-methylpyrrolidinone used for preparation of the polymers which facilitates the formation of crosslinks or complexes with the macromolecular chains.

Keywords: polyheteroarylenes, supercritical carbon dioxide, swelling, conformational rigidity, free volume, crosslinks.

1. Introduction

It is known that polyheteroarylenes exhibit high thermal stability and excellent mechanical properties determined by their conformational rigidity which differs significantly from that of analogous aliphatic polymers, from 10–15Å to thousands of Angstroms [1]. Most of these polyheteroarylenes are amorphous glassy polymers and most of their physical properties correlate well with their conformational rigidity [2]. At the same time, it is known that physical properties of amorphous glassy polymers depend not only on their chemical structure, but also on the history of their preparation, on the physical aging processes and others. In recent years a great interest was given to the modification of amorphous glassy polymers by supercritical carbon dioxide (sc CO_2) treatment with the aim of manipulating their physico-chemical properties [3]. It is believed that the swelling process with sc CO_2 can change some of these properties. If the swelling process is directly connected with the conformational rigidity of the polymers, it gives a good possibility to change their properties. Therefore, the study of the influence of the swelling process on glassy polymers of different chemical structure is very important.

Previously we have studied a polyetherimide containing hexafluoroisopropylidene groups which was subjected to supercritical CO_2 treatment under the temperature of 313 and 338 K, and the pressure of 150 kPa; we have found that under the temperature of 313 K microcavities were formed and an increase of the free volume of 23.1 % took place. In the case of treatment under 333 K we have obtained nanocavities and an increase of the free volume of 56.8 % [4].

Here we present a study of the dependence of glass transition temperature on conformational parameters and free volume for five groups of polyheteroarylenes and the swelling process of polymer films in the supercritical carbon dioxide.

2. Experimental

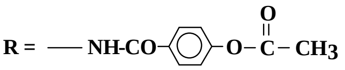
2.1. Preparation of Polymer Films

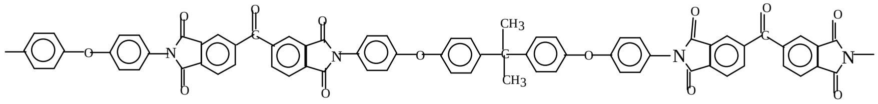
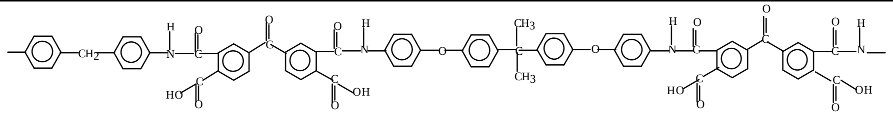
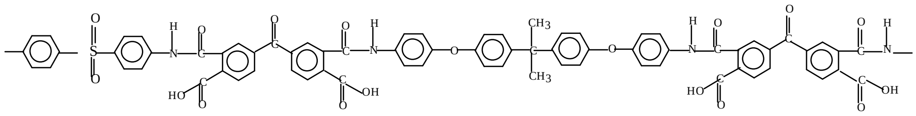
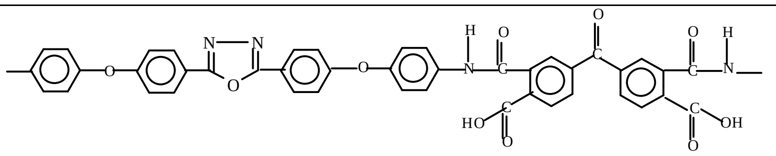
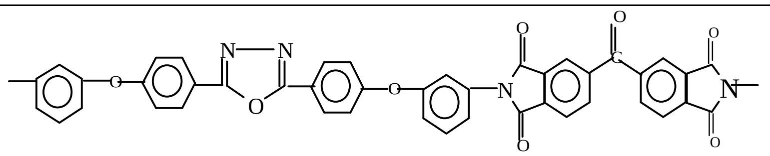
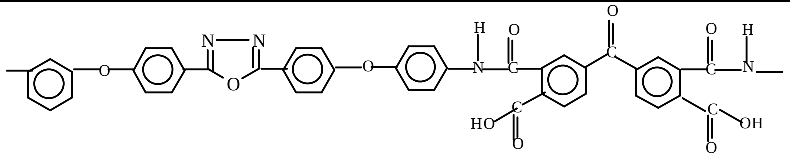
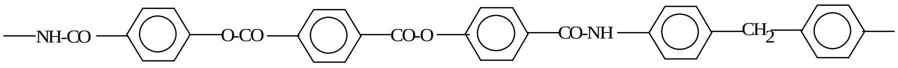
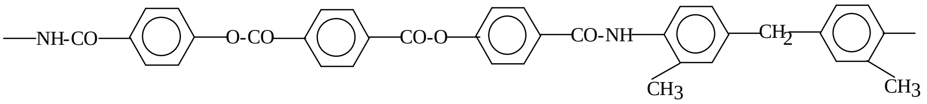
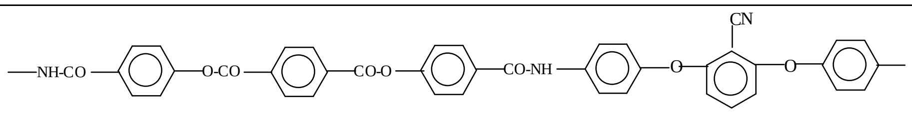
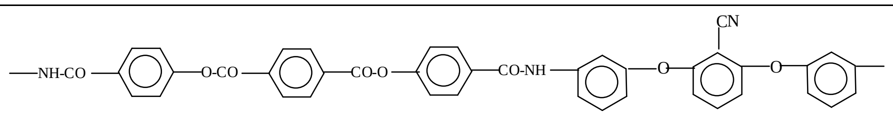
Five series of polymers have been studied and their synthesis was reported previously [5-13]. Thus, the series having the code AMIC contains one polyimide (1) and two polyamidic acids (2 and 3); the series having the code OXAD contains two polyoxadiazole-amidic acids (4 and 6) and one polyoxadiazole-imide (5); the series having the code PEAM contains six polyester-amides (7, 8, 9, 10, 11 and 12); the series having the code ACET contains three poly(oxadiazole-amide)s with pendant acetoxybenzamide groups (13, 14, 15); the series having the code CYAN contains four polyamidic acids (16, 18, 20, 22) and the corresponding four polyimides (17, 19, 21, 23) based on a diamine having cyano substituents and four dianhydrides containing pyromellitic, hexafluoroisopropylidene diphthalic, biphenylene or diphenylketone units, respectively

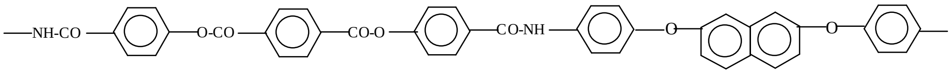
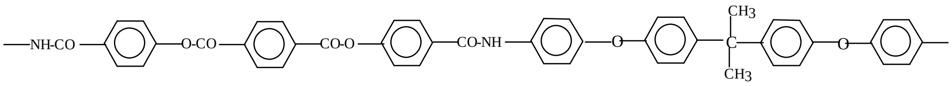
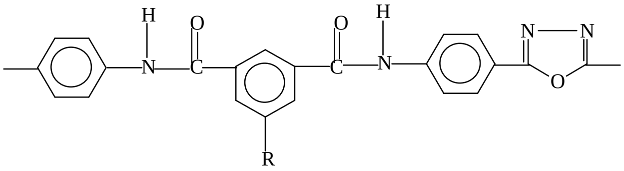
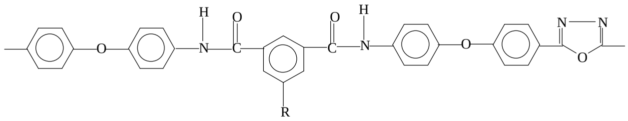
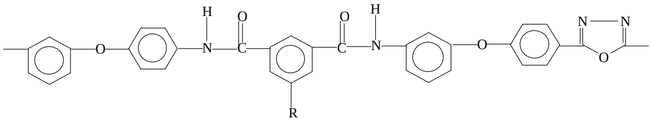
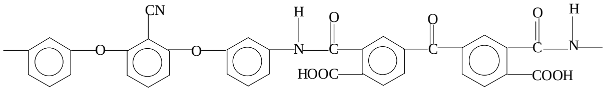
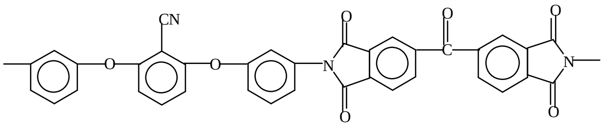
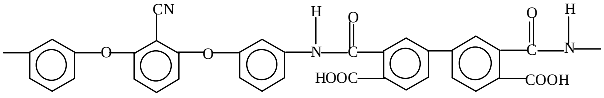
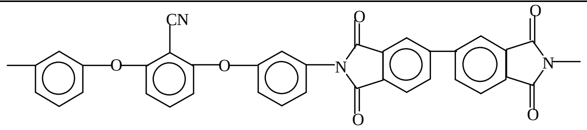
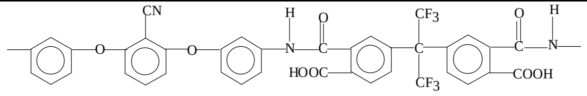
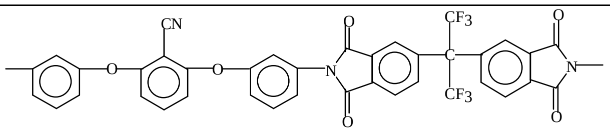
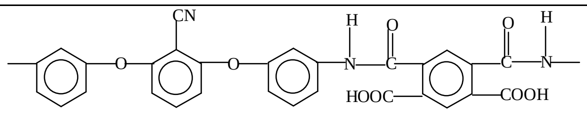
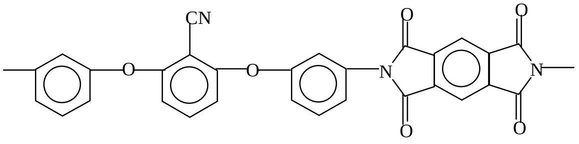
(Table 1). These polymers show good solubility in N-methylpyrrolidinone (NMP) and other polar amidic solvents having high boiling temperature. The films, having the thickness usually in the range of 30–40 mμ, were prepared by using solutions of polymers in N-methylpyrrolidinone, having the concentration of 15 %, which were cast onto glass plates and heated gradually up to 483 K. The films were carefully taken out of the substrate and were used afterwards for various measurements.

Table 1

Recurrent units of the studied polymers: AMIC, OXAD, PEAM, ACET and CYAN


$R = -NH\text{-}CO-C_6H_4-O-\overset{O}{\overset{\|}{C}}-CH_3$

Polymer	Series code	Recurrent unit
1	AMIC	
2	AMIC	
3	AMIC	
4	OXAD	
5	OXAD	
6	OXAD	
7	PEAM	
8	PEAM	
9	PEAM	
10	PEAM	

11	PEAM	
12	PEAM	
13	ACET	
14	ACET	
15	ACET	
16	CYAN	
17	CYAN	
18	CYAN	
19	CYAN	
20	CYAN	
21	CYAN	
22	CYAN	
23	CYAN	

2.2. Measurement of Density

To measure the density of polyheteroarylene films we used the hydrostatic weighing method. The study was performed with an equipment for density measurement and an electronic analytic balance Ohaus AP 250D, precision of 10^{-5} g, from Ohaus Corp US which was connected with computer. With the help of this equipment we measured the change of a sample weight during the experiment, with a precision of 0.001 g/cm^3 in the value of density. Ethanol was taken as a liquid with a known density. The studied polyheteroarylenes were not absorbed and were not dissolved in ethanol, which for these polymers had a low diffusion coefficient. Since the density of ethanol depends on temperature, every time it was measured using pycnometer. The characteristic diffusion times were in the domain of 10^4–10^5 s, which are 1-2 order of magnitude higher than the time of density measurement. That is why the sorption of solvent and the swelling of the film must have only insignificant influence on the value of the measured density. All measurements of the density were performed at 296 K. The density was calculated by the Eq. (1):

$$r_S = \frac{W_a}{W_a - W_1} r_1 \qquad (1)$$

where r_s is the density of the sample, W_a is the weight of the sample in the air, W_l is the weight of the sample in the liquid, r_l is the density of the liquid. The error of the density measurements was 0.1–0.3 %.

2.3. Measurement of Glass Transition Temperature

The glass transition temperature (T_g) of the polymers was measured by differential scanning calorimetry, using a Mettler DSC 12E apparatus. The samples were heated at the rate of 15°/min under nitrogen to above 573 K. Heat flow versus temperature scans from the second heating run was plotted and used for reporting the T_g. The mid point of the inflection curve resulting from the second heating run was assigned as the T_g of the respective polymers. The precision of this method is ±7–10 K.

2.4. Calculation of Conformational Parameter and Free Volume

We have taken the statistical Kuhn segment $\boldsymbol{A_{fr}}$, which was calculated by the Eq. (2) as the conformational parameter [1]:

$$A_{fr} = \lim_{n\to\infty}\left(\frac{< R^2 >}{nl_0}\right) \qquad (2)$$

where $<R^2>$ is the mean square distance between the ends of the chain calculated for all possible conformations; $L = nl_0$ is the contour length of the chain, a parameter which does not depend on the chain conformation; l_0 is the contour length of a recurrent unit. All the values of Kuhn segment were calculated by Monte Carlo method, the geometry of the recurrent unit was evaluated by the quantum chemical method AM1 [14].

To calculate the free volume we used the method previously described [15]. We built a model of the recurrent unit and its geometry was also evaluated by the quantum chemical method AM1. The atoms are described by spheres having Van der Waals radius equal to the corresponding radius of each type of atoms (Chart 1) [16].

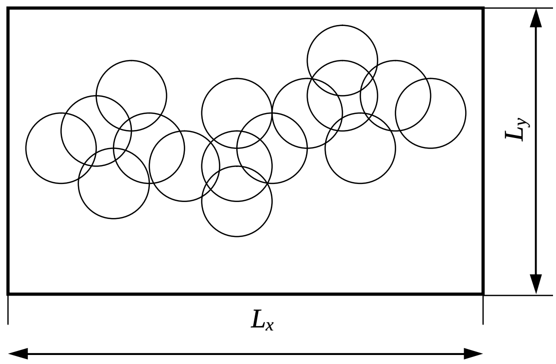


Chart 1. The monomer introduced in the box

This model was situated in a 3D rectangular box having the axes L_x, L_y, L_z given by the Eq. (3):

$$L_x = x_{\max} + R_{\max} - (x_{\min} - R_{\max}) = \\ = x_{\max} - x_{\min} + 2R_{\max} \qquad (3)$$

where $x_{\max}$ and $x_{\min}$ are the maximum and the minimum values of the coordinates of the atom corresponding to the recurrent unit; $R_{\max}$ is the maximum value of the radius of the atom corresponding to the recurrent unit. L_y and L_z were determined in the same way. The volume of this model was calculated by Monte Carlo method. Due to that, in the volume corresponding to the parameters of the box, random points were generated. The number of random points, landing in the recurrent unit, is m. At the beginning of the calculation m is equal to 0. For each random point the following conditions were verified:

$$\left|r_d - r_i\right| \le R_i, \qquad i = 1–n$$

where n is the number of atoms in the recurrent unit, $\left|r_d - r_i\right|$ is the distance between a given point and any other point in the recurrent unit.

In the case of achievement of these conditions for at least one atom, the procedure of verification stopped, the number of successful events began with (m+1), and the next random point was generated.

Van der Waals volume (V_w) was calculated by the formula (4):

$$V_w = \frac{m}{M} V_{box} \qquad (4)$$

where M is the total number of all points, V_{box} is the volume of the box.

The free volume ($\mathbf{V_f}$) was calculated by the formula (5):

$$V_f = \frac{1}{r} - \frac{N_A \cdot V_w}{M_o} \qquad (5)$$

where N_A is the number of Avogadro, r is the density of polymer, M_o is the molecular weight of the recurrent unit. The value V_f, thus calculated, shows the volume which is not occupied by macromolecules in one cm^3 of a polymer film. From this point on, we will call it a “free volume”.

2.5. Method of Treatment with Supercritical Carbon Dioxide

The experimental set-up and the method of impregnation with the supercritical carbon dioxide (sc CO_2) were described in previous papers [17-19]. This experimental set-up is composed of a generator which can provide CO_2 up to pressure of 35 MPa (High Pressure Equipment Company, USA). A system of valves ensures the CO_2 access to the reaction cell with the volume of 30 cm^3. The pressure generator and the reaction cell are provided with manometers for allowing to control the pressure and the letting-in and letting-out of the gas. The temperature control gives a better precision than ±0.2 K. The cell is designed for experiments at pressures up to 50 MPa and temperatures up to 393 K.

CO_2 desorption curves were obtained using the gravimetric technique [20]. Sample weight was measured with an Ohaus AP 250 D electronic balance interfaced with a computer.

The following experimental technique was applied: the polymer sample was weighed and placed into the cell. The sample had the form of a film (typically, a disk with 15 mm diameter and thickness in the range from several to tens microns). After purging the cell with CO_2 it was sealed. The pressure was increased up to the necessary value and the sample was exposed during a given time. The cell was decompressed, the polymer sample was placed on the electronic balance and the weight decrease during CO_2 desorption was recorded using a computer. Then the weight swelling degree at zero time (the moment of decompression) and the CO_2 diffusion coefficient were calculated. All experiments were done at 150 kPa and 313 K. The decompression speed of CO_2 was near 5 ml/s.

Approximate (asymptotic) formulas are typically used to analyze the desorption dynamics using gravimetric technique [21, 22]. Such formulas are valid only either for the initial or the final stage of the process. This approach can hardly give an answer to the question about the diffusion type: whether the diffusion is subjected to the Fick law or not. On the other hand, the progress of the computer technology during the recent years allows to realize numerically the analysis of the experimental data even when the complex exact solutions are used. We suppose that it makes the use of the approximate solutions superfluous. Therefore, we used the exact solutions of the diffusion problem with the uniform initial and zero bounda-

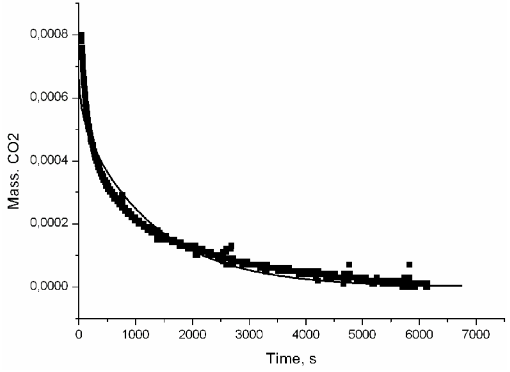


Fig. 1. Desorption curve of CO_2 for the polymer AMIC-2

Table 2

Diffusion coefficients (*D*) of CO_2 and equilibrium coefficient of swelling (Z_o) of the studied polymers

Polymer	*D*, 10^{-10} cm^2/s	Z_0, wt %	Polymer	*D*, 10^{-10} cm^2/s	Z_0, wt %
1	40	6.9	13	4.3	0.968
2	14	8.7	14	5.8	2.98
3	29	12.5	15	3.6	2.93
4	19	-	16	15	4.49
5	0.8	6.9	17	8.7	4.78
6	22	-	18	25.9	3.86
7	-	-	19	4.4	4.16
8	3.4	6.6	20	48	7.81
9	3.0	3.7	21	80.3	4.45
10	0.16	2.6	22	349	9.30
11	2.3	-	23	-	-
12	0.8	6.9	-	-	-

ry conditions valid in the Fick approximations. The equations describing the dependence of the sorbate weight on time $Z(t)$ are known from the diffusion theory [23]. For a film-like sample this equation has the form (6):

$$\frac{Z(t)}{Z_0}=\frac{8}{p^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left(\frac{-(2n+1)^2p^2Dt}{l^2}\right) \qquad (6)$$

where l is the film thickness; Z_0 is the equilibrium coefficient of swelling for “0” time; D is the diffusion coefficient.

A numerical algorithm to find the best fit for the experimental data was realized using the least squares method. Theoretical dependencies (6) were used as the fit functions and the parameters Z_0 and D were varied. Thus, the best fit allows to determine both the values of the diffusion coefficient and the initial sorbate weight (and therefore the equilibrium degree of the polymer swelling in sc CO_2). In the case when the exact solution (6), valid for $D = const$, gives a good fit for the experimental data, the diffusion is of normal type and it submits to the Fick law. Fig. 1 shows the typical desorption curve for the films of studied polyheteroarylene 4 and 5 and their fit with the theoretical dependence (6). As it can be seen in Fig. 1 our case corresponds to the normal diffusion (the experimental and theoretical curves coincide very well). Therefore, we can calculate the values of Z_0 and D. These values for the studied polyheteroarylenes are given in Table 2.

3. Results and Discussion

In order to understand how the physico-chemical properties of polyheteroarylenes change after treatment by supercritical carbon dioxide (sc CO_2), we analyzed such properties before and after treatment with sc CO_2. Table 3 shows the values of the glass transition temperature (T_g), Kuhn segment (A_{fr}) and Van der Waals volume (V_w) of all ivestigated polymers. The glass transition temperature of these polymers was in the range of 458–553 K and the conformational rigidity was in the domain of 12–72.5 Å. The dependence of T_g of these polymers on Kuhn segment is described by three straight lines having high correlation coefficients (Figs. 2a, b and c). For two samples OXAD (polymers 5 and 6) the values of T_g were identical. By using the equation $Y = 255.369 + 0.629X$, having such a high correlation coefficient R = 99.57 % , these T_g values can be calculated with high precision and, indeed, the difference was only 0.74 K, that situated beyond the accuracy limits of the T_g measuring method.

In the case of PEAM (Fig. 2a), the samples 8 and 12 are out of the straight line which is due to the low molecular weight of these two polymers. In such cases Gaussian coil has not been formed yet, the packing of the chains is loose, and the conformational transitions take place very easy in the glass transition state.

The dependence of the glass transition temperature on Kuhn segment in the case of ACET polymers is linear, with not a very high correlation coefficient (Fig. 2b). When measuring the glass transition temperature by using the differential scanning calorimetry (DSC) method, the error can be ±10 %. From the dependence of T_g on Kuhn segment, $Y = 260.35 + 0.391X$, we calculated the T_g of ACET polymers 14 and 15. They are 546.8 and 541.4 K, respectively. In one case it is 3.8 K higher and in the other case it is 1.6 K lower than the experimental values (543 K for both polymers). These differences are in the domain of experimental error of DSC method.

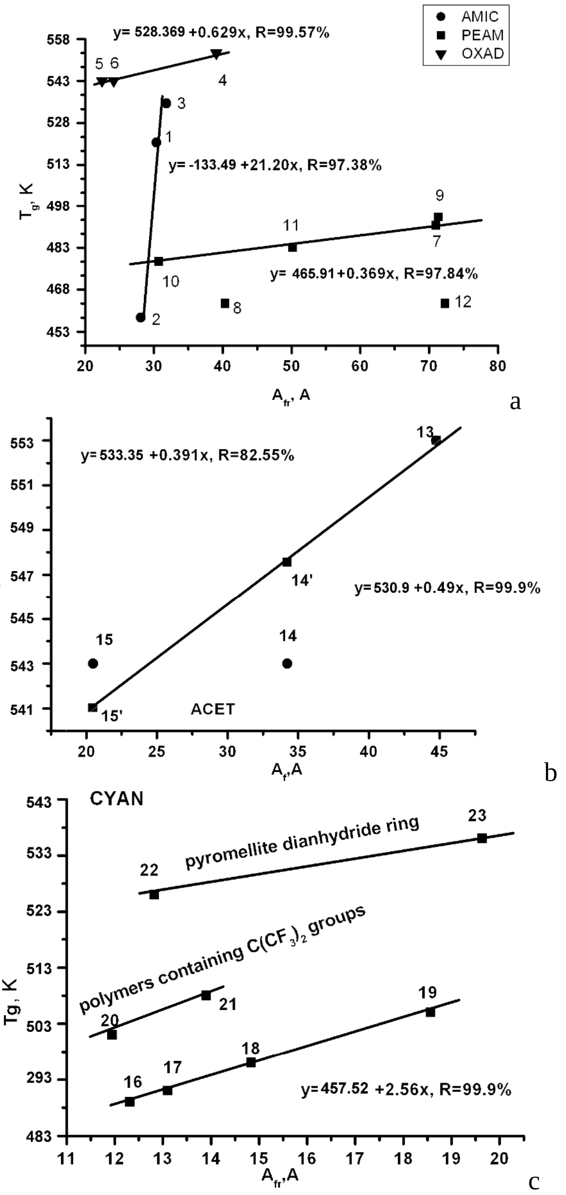


Fig. 2. Dependence of glass transition temperature (T_g) on Kuhn segment (A_{fr}) for the studied polymers:
AMIC, OXAD, PEAM (a), ACET (b) and CYAN (c)

The dependence of glass transition temperature on Kuhn segment for the CYAN polymers is described by three lines (Fig. 2c). The first line is for polymers 22 and 23 based on pyromellitic dianhydride, the second is for polymers 20 and 21 based on hexafluoroisopropylidene diphthalic dianhydride and the third line is for polymers 16, 17, 18 and 19 based on the dianhydride containing diphenylketone or biphenylene segment. Fig. 2 shows that the polymers AMIC, OXAD, PEAM, ACET and CYAN behave normally, which means that the glass transition temperature increases with increasing the rigidity [2].

Now we examine the modification of the polymers density after swelling and desorption of sc CO_2. We can presume that after treatment by sc CO_2 the density of polymers should decrease due to the possible formation of nano- and micro-cavities [13, 19, 24]. Table 3 shows the density values before (ρ_1) and after (ρ_2) treatment by sc CO_2.

The equilibrium coefficients of swelling with CO_2 of these polyheteroarylenes are low (Table 2). In order to find an explanation of this behavior we examine now the dependence of glass transition temperature on the free volume which was calculated by the Eq. (5) taking into consideration the Van der Waals volume and the density of the studied polymers. It is known that when the free volume of the polymers increases their glass transition temperature decreases because the conformational transitions take place easier by heating. The macromolecular chains start moving easier towards each other and the amorphous polymers soften.

After treatment by sc CO_2 the density of the polymers modified: for some of them the density decreased, therefore the swelling did take place, while for other polymers the density increased. To explain such a behavior, we examine now the dependence of glass transition temperature on a free volume, and the dependence of the free volume on the conformational rigidity.

The degree of swelling is not high in comparison with the degree of swelling of polyimides [4] and, therefore, the experimental measurements of the glass transition temperature after swelling with sc CO_2, by using the DSC method are not reasonable.

Table 3

Glass transition temperature, density, conformational parameter, Van der Waals volume, free volume and the changing of the density and free volume after swelling in supercritical CO_2

Polymer	T_g, K	A_{fr}, Å	V_w, $Å^3$	r_1, g/cm^3	V_{f0}, cm^3/g	r_2, g/cm^3	V_{f1}, cm^3/g	Δr, g/cm^3	ΔV, cm^3/g
1	521	30.37	1031.648	1.317	0.2342	1.319	0.2330	- 0.002	-0.0012
2	458	32.84	1087.52	1.311	0.2384	1.295	0.2479	0.016	**0.0095**
3	535	30.02	1096.54	1.329	0.2035	1.322	0.2075	0.007	**0.004**
4	553	39.05	651.013	1.391	0.3672	1.411	0.3570	- 0.020	-0.0102
5	543 542.82	22.45	624.822	1.369	0.3817	1.366	0.3833	0.003	**0.0016**
6	543 543.56	24.14	654.141	1.364	0.3798	1.376	0.3734	- 0.012	-0.0064
7	491	72.53	521.673	1.259	0.2416	1.302	0.2154	- 0.043	-0.0262
8	463	72.34	553.099	1.256	0.2385	1.246	0.2441	0.010	**0.0056**
9	494	71.39	614.855	1.308	0.2358	1.313	0.2328	- 0.005	-0.003
10	478	28.08	614.851	1.296	0.2428	1.315	0.2317	- 0.019	-0.0111
11	483	41.86	642.950	1.299	0.2538	1.344	0.2280	- 0.045	-0.0258
12	463	40.61	721.688	1.233	0.2673	1.259	0.2506	- 0.026	-0.0167
13	553	44.77	495.140	1.383	0.171	1.378	0.174	0.005	**0.002**
14	543 546.8	34.23	663.816	1.360	0.198	1.335	0.212	0.025	**0.014**
15	543 541.4	20.48	1096.54	1.336	0.216	0.311	0.230	0.025	**0.014**
16	489	12.32	546.402	1.316	0.246	1.339	0.233	-0.023	-0.013
17	496	14.84	518.139	1.330	0.235	1.309	0.247	0.021	**0.012**
18	491	13.11	527.414	1.325	0.236	1.343	0.226	-0.018	-0.010
19	505	18.57	501.620	1.364	0.208	1.350	0.216	0.014	**0.008**
20	501	11.95	608.868	1.392	0.237	1.411	0.227	-0.019	-0.010
21	508	13.91	582.420	1.407	0.227	1.382	0.240	0.025	**0.013**
22	531	12.83	451.458	1.379	0.222	1.358	0.228	-0.021	-0.008
23	541	17.51	424.690						

Notes: T_g –glass transition temperature; A_{fr} – Kuhn segment; V_w – Van der Waals volume; r_1 – density before swelling; r_2 – density after swelling; V_{f0} – free volume before swelling; V_{f1} – free volume after swelling; $\Delta r = r_1 – r_2$ is modification of density; $\Delta V = V_{f1} – V_{f0}$ is modification of free volume.

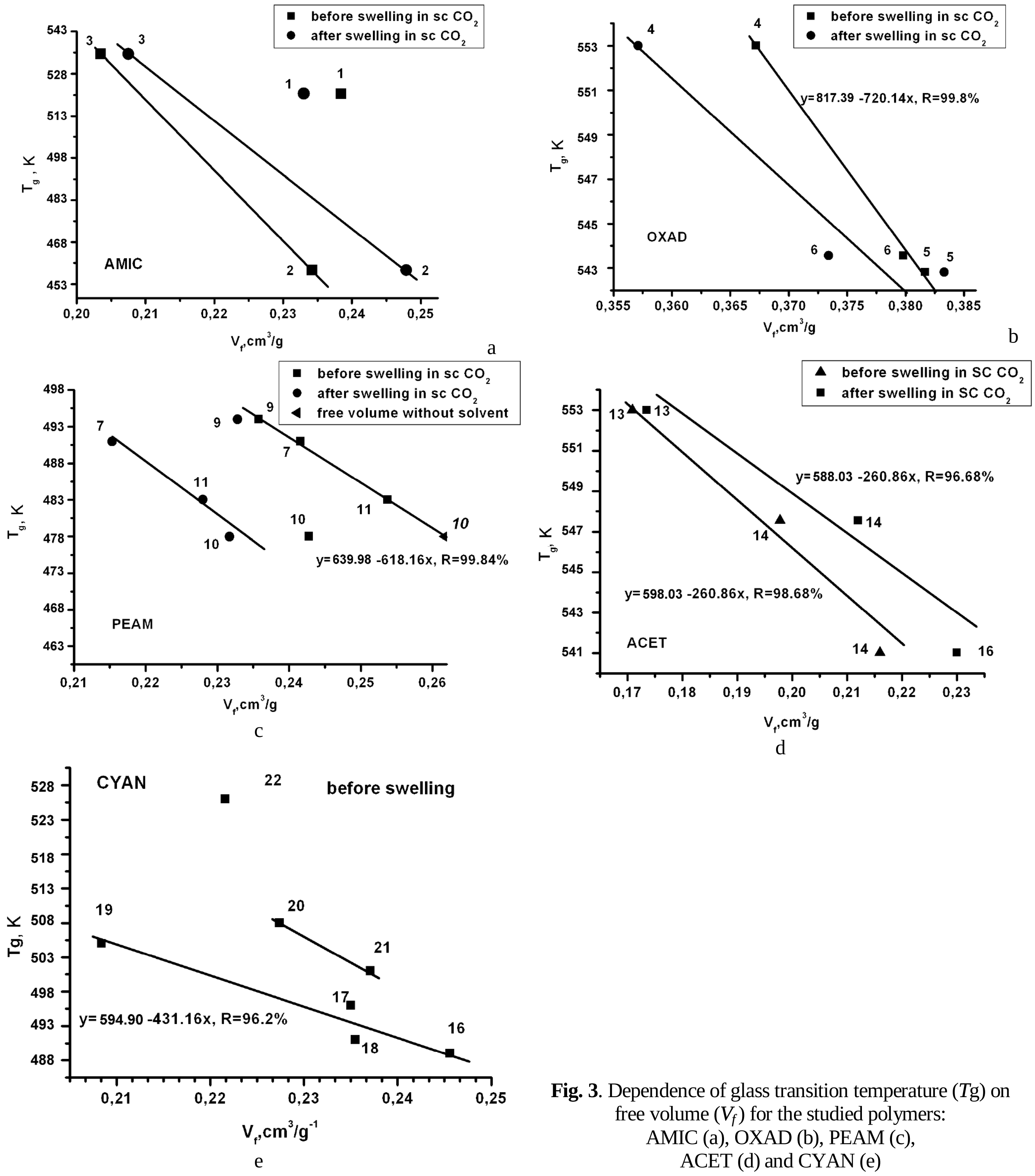


Fig. 3. Dependence of glass transition temperature (*T*g) on free volume (V_f) for the studied polymers: AMIC (a), OXAD (b), PEAM (c), ACET (d) and CYAN (e)

Fig. 3 presents the dependence of glass transition temperature on the free volume for five series of polymers before and after swelling in sc-CO_2. As can be seen in Figs. 3a and 3d, only in the series AMIC and ACET the line showing the free volume of the polymers after swelling in sc CO_2 is on the right side, which means that the swelling of polymers did take place, although not in a significant degree. Polymer AMIC 1 is out of both cases. It shows that polymers AMIC 2 and AMIC 3 contained residual solvent *N*-methylpyrrolidinone (NMP) which was partially eliminated from these polymers by swelling in sc CO_2. If this would not have been observed, after swelling in sc CO_2 all points had been situated on the same line.

For the polymers in series OXAD (Fig. 3b), the density of polymers 4 and 6 after swelling in sc CO_2 increases, and only for polymer 5 it decreases below the initial value. The dependence of glass transition temperature on the free volume is linear, with a high correlation coefficient. The increase of density after modification in sc CO_2 could be explained by absorption of CO_2 in the polymer matrix, due to the formation of hydrogen bonds between CO_2 and hydrogen atoms of amide groups. It is known that CO_2 molecule is quadruple, in the two ends having oxygen atoms with a pair of non-participating electrons. These electrons may participate in the formation of hydrogen bonds with hydrogen atoms from the polymer matrix. In this case it can be the hydrogen of amide groups. If the distance between hydrogen atoms of the recurrent unit and oxygen atom of CO_2 is smaller than the sum of Van der Waals radii, and the energy of formation of the complex decreases, then the hydrogen bond is formed. To verify this hypothesis, calculations were performed, by using the quanto-chemical method AM1 [14]. If we consider that the formation energy of the recurrent unit is E_1 and the formation energy of CO_2 is E_2, then the total energy of the two independent units (recurrent unit and CO_2 molecule) is: $E = E_1 + E_2 = -761.49$ kJ/mol. The calculated formation energy of the complex of these two units was –768.40 kJ/mol which is 6.91 kJ/mol lower. Therefore, the formation of the complex is more probable than the existence of separated units. On the other hand, the sum of Van der Waals radii of oxygen and hydrogen atoms is 2.53 Å [16]. The calculations showed that the distance between the oxygen atom of the carbonyl group and the hydrogen atoms of the amide group is 2.27 Å, which is 0.26 Å shorter than the sum of Van der Waals radii of these atoms. Thus, it was proved the possibility of formation of complexes between amide groups in the polymer matrix and CO_2 molecules. In such a case it is understandable why a part of CO_2 during decompression remains in polymers 4 and 6: because in series OXAD only these two polymers contain amide groups. Similar specific interaction of CO_2 with polymers was also observed earlier [25]. This is confirmed by diffusion coefficients of CO_2 in these polymers (Table 2).

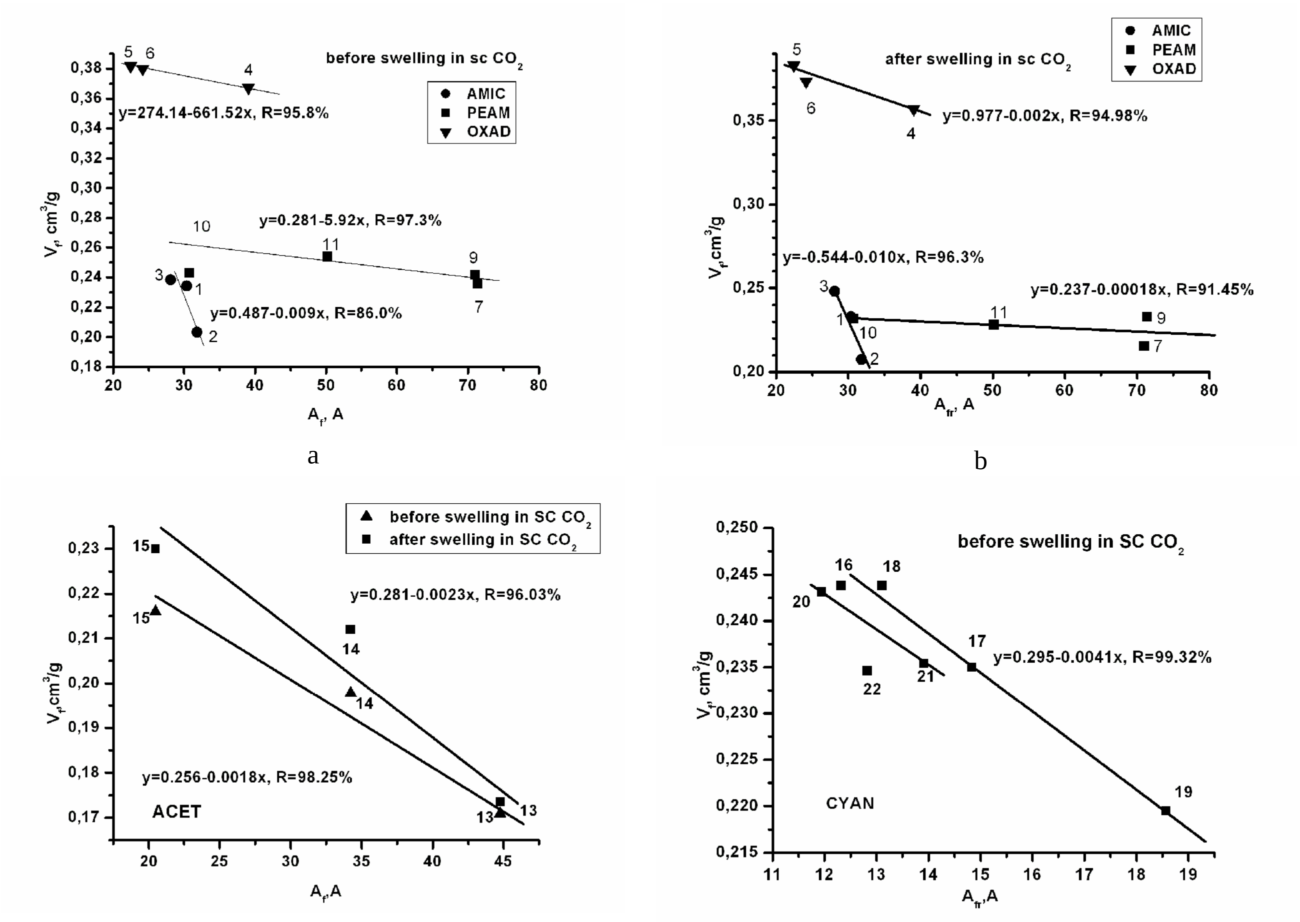
In the polymer series PEAM (Fig. 3c) the dependence of the glass transition temperature on the free volume is linear for three polymers: 7, 9 and 11. In the case of sample 10 the free volume is significantly smaller than it should be according to the general dependence in this series. It shows that in the case of this polyheteroarylene, when the film was prepared, the part of the solvent remained inside it and did not evaporate by drying until constant weight. This part of the free volume can be calculated. The solvent used to cast the films was *N*-methylpyrrolidinone (NMP). We calculated its Van der Waals volume. We started from the equation showing the dependence of the glass transition temperature on the free volume and we found that the free volume of polymer 10 before treatment by sc CO_2 is 0.262 cm^3/g. The difference between the experimental value of the free volume and the calculated one is 0.0192 cm^3/g or 7.9 % of the free volume of this polymer. That is the part of the free volume which is occupied by the solvent and that is why the density of the polymer is higher. The value of the free volume occupied by the solvent corresponds to 2.4 %. After swelling in sc CO_2 the free volume of these polymers, with the exception of 8, decreases significantly (Table 3): for polymer 9 it decreases by 1.4 %, while for polymer 11 it decreases by 10.2 % It shows that the absorption of CO_2 in the polymer matrix is similar to the polymers in series OXAD, but it occurs at different degrees for each polymer. The diffusion coefficients which are given in Table 2 confirm the formation of hydrogen bonds in these polymers because they are lower in comparison with the diffusion coefficient of polymer 9. In the case of this latter polyheteroarylene the diffusion coefficient is high enough and a big part of CO_2 leaves the polymer matrix during decompression.

Fig. 3d shows the dependence of the glass transition temperature on the free volume of the ACET polymers before and after swelling with sc CO_2. It can be seen here that the line referring to the free volume after swelling is situated in the right side which means that the swelling of the polymers did take place, although not to the same degree. The degree of swelling is not high in comparison with the degree of polyimides swelling [4] and, therefore, the experimental measurements of the glass transition temperature after swelling with sc CO_2, by using the DSC method is not reasonable. Both dependences shown in Fig. 3d have high correlation coefficients. The degree of swelling of the polymers in this group differs significantly from each other. In the case of polymer 13, the free volume increases by 1.7%, while in the case of polymer 15 it increases by 6.5 %. This behavior is connected with the conformational rigidity of the polymers which decreases from 44.77 Å in the case of polymer 13 to 20.48 Å in the case of polymer 15 (Table 3). While the rigidity of the polymer increases, their free volume decreases (Fig. 4). When the number of flexible bridges (Ph–O–Ph) increases, in the case of polymers 14 and 15, and therefore the probability of conformational transitions in polymer chains increases during treatment by sc CO_2 leading to the formation of nanocavities, the free volume of the polymer increases. The voluminous side groups R (structures shown in Table 1) play a significant role here since they do not allow the polymer chains in the initial films to pack tightly, which increases the probability of conformational transitions around the flexible bridges.

A completely different behavior is observed in the case of CYAN polymers when we examine the dependence of glass transition temperatures on the free volume (Fig.

3e). Before swelling with CO_2 the dependence of the glass transition temperature on the free volume (Fig. 3e) and the dependence of the glass transition temperature on Kuhn segment (Fig. 2c) divides in three sub-groups: polymers 16, 17, 18 and 19 which contain diphenylketone or biphenylene unit in the dianhydride segment; polymers 20 and 21 containing hexafluoroisopropylidene diphthalic units in the dianhydride segment; polymers 22 and 23 containing pyromellitic unit in the dianhydride segment. Since the polymer 23 is partially crystalline, it will not be taken into consideration in the next discussion. The dependence of the free volume on Kuhn segment is divided in the same three sub-groups (Fig. 4d).

The data given in Fig. 4 showing the dependences of the free volume before and after swelling in CO_2 upon its conformational rigidity confirm the conclusions made on the basis of Fig. 3. With increasing the rigidity, the free volume decreases. Both of the dependencies (before and after swelling) have high coefficients of correlation, but after swelling in CO_2 only for polymers AMIC the correlation coefficient increases, while for the polymers OXAD, PEAM and ACET it has a slight decrease. This is directly connected with the presence of the solvent in polymers before and after swelling, and with the presence of residual CO_2 participating in the formation of hydrogen bonds with amide groups.

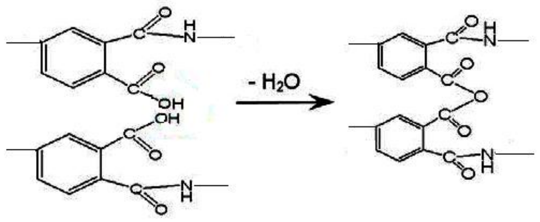


a b c d

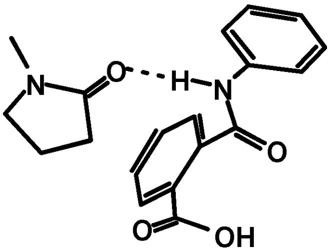
Fig. 4. Dependence of free volume on the conformational rigidity (Kuhn segment) of the studied polymers

The swelling of the CYAN polymers takes place in the polymers 17, 19 and 21, containing imide rings, and it increases with the increase of the flexibility (Table 3). To explain such a difference, we can refer to a previously published paper [26] presenting a study of the IR spectra of the polyamidic acids prepared in various solvents. There, it was shown that in the synthesis or dissolution in *N*-methylpyrrolidinone (NMP) followed by heating up to 473 K to remove the solvent, two competitive processes may take place:

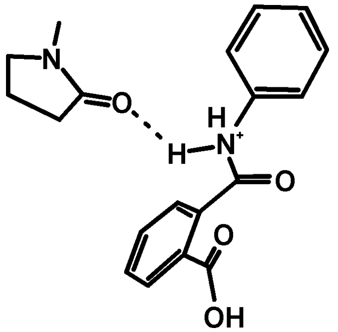
– the first is the formation of crosslinks between the chains of polyamidic acids:



– the second is the formation of polymer/NMP complex:



The energy of the formation of the complex = –31 kJ/mol



The energy of the formation of the complex = –74 kJ/mol

Thus, the formation of crosslinks in the polyamidic acids prevents their swelling with sc CO_2. The formation of complexes between NMP and amide groups hinders the free rotation around N–Ph bond and also leads to the formation of inter-chain bonds. Also, the low degree of swelling from 3.8 to 7 % found in polyimides 17, 19 and 21 is connected with the fact that during imidization of the polymers in NMP, it is possible to form anhydride bridges leading to crosslinks between chains. But in the case of polyimides such crosslinks are less frequent than in the case of the corresponding polyamidic acids.

Now we look at Table 2 which presents the diffusion coefficients of CO_2 obtained during desorption of CO_2 and equilibrium degree of swelling Z_0. Both these parameters are determined by moderate degree of precision. The diffusion coefficients and equilibrium degree of swelling Z_0 of these polyheteroarylenes show the strong connection of these values with the chemical structure and the properties of polymers. Thus, in the case of series AMIC, the polymer 1 shows the highest value of diffusion coefficient D, and a medium value of equilibrium degree of swelling Z_0, which can be explained by a lower coefficient of molecular packing, and a higher rigidity of the polymer. The polymers in series OXAD show high values of D for 4 and 6, in comparison with 5, which can be connected with the formation of specific interaction between CO_2 and amide groups. Finally, the series PEAM shows low values of D and Z_0, and among them the polymer 12 exhibits the highest coefficient of molecular packing and one of the lowest values of D. For the ACET polymers 14 and 15, they are close to each other, regardless the significantly different rigidity. At the same time the values of the free volume increase which are also very close; they were calculated on the basis of density change and Van der Waals volume of the recurrent unit. The diffusion coefficients of the CYAN polymers 17, 19 and 21 are very close to each other, with the exception of polymer 21 which contains hexafluoroisopropylidene bridges, while the coefficients of swelling of these three polyimides are almost identical. In the case of CYAN polymers 16, 18 and 20 the coefficients of swelling are different and they increase with the decrease of the rigidity. The increase of rigidity enables the increase of the number of crosslinks due to the formation of anhydride bridges. In case of polymer 21 both diffusion coefficient and equilibrium coefficient of swelling are high probably because of a stronger sorption of carbon dioxide during swelling and its possible retention in the polymer matrix due to the weak interactions between hydrogen in amide groups and oxygen in carbon dioxide.

4. Conclusions

This study shows that the swelling process of polyheteroarylenes with supercritical carbon dioxide is connected with the history of the polymer film preparation. However, the conformational analysis allows to determine certain factors which influence this process. Thus, with the increase of conformational rigidity, the degree of swelling of the polymers is lower. The presence of voluminous side groups facilitates the swelling process. Due to the presence of residual solvent the advanced drying of the polymer film is necessary before treatment by supercritical carbon dioxide. After treatment by supercritical carbon dioxide it is also necessary to maintain the film at high temperature for some time in order to evolve the CO_2 gas.

The free volume in polymers depends on their conformational rigidity. When the films are prepared from polymer solutions, solvents having low boiling point should be used in order to prevent the influence of the residual solvent on the swelling process of the polymers in supercritical CO_2. The polymers containing amide groups easily form hydrogen bonds with CO_2 which hinders significantly their swelling**.** The study of the dependence of the glass transition temperature on the free volume and on Kuhn segment, before and after swelling with supercritical carbon dioxide, of two groups of polyheteroarylenes, ACET and CYAN, showed that the swelling degree is low, below 7 %, and it depends significantly on the structure of the recurrent units, for example on the presence of voluminous side substituents and flexible brigdes such as Ph–O–Ph. The use of high boiling solvent N-methylpyrrolidinone (NMP) in the synthesis of polyheteroarylenes may lead to the formation of complexes between NMP and polymer chains which give rise to crosslinks and increase the rigidity and thus reduce the degree of swelling with supercritical carbon dioxide.

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НАБУХАННЯ У СУПЕРКРИТИЧНОМУ ДІОКСИДІ ВУГЛЕЦЮ ПОЛІГЕТЕРОАРИЛЕНІВ, СИНТЕЗОВАНИХ У *N*-МЕТИЛПІРОЛІДОНІ

Анотація. *Досліджено фізичні властивості п'яти полігетероариленів до і після набухання їх в суперкритичному діоксиді вуглецю. При вивченні залежності температури склування та вільного об'єму полімерів від їх конформаційної жорсткості встановлено, що значний вплив на процес набухання у суперкритичному діоксиді вуглецю мають об'ємні бічні групи полімеру і висококиплячий розчинник N-метилпіролідон, що використовується для приготування полімерів, які сприяють утворенню зшитих зв'язків або комплексів з макро молекулярними ланцюгами.*

Ключові слова: *полігетероарилени, суперкритичний діоксид вуглецю, набухання, конформаційна жорсткість, зшиті зв'язки.*