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^{129}Xe-NMR study of free volume in amorphous perfluorinated polymers: comparsion with other methods

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Abstract

The ^{129}Xe-NMR method was used for evaluation of the sizes of free volume elements in amorphous glassy materials—random copolymers of tetrafluoroethylene and perfluorodioxoles of different structures. ^{129}Xe chemical shifts were measured at different pressures up to 1060 Torr. The zero pressure chemical shifts obtained by extrapolation were used for calculation of the diameters of microcavities having spherical and cylindrical shapes. The sizes of microcavities are consistent with those found by means of positron annihilation lifetimes and inverse gas chromatography methods.

Keywords: Free volume; Glassy polymers; ^{129}Xe nuclear magnetic resonance

1. Introduction

The free volume theory has been proposed to describe molecular motion, microstructure, and properties of polymers [1,2]. First, the free volume was merely regarded as a theoretical concept that could explain many aspects of polymer behaviour but could not be determined directly. A stride in quantitative application of the free volume approach has been made thanks to an appearance of physical methods for estimation of mean free volume size and size distribution in polymers.

Several techniques have been successfully applied for measuring free volume in polymers such as the methods of spin, photochromic and electrochromic probes, [3–6] inverse gas chromatography (IGC), [7] small-angle X-ray and neutron diffraction methods [8,9]. However, the most detailed information on free volume has been accumulated owing to the application of positron annihilation lifetime spectroscopy (PALS) [10–12]. For many polymers free volume sizes have been measured using this method as a function of their chemical structure, as well as temperature, pressure, time of aging, degree of crystallinity and mechanical deformation. The results of the PALS method were especially fruitful, when a group of structurally related polymers was studied.

Thus, today sufficiently abundant information has been accumulated on free volume in diverse polymers. Usually, free volume was estimated by a single method in groups of polymers with varying chemical structure. [3,13,14] A general observation made in such studies is that the polymers with large free volume as evaluated by one method, also reveal large free volume when being probed by other techniques. However, the quantitative results of applications of different methods for estimation of free volume have been seldom, if ever, compared to each other. Such task seems to be very relevant now, when free volume in many polymers has been studied using different methods. This comparison is also interesting in relation to recent results of computer molecular modeling aimed to determine free volume size distribution in polymers. [15–17]

^{129}Xe-NMR spectroscopy is another method, which can be useful for investigation of free volume in polymers [18–21]. The chemical shift of a ^{129}Xe atom sorbed in a microporous material (e.g. polymer matrix) is sensitive to the size of the microcavity hosting it. Indeed, it was shown

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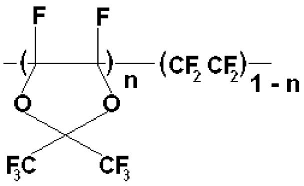
that the chemical shift depends on density of polymers and organic liquids, and, hence, basing on certain assumptions, can characterize free volume [22]. This method, first, revealed interesting results in studies of the size of microcavities in zeolites and other porous media [23]. Recently, an attempt was made to compare the results of estimation of free volume size on the basis of PALS and ^{129}Xe-NMR studies of a group of polymers having widely varying chemical structure and properties (amorphous and semicrystalline) [24].

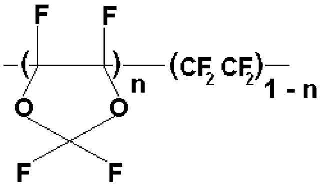
The present work is aimed to investigate, using this method, a group of perfluorinated amorphous glassy copolymers having similar chemical structure: copolymers of tetrafluoroethylene and perfluorodioxole with different side groups.

Their chemical structure is shown below. Amorphous Teflons AF (DuPont Co) differ by a content of cyclic comonomer perfluoro-2,2-dimethyldioxole (PDD):



where $n = 0.87$ and 0.65 for the copolymers AF2400 and AF1600, respectively.

Hyflons AD (Ausimont®) also have different content of perfluorodioxole comonomer 2,2,4-trifluoro-5-trifluoromethoxy-1,3-dioxole (TTD):



$n = 0.85$ and 0.6 for Hyflon AD 80X and Hyflon AD 60X, respectively.

The results of the application of ^{129}Xe-NMR technique are compared with the data of other probe methods (PALS, IGC).

2. Background

According to Fraissard and Ito [23], NMR chemical shift of ^{129}Xe atoms sorbed in nano-porous medium in the absence of paramagnetic particles or particles that form local electrostatic field (e.g. cations) can be presented as a sum

$$\delta_\Sigma = \delta_o + \delta_s + \delta_{Xe/Xe}\rho \quad (1)$$

where δ_o is the reference value, δ_s is the value related to the collisions with the wall, $\delta_{Xe/Xe}$ is the chemical shift related to collisions of Xe molecules in gas phase, and ρ is the density of the gas phase. Therefore, if the δ_Σ value is extrapolated to the zero pressure of Xe gas, the difference $\delta = (\delta_\Sigma - \delta_o)$ characterizes only the collisions with the walls of microcavities. An empiric equation was proposed [23] based on the data for various zeolites

$$\delta = 499.1/(2.054 + \lambda) \quad (2)$$

where λ (Å) is the mean free path of Xe atom in a microcavity. Note that the chemical shift δ (ppm) is dimensionless quantity as the ratio in the right part of Eq. (2). Depending of the geometry of microcavity the λ value can be related to the diameter of spherical hole (D_{sp}) or cylindrical hole (D_c) with the length much larger than the diameter:

$$\lambda = 1/2(D_{sp} - 4.4) \quad (3)$$

$$\lambda = D_c - 4.4 \quad (4)$$

Note that in these formulas, λ, D_{sp}, and D_c are expressed in Å, and the value 4.4 Å is the atomic diameter of Xe according to Breck [25]. Other values of atomic diameter of Xe have been reported in the literature; this circumstance will be discussed later.

In the present work, it is intended to compare the estimation of the sizes of microcavity made using ^{129}Xe-NMR method with those found by means of other probe methods, namely the PALS and IGC techniques for the same polymers.

In the PALS methodology, the radius of free volume elements (FVE) can be related to the longest lifetimes [26, 27]:

$$\tau_i = 1/2[1 - (R_i/R_o) + (1/2\pi)\sin(2\pi R_i/R_o)]^{-1} \quad (5)$$

where τ_i is the longest or o-Positronium lifetime and R_i is the corresponding radius of FVE elements, expressed in ns and Å, respectively; $R_o = R_i + \Delta R$, where $\Delta R = 1.66$ Å is the fitted empirical parameter that characterizes electron layer thickness. This equation was obtained in assumption of the spherical form of FVE, that is the volume of microcavity is $4/3(\pi R_i^3)$, Å^3. When analyzing free volume in polymers, it has been noted (see, e.g. [12,28]) that cylindrical or ellipsoid shape of FVE can be a more realistic model for polymers. Recently, an equation was proposed for the size (diameter) of cylindrical FVE in polymers [29]:

$$\tau_i = [8.6(\Delta R/R_i)^3(1 - 3\Delta R/4R_i)]^{-1} \quad (6)$$

where ΔR is defined just as before and R_i is the radius of the cylinder. Both approaches will be employed in this work to evaluate the size of FVE on the basis of positron annihilation lifetime data.

It can be noted that the ^{129}Xe-NMR method predicts greater diameters of microcavity in the assumption of spherical symmetry (Eqs. (3) and (4)), whereas the PALS methods gives the opposite prediction using Eqs. (5) and (6).

The IGC method enables a determination of excess enthalpy of mixing at infinite dilution to be made. It has been shown that in all glassy polymers studied, this value passes through a minimum for a series of sorbates with increasing size [7,30,31] The coordinates of those minima (critical or van der Waals volumes of sorbates) can be identified as the average sizes of FVE in glassy polymers. Assuming spherical shapes of FVE corresponding radii of FVE can be calculated.

3. Experimental

Several properties of the polymers studied are presented in Table 1. All the polymers were studied in the form of films except one sample of amorphous Teflon AF2400 that was also studied in the form of powder. The films were obtained in Petri dishes by slow evaporation of the solvent (Galden® HT70, Ausimont®, a mixture of perfluoro ethers). Transparent films were cut in disks (7.5 mm diameter.) and packed at the bottom of 10 mm NMR tubes fitted with valves for evacuation and inlet of xenon gas. The samples were evacuated up to at least 10^{-8} atm prior to Xe sorption.

The chemical shift δ of the sorbed ^{129}Xe at different pressures has been measured on a Bruker MSL400 spectrometer (90° pulse duration 10 μs, delay time 16 s). The magnetic field was 9.4 T (110.6 MHz) and the spectral width was 35700 Hz. The signal of Xe in the gas phase in all runs has been considered to be at 0 ppm.

Manometric measurements of sorption of Xe gas in the polymers studied was carried out in a glass vacuum vessel using Edwards Datametrics pressure transducer in the range of 0–1000 Torr.

4. Results and discussion

Sorption isotherms of Xe in all the perfluorinated polymers are linear in the pressure range 0–1.4 atm. In spite of the fact that all the polymers are glassy, no changes in the slopes of isotherms are discernable. In other words, no dual mode sorption behaviour can be noted at these pressures. It is known that rapid change of the slopes of sorption isotherms starts as pressure approaches $p_c = 1/b$, where b is Langmuir affinity parameter. A unified linear correlation of b in various polymers with critical temperature of the solutes has been reported [35]. Using this correlation, one can conclude that for Xe, b should be close to 0.12 atm^{-1}. It means that the curvature can be observed at pressures approaching 8 atm. As experimental pressures were always lower than 1.4 atm, the linear sorption isotherms were observed. Solubility coefficients of Xe calculated from the isotherms are presented in Table 1. It is seen that they correlate with free volume, the glass transition temperature and permeability of the considered perfluorinated polymers.

A typical ^{129}Xe-NMR spectrum is shown in Fig. 1. A linear increase of δ with gas pressure at 25 °C was observed up to about 1.3 atm for all of the fluorinated polymers studied (Fig. 2). For all the polymers the lines have approximately the same slope. This is consistent with Eq. (1), which shows that the slope is determined by gas density, whereas the chemical shift $\delta_{\text{Xe/Xe}}$ should be independent of the nature of the polymer material. The δ_0 values extrapolated to zero sorbate loading (or gas pressure), range from 65 to 84 ppm, and the increasing values of δ_0 are observed, when fractional free volume of the four polymers decreases.

Using Eq. (2), the mean free path λ (Å) for all the polymers was calculated. The λ values together with the radii of microcavities having spherical or cylindrical geometry found by mean Eqs. (3) and (4) are given in Table 2. They are compared with the radii of FVE computed on the basis of the PALS data using Eqs. (5) and (6). In addition, other polymers, which have been studied using the ^{129}Xe-NMR, PALS and IGC methods are also included for a comparison. Several conclusions can be made after examining this Table.

First, the ^{129}Xe chemical shifts can be regarded as reliable characteristics of a polymer. Independent studies of different samples of the same polymers (e.g. LDPE or PC) resulted in very close values of δ. However, further, more precise assignment of the chemical shift is hardly possible, because not in all cases the δ values extrapolated to zero pressure were reported. On the other hand, a variation in the disperse state of polymer samples (powder or films) can affect the observed δ values as the results obtained for AF2400 copolymer show.

An analysis of Table 2 indicates that for sufficiently great number of polymers that have been studied so far using

Table 1
Physical properties of glassy amorphous perfluorinated polymers

Polymer	Composition (mol%)		T_g (°C)	FFV (%)	P(O_2) (Barrer)	S(Xe) (cm^3(STP)/g atm)
	TTD	PDD				
Hyflon AD 60X	60	–	110 [32]	9.4 [32]	51.4 [32]	0.19
Hyflon AD 80X	85	–	134 [32]	9.5 [32]	194 [32]	0.19
AF1600	–	65	160 [33]	32.0 [34]	170 [34]	0.36
AF2400	–	87	240 [33]	37.4 [34]	1140 [34]	0.74

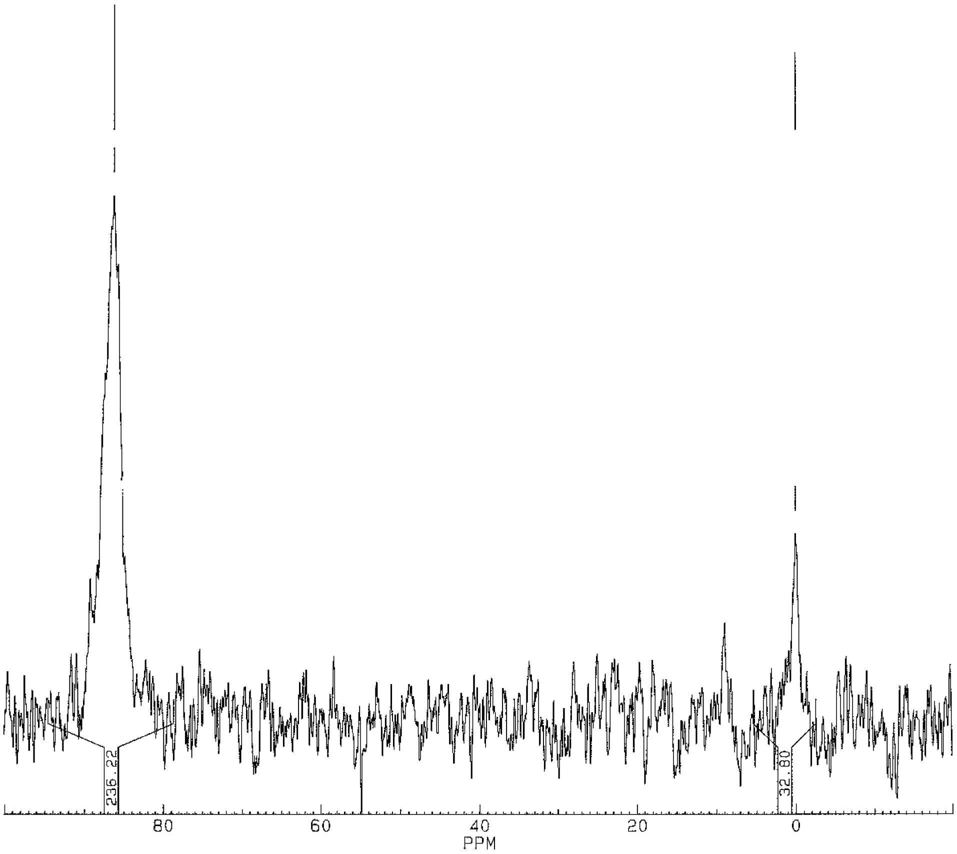


Fig. 1. NMR spectrum of ^{129}Xe sorbed in Hyflon AD 60X® Conditions: temperature 25 °C, $p_{Xe} = 0.54$ atm, NS = 2327, pulse width 10 μs ($\theta = 30°$), spectral width 35700 Hz, digital resolution 4.4 Hz, repetition time 16 s, LB = 20 Hz, acquisition time 0.22 s.

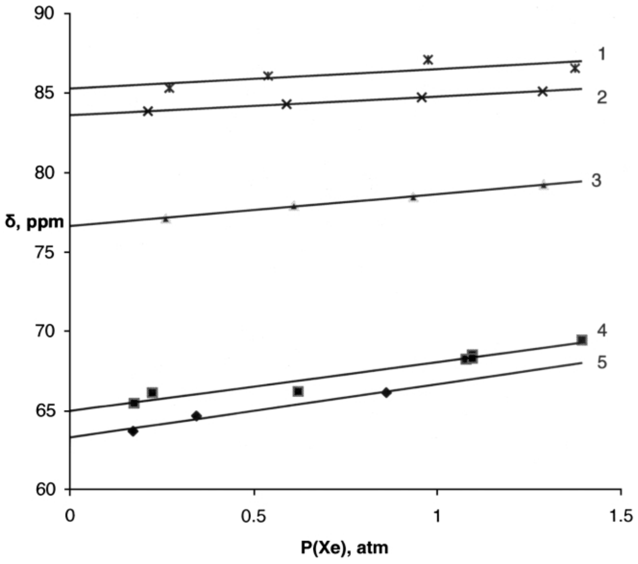


Fig. 2. Effect of gas pressure on ^{129}Xe chemical shifts in equilibrium with different polymers at 25 °C: 1 Hyflon AD 60X, 2 Hyflon AD 80X, 3 AF1600, 4 AF2400 (film), 5 AF2400 (powder).

Table 2
Free volume sizes (radii R, Å) in polymers based on ^{129}Xe-NMR and other probe methods

Polymer	δ (ppm)	λ (Å)	^{129}Xe-NMR		PALS		IGC
			R_{sp}	R_c	R_{sp}	R_c	
AF2400	63.3[a]	5.83	8.04	5.12	5.95 [14]	6.33	6.4 [30]
	64.7[b]	5.63	7.83	5.02			
AF1600	76.7	4.46	6.66	4.43	4.89 [14]	5.43	5.8 [31]
AD 80X	83.6	3.92	6.12	4.16	–	–	
AD 60X	85.3	3.8	6	4.1	–	–	
PTFE [24]	90	3.49	5.69	3.94	4.2 [24]	4.9 [24]	
PPO	180 [24]	0.72	2.92	2.56	3.4 [24]	4.2 [24]	3.4 [37]
	185 [36]	0.64	2.84	2.52			
LDPE	203 [24]	0.4	2.6	2.4	3.3 [24]	4.1 [24]	
	200 [20]	0.44	2.64	2.42			
	200 [22]	0.44	2.64	2.42			
PC	214 [24]	0.28	2.48	2.34	2.9 [24]	3.8 [24]	
	212 [20]	0.3	2.5	2.35			
PS [21]	210	0.32	2.52	2.36	2.88 [35]	3.76 [38]	
PEMA [22]	203	0.4	2.6	2.4	3.0 [36]	3.9 [39]	

PTFE—polytetrafluoroethylene, PPO—polyphenyleneoxide, LDPE—low density polyethylene, PC—polycarbonate, PS—polystyrene, PEMA—poly(ethyl methacrylate).

[a] Powder.

[b] Film.

^{129}Xe-NMR method, the radii of spherical microcavities are in the range 2.3–8 Å (or 2.3–5 Å in the assumption of cylindrical symmetry). For comparison, the ranges of radii as determined by means of the PALS method are 2.8–6 and 3.0–6.3 Å, respectively. Thus, the results of the two methods are in reasonable agreement. One can observe also correlations of the ^{129}Xe-NMR data with other properties of polymers. Thus, the AF Teflons having the highest gas permeability and large fractional free volume reveal the smallest δ values and the largest radii R_{sp} and R_c according to the ^{129}Xe-NMR method.

Table 2 shows, aside of the correlation between the ^{129}Xe-NMR and PALS data, that both methods find relatively higher R values for FVE in the perfluorinated polymers shown in the top of this table. It should be emphasized that a conclusion that high free volume is a generic property of perfluorinated polymers as compared to others, hydrogen based materials would be far-fetched. Table 3 shows as an illustration the sizes of several other highly permeable Si- and F-containing polymers (but not perfluorinated), which have been studied by means of the PALS method (but not yet by ^{129}Xe-NMR). It is seen that some of these polymers have even larger sizes of microcavities in comparison with perfluorinated polymers. As there is a good correlation between the size of free volume as measured by PALS in glassy polymers and their gas permeability, other highly permeable polymers [42–44] would probably show large radii of FVE.

Interactions of Xe atoms with walls of microcavities can also affect the observed chemical shifts. According to Fraissard and Ito [23], Eq. (1) is valid provided there are no electrostatic or paramagnetic perturbations on Xe electrons in vicinity of hole walls. The C–F bonds are more polar than C–H, polarizibilities of these bonds are also different as can be judged by extremely low refractive index of perfluorinated polymers (e.g. $n_D = 1.29$ for AF2400 [33]). We believe, however, that this factor should exert only minor effect on chemical shift, because larger sizes of FVE in these polymers are also proven by the PALS and IGC techniques.

The accuracy of determination of the hole radii should not be overestimated. On the one hand, an assumption that FVE have the shapes of spheres and cylinders with single diameter is rather rough, especially for high free volume polymers. Thus, it has been shown [17] that free volume in PTMSP can be represented as a system of interpenetrating pores with widely varying diameters. Recently, it has also been demonstrated [45] that Teflon AF2400 also includes elongated pores with diameter in the range 3–18 Å surrounded by densely packed matrix.

Table 3
Radii of free volume in polymers found using the PALS method

Polymer	R_{sp}, (Å)	Reference
PTMSP	6.8	[14]
PPrSiDPA	6.4	[14,40]
PVTMS	4.35	[14]
PFPNB	4.1	[41]

PTMSP—poly(trimethylsilyl propyne), PPrSiDPA—poly[1-phenyl-2[p(triisopropylsilyl)phenyl]acetylene, PVTMS—poly(vinyltrimethyl silane), PFMNB—poly[5,5-difluoro-6,6-bis(trifluoromethylnorbornene)].

Other problem, which can influence the accuracy of estimation of free volume size using the ^{129}Xe-NMR method, is related to uncertainty of van der Waals size of Xe atom (3.2–4.9 Å according to different scales, see, e.g. [46]). Therefore, depending of a choice of Xe size the radii of FVE as detemined by the NMR method would be 7.2–8.1 or 4.4–5.3 Å for spherical and cylindrical geometry of the hole, respectively.

In relation to this problem, it is worthwhile to consider the results of recently reported experiments on incorporation of ^{129}Xe atoms inside the cavity of fullerene C_{60} [47]. By heating C_{60} in high pressure atmosphere of ^{129}Xe gas these authors succeeded to prepare and then separate the inclusion compound Xe@C_{60} and then to measure its ^{129}Xe-NMR spectrum. This result looks like unexpected, because the usually accepted diameter of Xe atom is 4.4 Å [25], whereas the inner diameter of the cavity inside C_{60} is only 4 Å (if one assumes that the thickness of the layer, where van der Waals interactions take place, is about 1.5 Å) [48]. On the one hand, it can imply that smaller van der Waals radii suggested for Xe atom are more realistic. On the other hand, the measured chemical shift of ^{129}Xe inserted in the cavity of C_{60} is 179.24 ppm relative to ^{129}Xe gas. If we apply Eqs. (2) and (3) to calculate the diameter of the cavity, we will obtain 5–6 Å (similar to that of PPO, see Table 2). It seems unlikely that such calculation is fully justified: a Xe atom incorporated inside C_{60} would, probably, interact with several or, maybe, all 60 carbon atoms of fullerene. [49] These interactions should cause greater chemical shifts than those in larger cavities, where Xe atom is inserted in 'free volume'. That is, the effects of walls here cannot be neglected.

Fig. 3 shows a correlation between the radii of microcavities having different symmetry and estimated using ^{129}Xe-NMR and PALS methods. These two methods are based on application of the probes (Xe and o-Ps atoms) having significantly differing dimensions. As the size of microcavities is getting smaller and closer to the size of Xe probe, two methods should give more and more conflicting results. If one assumes a linear extrapolation to smaller PALS radii, the lines would cross the horizontal axis at about 2 Å, i.e. the size of Xe atom. On the other hand, one can also suppose that the correlations stop to be linear and approach the origin of the graph. Unfortunately, at present there is no experimental data for polymers with small microcavities to make a distinction between these two possibilities. Meanwhile, such polymers exist and have been studied using the PALS method. For example, the Vectra copolyester has an extremely short o-Positronium lifetime of 1.29–1.38 ns, that is the radii of microcavity is as small as 2.1–2.2 Å. [50,51] In terms of the results of the

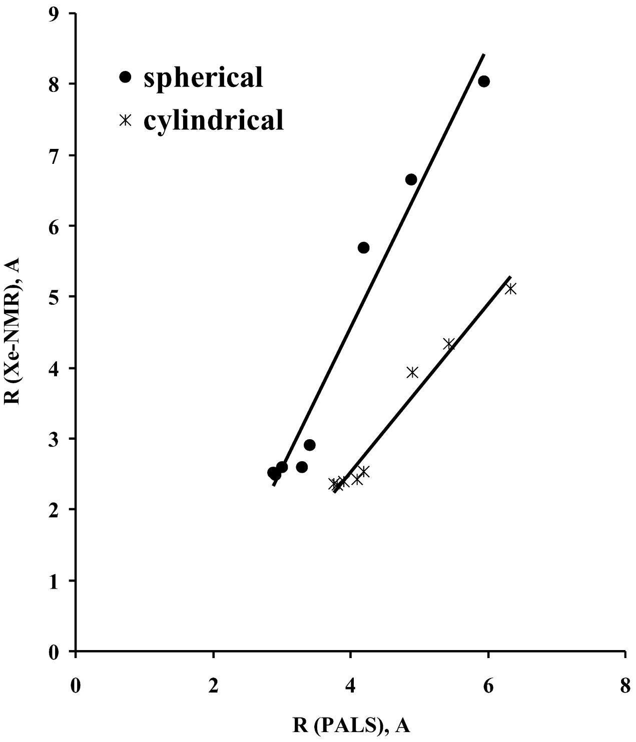


Fig. 3. Correlations of the radii of spherical and cylindrical microcavities as determined by ^{129}Xe-NMR and PALS method.

^{129}Xe-NMR method and the correlation shown in Fig. 3, for such a material mean free path λ close to zero and the chemical shift 243 ppm should be observed. Further studies of such materials are needed to resolve this problem and define the range of applicability of the ^{129}Xe-NMR method.

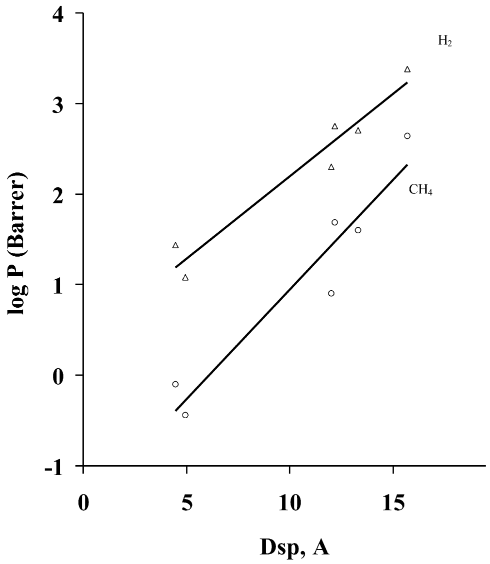


Fig. 4. Permeability coefficients of hydrogen and methane versus the diameters of microcavities in polymers estimated using ^{129}Xe-NMR method (polymers: perfluorinated polymers studied in this work, PS and PC).

Gas permeability is among the properties that should be sensitive to the sizes of FVE. Fig. 4 indicates that the diameter of microcavity as determined by the ^{129}Xe-NMR method reasonably well correlates with permeability coefficients of gases in different polymers. A similar correlation holds for the D_c values. A fulfillment of such correlations is consistent with the observation that concentration of FVE is approximately the same in various polymers. [14]

In conclusion, the results of this work show that the ^{129}Xe-NMR method gives reasonable estimates of the sizes of FVE in polymers, which are consistent with the data of other probe methods.

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