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Inga A. Ronova[a]; Lev N. Nikitin[a]; Ekaterina A. Sokolova[a]; Irina Bacosca[b]; Ion Sava[b]; Maria Bruma[b]
[a] Russian Academy of Sciences, Nesmeyanov Institute of Organoelement Compounds, Moscow, Russia
[b] Aleea Grigore Ghica Voda, "Petru Poni" Institute of Macromolecular Chemistry, Iasi, Romania

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Swelling of Polyheteroarylenes in Supercritical Carbon Dioxide

INGA A. RONOVA[1], LEV N. NIKITIN[1], EKATERINA A. SOKOLOVA[1], IRINA BACOSCA[2], ION SAVA[2] and MARIA BRUMA[2,*]

[1]*Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilov st. 28, Moscow 119991, Russia*
[2]*"Petru Poni" Institute of Macromolecular Chemistry, Aleea Grigore Ghica Voda 41A, Iasi 700487, Romania*

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Two series of polyheteroarylenes have been investigated with regard to their physical properties before and after swelling with supercritical carbon dioxide. The study of the dependence of glass transition temperature and free volume of polymers on their conformational rigidity showed that the process of swelling in supercritical carbon dioxide is influenced by the voluminous side groups and by the high boiling solvent N-methylpyrolidinone used for the 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 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, the physical aging processes, etc. In recent years, great interest was given to the modification of amorphous glassy polymers by treatment with supercritical carbon dioxide (sc CO_2) with the aim to manipulate 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, this provides 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 the treatment with supercritical CO_2 under a temperature of 40°C and 65°C, and a pressure of 150 bar; we have found that under the temperature of 40°C microcavities were formed and an increase of the free volume of 23.1% took place. In the case of treatment under 60°C, 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 two groups of polyheteroarylenes and the swelling process of polymer films in supercritical carbon dioxide.

2 Experimental

2.1 Preparation of Polymer Films

Two series of polymers have been studied whose synthesis was performed according to previously published methods (5–9). Thus, the series having the code **ACET** contains three poly(oxadiazole-amide)s with pendant acetoxybenzamide groups (**1**, **2**, **3**); the series having the code **CYAN** contains four polyamidic acids (**4**, **6**, **8**, **10**) and the corresponding four polyimides (**5**, **7**, **9**, **11**) 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 μm, were prepared by using solutions

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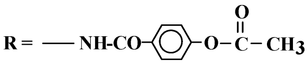
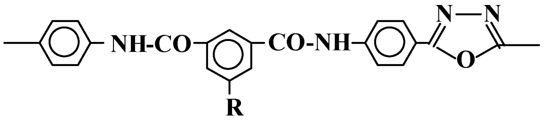
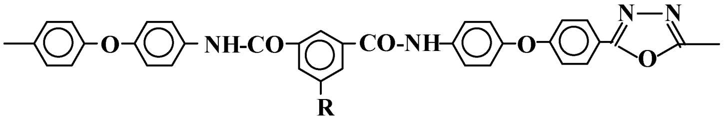
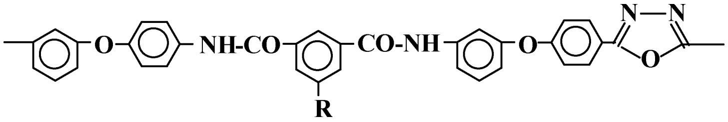
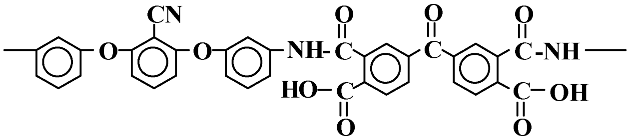
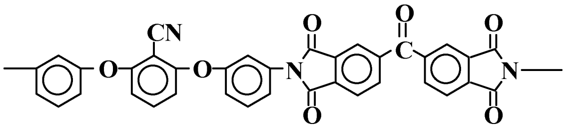
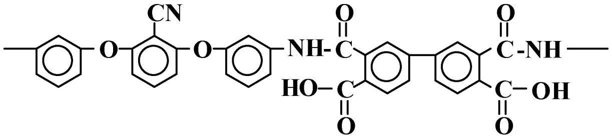
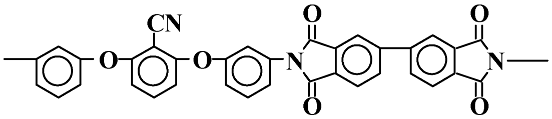
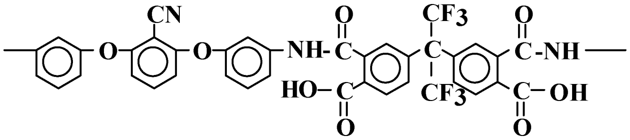
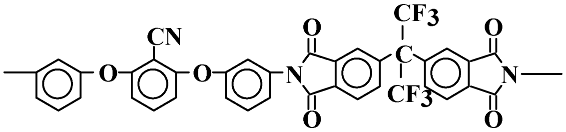
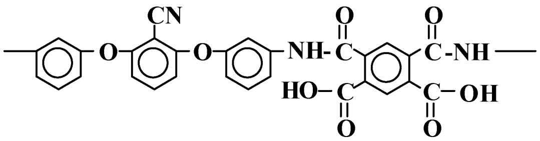
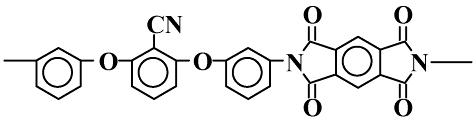
*Address correspondence to: Maria Bruma, "Petru Poni" Institute of Macromolecular Chemistry, Aleea Grigore Ghica Voda 41A, Iasi 700487, Romania. E-mail: mbruma@icmpp.ro

Table 1. Repeating units of **ACET** and **CYAN** polymers:



Polymer	*Series code*	*Repeating unit*
1	**ACET**	
2	**ACET**	
3	**ACET**	
4	**CYAN**	
5	**CYAN**	
6	**CYAN**	
7	**CYAN**	
8	**CYAN**	
9	**CYAN**	
10	**CYAN**	
11	**CYAN**	

of polymers in NMP, having the concentration of 15%, which were cast onto glass plates and heated gradually up to 210°C until a constant weight. The films were carefully taken out of the substrate and were used afterwards for various measurements.

2.2 Measurement of Density

To measure the density of polyheteroarylene films, we used the hydrostatic weighing method. The study was performed with equipment for density measurement and an electronic analytic balance Ohaus AP 250D, precision of 10^{-5} g, from Ohaus Corp US which was connected to a computer. With this equipment, we measured the change of 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 known density. The studied polyheteroarylenes did not absorb and did not dissolve in ethanol, which for these polymers had a low diffusion coefficient. Since the density of ethanol depends on temperature, it was measured every time using a 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. This is why the sorption of solvent and the swelling of the film must have only an insignificant influence on the value of the measured density. All measurements of the density were performed at 23°C. The density was calculated with Equation 1:

$$\rho_s = W_a/(W_a - W_l)\rho_l \tag{1}$$

where $\boldsymbol{\rho}_s$ is the density of the sample, $\mathbf{W}_a$ is the weight of the sample in air, $\mathbf{W}_l$ is the weight of the sample in liquid, $\boldsymbol{\rho}_l$ is the density of liquid. The error of the density measurements was 0.1–0.3%.

2.3 Measurement of Glass Transition Temperature

The glass transition temperature (Tg) of the polymers was measured by differential scanning calorimetry, using a Mettler DSC 12E apparatus. The samples were heated at a rate of 15°C/min under nitrogen to above 300°C. Heat flow vs. temperature scans from the second heating run were plotted and used for reporting the Tg. The mid point of the inflection curve resulting from the second heating run was assigned as the Tg of the respective polymers. The precision of this method is ±7–10°C.

2.4 Calculation of Conformational Parameter and Free Volume

As a conformational parameter, we have taken the statistical Kuhn segment $\boldsymbol{A}_{fr}$, which was calculated with the Equation 2 (1):

$$\mathbf{A}_{fr} = \lim_{n\to\infty}\left(\frac{<\mathbf{R}^2>}{\mathbf{nl}_o}\right), \tag{2}$$

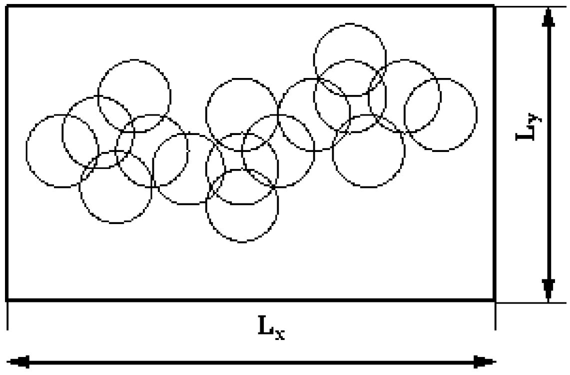


Chart 1. The repeating unit introduced in the box.

where $\boldsymbol{R}^2$ is the mean square distance between the ends of the chain calculated for all possible conformations; $\boldsymbol{L} = \boldsymbol{nl}_o$ is the contour length of the chain, a parameter which does not depend on the chain conformation; $\boldsymbol{l}_o$ is the contour length of a repeating unit. All the values of the Kuhn segment were calculated with the Monte Carlo method, geometry of the repeating unit summarized by the quantum chemical method AM1 (10).

To calculate the free volume we used the method previously described (11). We built a model of the repeating unit and its geometry was also summarized by the quantum chemical method AM1. The atoms are described by spheres having the Van der Waals radius equal to the corresponding radius of each type of atoms (Chart 1) (12).

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

$$\mathbf{L}_x = \mathbf{x}_{max} + \mathbf{R}_{max} - (\mathbf{x}_{min} - \mathbf{R}_{max}) = \mathbf{x}_{max} - \mathbf{x}_{min} + 2\mathbf{R}_{max}, \tag{3}$$

where $\mathbf{x}_{max}$ and $\mathbf{x}_{min}$ are the maximum and the minimum values of the coordinates of atom corresponding to the repeating unit, $\boldsymbol{R}_{max}$ is the maximum value of the radius of atom corresponding to the repeating unit. $\mathbf{L}_y$ and $\mathbf{L}_z$ were determined in the same way. The volume of this model was calculated with the Monte Carlo method; in the volume corresponding to the parameters of the box, random points were generated. The number of random points, landing in the repeating unit, is $\boldsymbol{m}$. In the beginning of the calculation $\boldsymbol{m}$ is equal to zero. For each random point the following conditions were verified:

$$|\mathbf{r}_d - \mathbf{r}_i| \le \mathbf{R}_i, \quad \mathbf{i} = \mathbf{1}\ldots\mathbf{N},$$

where $\boldsymbol{N}$ is the number of atoms in the repeating unit, $|\boldsymbol{r}_d - \boldsymbol{r}_i|$ is the distance between a given point and any other point in the repeating unit. In 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 ($\mathbf{V}_w$) was calculated with the formula (4):

$$\mathbf{V_w = (m/M)V_{box}} \tag{4}$$

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 with the formula (5):

$$\mathbf{V_f} = \frac{1}{\rho} - \frac{\mathbf{N_A \bullet V_w}}{\mathbf{M_o}} \qquad (5)$$

where $\mathbf{N}_A$ is the number of Avogadro, ρ is the density of polymer, $\mathbf{M_o}$ is the molecular weight of the repeating unit. The value $\mathbf{V_f}$, thus calculated, shows the volume which is not occupied by the macromolecules in one cm^3 of polymer film. From this point on, we will call it "free volume".

2.5 Method of Treatment with Supercritical Carbon Dioxide

The experimental set-up and the method of impregnation with supercritical carbon dioxide (sc-CO_2) were described in previous papers (13–15). This experimental set-up is composed of a generator which can provide CO_2 up to 35 MPa pressure (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 to allow control of the pressure and the letting-in and letting-out of gas. The temperature control allows a precision better than ±0.2°C. The cell is designed for experiments at pressures up to 50 MPa and temperatures up to 120°C.

CO_2 desorption curves were obtained using the gravimetric technique (16). 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 bar and 40°C. 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 (17, 18). Such formulas are only valid 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 us to realize numerically the analysis of the experimental data even when the complex exact solutions are used. We believe that this makes the use of the approximate solutions superfluous.

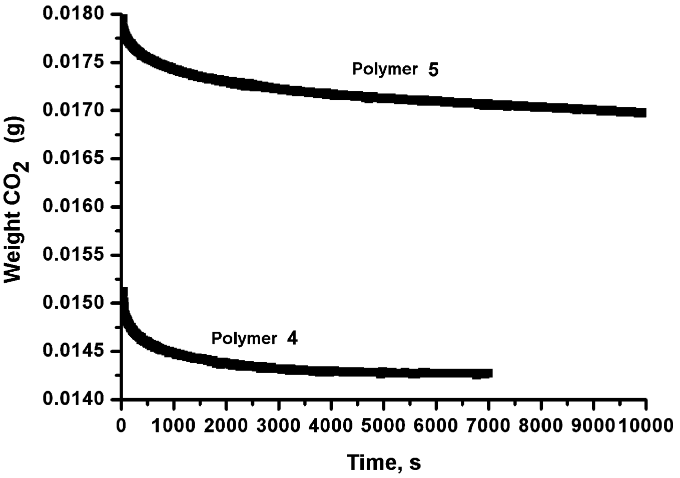


Fig. 1. Desorption curve of CO_2 for the polymers CYAN **4** and CYAN **5**.

Therefore, we used the exact solutions of the diffusion problem with the uniform initial and zero boundary 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 (19). For a film-like sample, this equation has the form (6):

$$\frac{\mathbf{Z(t)}}{\mathbf{Z}_0} = \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(\mathbf{2n+1})^2}\mathbf{exp}\left(\frac{-(2n+1)^2\pi^2\mathbf{Dt}}{\mathbf{l}^2}\right) \qquad (6)$$

where l is the film thickness; Z_0 is equilibrium coefficient of swelling for the "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 a normal type and it obeys the Fick law. Figure 1 shows the typical desorption curve for the films of studied polyheteroarylene **4** and **5** and their fit with the theoretical dependence (6). As can be seen in Figure 1, our case corresponds to the normal diffusion (the experimental and theoretical curves coincide very well). Therefore, we can calculate the values of $\mathbf{Z}_0$ and $\mathbf{D}$. The values of $\mathbf{Z}_0$ and $\mathbf{D}$ 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 with supercritical carbon dioxide (sc CO_2), we analyzed such

Table 2. Diffusion coefficients (**D**) of CO_2 and equilibrium coefficients of swelling (**Z_o**) of the studied polymers

Polymer	*D, 10^{-9} cm^2/s*	*Z_o, weight %*
1	0.43	0.968
2	0.58	2.98
3	0.36	2.93
4	1.5	4.49
5	0.87	4.78
6	2.59	3.86
7	0.44	4.16
8	4.80	7.81
9	8.03	4.45
10	34.9	9.30

properties before and after treatment with sc CO_2. Table 1 shows the chemical structures of the repeating units of the studied polymers.

Two series of polymers have been investigated, **ACET** and **CYAN**. The series having the code **ACET** contains three poly(oxadiazole-amide)s with pendant acetoxybenzamide groups (**1**, **2**, **3**); the series having the code **CYAN** contains four polyamidic acids (**4**, **6**, **8**, **10**) and the corresponding four polyimides (**5**, **7**, **9**, **11**) based on a diamine having cyano substituents and four dianhydrides containing pyromellitic, hexafluoroisopropylidene diphthalic, biphenylene or diphenylketone units, respectively. The synthesis of these polymers was performed according to previously published methods (5–9). Table 3 shows the values of glass transition temperature (Tg), Kuhn segment (A_{fr}) and Van der Waals volume (V_w) of these polymers. The glass transition temperatures of these polymers are in the range of 216°C–280°C. The conformational rigidity, that is Kuhn segment value (A_{fr}), is in the range of 12 Å –45 Å. The dependence of glass transition temperature on Kuhn segment in the case of **ACET** polymers is linear, with not a very high correlation coefficient (Figure 2). When measuring the glass transition temperature by using the differential scanning calorimetry (DSC) method, the error can be ± 10%. From the dependence of Tg on Kuhn segment, $y = 260.35 + 0.391x$, we calculated the Tg of **ACET** polymers **2** and **3**. They are 273.8°C and 268.4°C, respectively. In one case, it is 3.8°C higher and in the other case it is 1.6°C lower than the experimental values (270°C for both polymers). These differences are in the domain of experimental error of the DSC method.

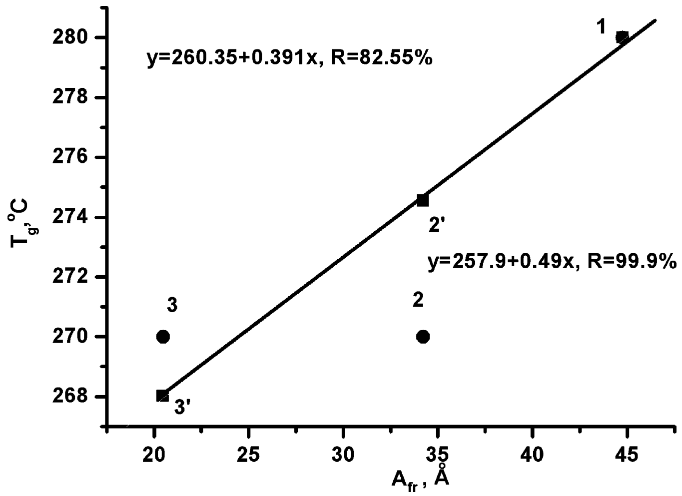


Fig. 2. Dependence of glass transition temperature (**Tg**) on Kuhn segment (**A_{fr}**) of **ACET** polymers (**1**, **2** and **3**: experimental values of Tg; **2′** and **3′**: calculated values of Tg).

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 (°C)*	*A_{fr} (Å)*	*V_w (Å^3)*	*ρ_1 (g/cm^3)*	*V_{f0} (cm^3/g)*	*ρ_2 (g/cm^3)*	*V_{f1} (cm^3/g)*	*$\Delta\rho$ (g/cm^3)*	*ΔV (cm^3/g)*
1	280	44.77	495.140	1.383	0.171	1.378	0.174	0.005	**0.002**
2	270 273.8	34.23	663.816	1.360	0.198	1.335	0.212	0.025	**0.014**
3	270 268.4	20.48	1096.54	1.336	0.216	0.311	0.230	0.025	**0.014**
4	216	12.32	546.402	1.316	0.246	1.339	0.233	−0.023	−0.013
5	223	14.84	518.139	1.330	0.235	1.309	0.247	0.021	**0.012**
6	218	13.11	527.414	1.325	0.236	1.343	0.226	−0.018	−0.010
7	232	18.57	501.620	1.364	0.208	1.350	0.216	0.014	**0.008**
8	228	11.95	608.868	1.392	0.237	1.411	0.227	−0.019	−0.010
9	235	13.91	582.420	1.407	0.227	1.382	0.240	0.025	**0.013**
10	253	12.83	451.458	1.379	0.222	1.358	0.228	−0.021	−0.008
11	263	17.51	424.690						

Tg = glass transition temperature; A_{fr} = Kuhn segment; V_w = Van der Waals volume; ρ_1 = density before swelling; ρ_2 = density after swelling; V_{f0} = free volume before swelling; V_{f1} = free volume after swelling; $\Delta\rho = \rho_1 - \rho_2$ = modification of density; $\Delta V = V_{f1} - V_{f0}$ = modification of free volume.

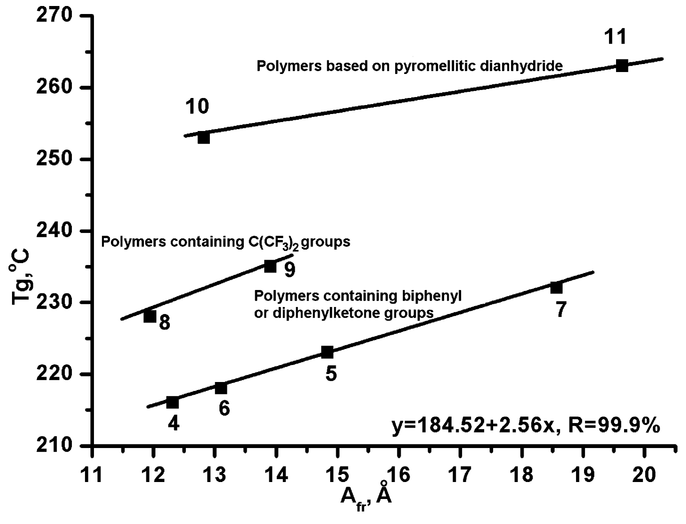


Fig. 3. Dependence of glass transition temperature (**Tg**) on Kuhn segment ($\mathbf{A}_{\mathrm{fr}}$) of **CYAN** polymers.

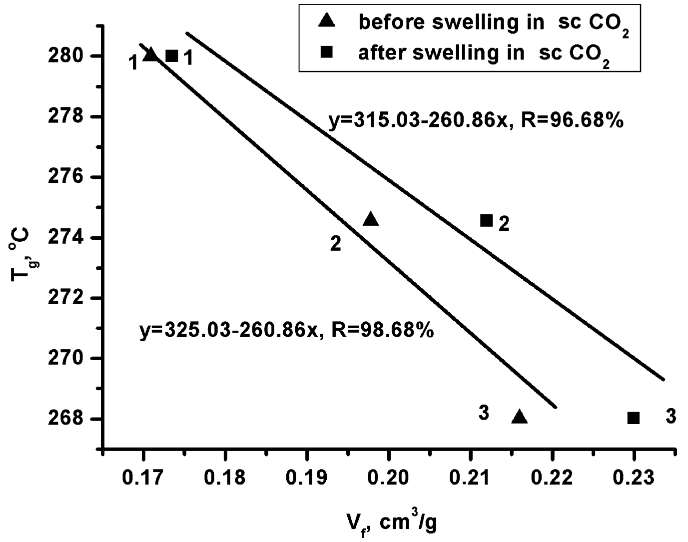


Fig. 4. Dependence of glass transition temperature (**Tg**) on free volume ($\mathbf{V}_{\mathrm{f}}$) for **ACET** polymers.

The dependence of glass transition temperature on Kuhn segment for the **CYAN** polymers is described by three lines (Figure 3).

The first line is for polymers **10** and **11** based on pyromellitic dianhydride, the second is for polymers **8** and **9** based on hexafluoroisopropylidene diphthalic dianhydride and the third line is for polymers **4**, **5**, **6** and **7** based on the dianhydride containing diphenylketone or biphenylene segment. Figures 2 and 3 show that the polymers **ACET** and **CYAN** behave normally, which means that the glass transition temperature increases with increasing the rigidity (2).

Now we examine the modification of density of the polymers after swelling and desorption of sc CO_2. We can presume that after treatment with sc CO_2, the density of polymers should decrease due to a possible formation of nano- and micro-cavities (15). Table 3 shows the density values before (ρ_1) and after (ρ_2) treatment with sc CO_2. The equilibrium coefficients of swelling with CO_2 of these polyheteroarylenes are not high (Table 1). In order to find an explanation of this behavior, we now examine the dependence of glass transition temperature on the free volume which was calculated with the Equation 5 taking into consideration the Van der Waals volume and 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.

Here, it can be seen 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 in the same degree. 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 is not reasonable. The low degree of swelling of **ACET** polymer films is connected with their preparation by using solutions in NMP. The influence of this solvent on the formation of polymer films will be discussed later in connection with the swelling of **CYAN** polymers. Both dependences shown in Figure 4 have high correlation coefficients. The degree of swelling of the polymers in this group differs significantly from each other. In the case of polymer **1**, the free volume increases with 1.7%, while in the case of polymer **3** it increases with 6.5%. This behavior is connected with the conformational rigidity of the polymers which decreases from 44.77 Å in the case of polymer **1** to 20.48 Å in the case of polymer **3** (Table 3). While the rigidity of the polymer increases, its free volume decreases (Figure 5). When the number of flexible bridges (Ph–O–Ph) increases, in the case of polymers **2** and **3**, and therefore the probability of conformational transitions in polymer chains increases during treatment with 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) have 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 free volume (Figure 6). Before swelling with CO_2, the dependence of glass transition temperature on free volume (Figure 6) and the dependence of glass transition temperature on the Kuhn segment (Figure 3) divides into three subgroups: polymers **4**, **5**, **6** and **7** which contain diphenylketone or biphenylene unit in the dianhydride segment; polymers **8** and **9** containing hexafluoroisopropylidene diphthalic units in the dianhydride segment; polymers **10** and **11** containing pyromellitic unit in

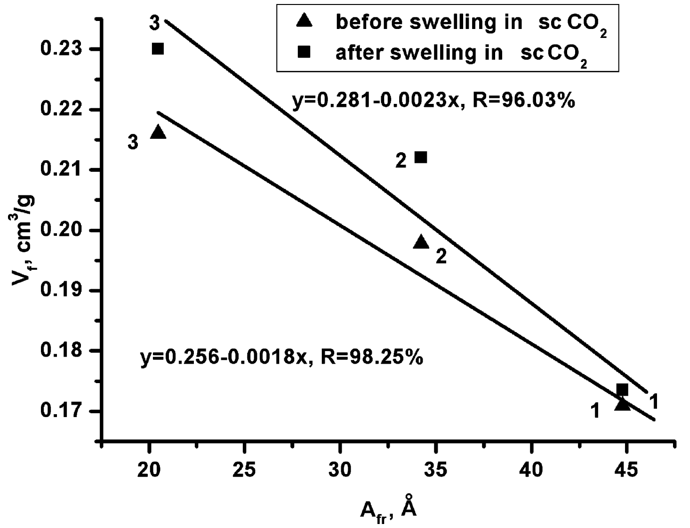


Fig. 5. Dependence of free volume (V_f) on the Kuhn segment (A_{fr}) before and after swelling in sc CO_2 for **ACET** polymers.

the dianhydride segment. Since the polymer **11** is partially crystalline, it will not be taken into consideration in the next discussion. The dependence of free volume on Kuhn segment divides in the same three subgroups (Figure 7).

The swelling of the **CYAN** polymers takes place in the polymers **5**, **7** and **9**, 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 (20) 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 200°C to remove the solvent, two competitive processes may take place:

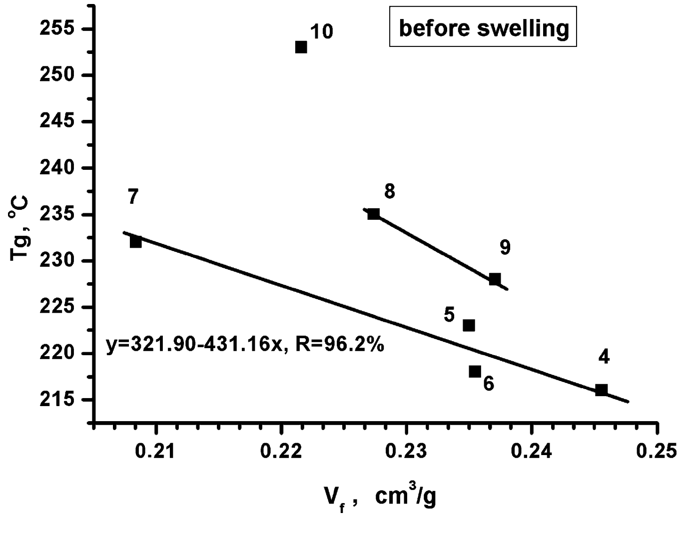


Fig. 6. Dependence of glass transition temperature (**Tg**) on free volume (V_f) for **CYAN** polymers.

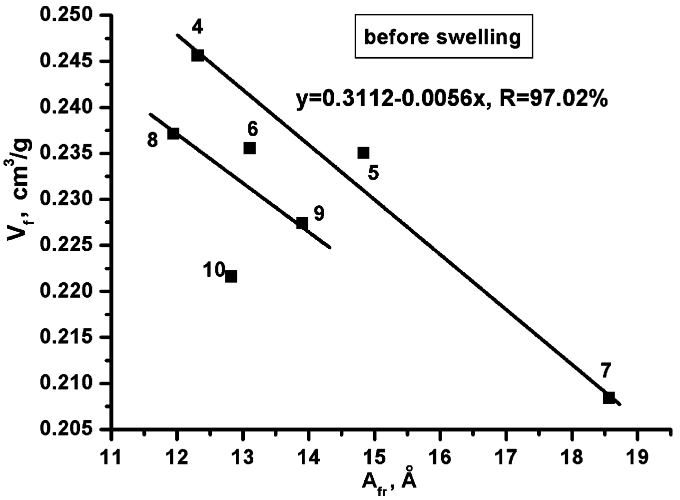
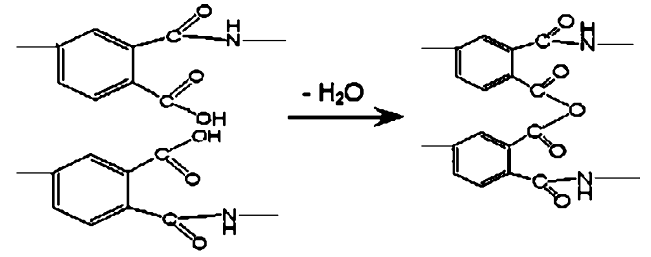
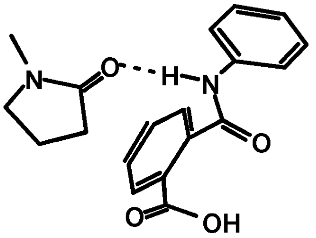


Fig. 7. Dependence of free volume (V_f) on the Kuhn segment (A_{fr}) for **CYAN** polymers.

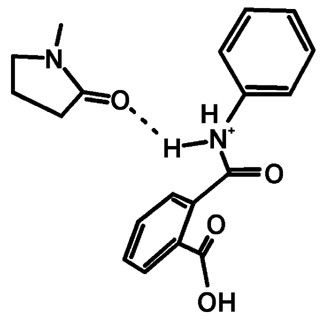
- the first is the formation of crosslinks between the chains of polyamidic acids:



- 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 leads also to the formation of inter-chain bonds. Also, the low degree of swelling of 3.8% to 7% found in polyimides **5**, **7** and **9** is connected with the fact that during the imidization of the polymers in NMP, it is possible the formation of anhydride bridges leading to crosslinks between chains. But in the case of the polyimides such crosslinks are less frequent than in the case of the corresponding polyamidic acids.

Now we look into the Table 2 which presents the diffusion coefficients of CO_2 obtained during desorption of CO_2 and the equilibrium coefficients after swelling. Both these parameters are determined with a moderate degree of precision. For the **ACET** polymers **2** and **3**, they are close to each other, regardless the significantly different rigidity. At the same time, also very close are the values of the free volume increase which were calculated on the basis of the change of density and Van der Waals volume of the repeating unit. The diffusion coefficients of the **CYAN** polymers **5**, **7** and **9** are very close to each other, with the exception of polymer **9** which contains hexafluoroisopropylidene bridges, while the coefficients of swelling of these three polyimides are almost identical. In the case of **CYAN** polymers **4**, **6** and **8,** 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 the case of polymer **10,** both diffusion coefficient and equilibrium coefficient of swelling are highly probable because of a stronger sorption of carbon dioxide during swelling and its possible retention in the polymer matrix due to week interactions between hydrogen in amide groups and oxygen in carbon dioxide.

4 Conclusions

The study of the dependence of glass transition temperature on free volume and on the Kuhn segment, before and after swelling with supercritical carbon dioxide, of the 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 repeating 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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