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Polymer 40 (1999) 1745–1752

polymer

Study of high permeability polymers by means of the spin probe technique

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Received 17 February 1998; accepted 13 May 1998

Abstract

The spin probe technique was systematically applied to study a family of high permeability and high free volume glassy polymers. Rotation correlation times τ_c or frequencies $\nu = 1/\tau_c$ of 2,2,6,6-tetramethylpyperidine-1-oxyl (TEMPO) were measured in amorphous teflons — random copolymers of tetrafluoroethylene and 2,2-bistrifluoromethyle-4,5-difluoro-1,3-dioxole, polyacetylenes and polynorbornenes. Polymers distinguished by unusually high, for the glassy state, permeability and free volume exhibit large rotational mobility of TEMPO. The correlation times correspond to fast rotation of the spin probe previously observed only in rubbery polymers. Correlations between the frequency ν and gas permeability and diffusion coefficients were observed. However, in some polymers, the spin probe's rotation rate is also sensitive to side-chain local mobility, which does not affect translational diffusion coefficients of gas molecules in polymers.

Keywords: High permeability polymers; Spin probe technique; Glassy polymers

1. Introduction

The search for novel polymeric materials with optimized combinations of gas permeability and permselectivity is an important problem in membrane science. A rational basis for this search is the determination of relationship between chemical structure, physical properties and transport parameters such as permeability and diffusion coefficients. While many physical properties can influence gas permeability, free volume or free volume size distribution seems to be the most important property related to gas transport and even sorption parameters of polymers. As a result, several methods have been proposed to probe free volume in polymers. A common feature of such methods as positron annihilation [1], inverse gas chromatography [2], electrochromic [3], photochromic [4], and spin probe [5] methods is that different probe particles are introduced into a material under investigation and, after following their behaviour in the polymer, certain conclusions can be made regarding free volume or average free volume element size in the material. Some of these methods, e.g. positron annihilation, have proven to be effective as standard approaches for reliable characterization of free volume in polymers. In contrast, the spin probe technique has only been only sporadically used in relation to free volume in and transport properties of polymers.

One of earliest results of the use of spin probes to study mass transfer properties of polymers was reported by Wasserman et al. [6] who demonstrated the correlation between rotational and translational diffusion coefficients of the stable free radical (spin probe) TEMPO. This result suggested that correlations might exist between gas diffusion coefficients and the rotation frequency of spin probes; and, in fact, such correlations were observed [7]. It was also shown that the rotation frequency of spin probes and gas diffusion coefficients exhibit a similar dependence on glass transition temperatures [8]. This effect could be explained by the analogous effects of free volume on these parameters. Whether or not a spin probe can be accomodated by a free volume element depends sensitively on the size of the spin probe and is reflected in the frequency of the probe's rotation as sensed by ESR method [9]. Based on studies with spin probes of various sizes, a rough estimate of the size of free volume elements can be made.

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0032-3861/99/$ - see front matter
PII: S0032-3861(98)00395-4

Interestingly, such estimates are in a reasonable agreement with the results of other methods, e.g. inverse gas chromatography [10].

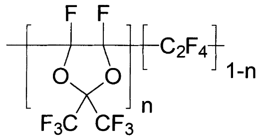
A disadvantage of these earlier studies is that the spin probe technique has been applied only to a limited set of conventional polymers with relatively low free volume. It is quite desirable to apply this method to glassy polymers such as poly(1-trimethylsilyl-1-propyne) (PTMSP) and other amorphous polyacetylenes which exhibit extremely high free volume. Additionally, this method has rarely been used to characterize a systematic series of structurally related polymers. Meanwhile, this approach is common in studies of gas permeability and diffusivity of polymers, because it allows the rationalization of structure–properties relationships in polymers. This work is meant to fill this gap.

The aim of this study is to investigate the mobility of the spin probe TEMPO in a large group of polymers belonging to different classes, including PTMSP and other polyacetylenes, high permeability, high free volume amorphous glassy fluoropolymers produced by E.I.DuPont Co. (AF2400 and AF1600), a substantial group of norbornene polymers. For most of these materials, gas permeability and diffusion coefficients are known, which allows a comparison between parameters characterizing translation and rotational diffusion of low molecular mass compounds in polymers, as well as the role of free volume and local group mobility on spin probe parameters. In other words, a question can be asked and probably answered if free volume effects are the main factor that influences a spin probe rotation frequency in glassy polymers, i.e. in the absence of segmental mobility, or there are other factors that affect the spin probe mobility.

2. Experimental

2.1. Polymers

Amorphous glassy perfluorinated copolymers purchased from E.I. DuPont Co. were used as-received in the form of powder. Two copolymers of 2,2-bisfluoromethyl-4,5-difluoro-1,3-dioxole and tetrafluoroethylene had the following structure, composition, and physical properties (glass transition temperature, molecular mass and fractional free volume):



	n	Tg, °C	M_w	FFV, %
I	0.87	240	300,000	37.4
II	0.65	165	100,000	32.0

Their transport parameters have been reported elsewhere [11].

The repeat unit structures and catalysts used to prepare the polyacetylenes are shown in Table 1. All of the polymers have molecular mass in the range of 400 000–2 000 000 and were studied in powder form. All of these polyacetylenes, with the possible exception of partially cross-linked poly(trimethylsilyl acetylene) (III), are soluble in common organic solvents and form good films. As a rule, the glass transition temperatures of these polymers are very high (often above the onset of decomposition) and usually are not detectable in DSC scans.

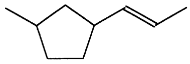
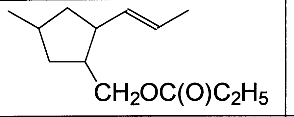
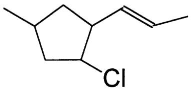
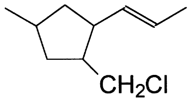
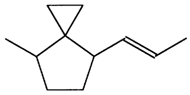
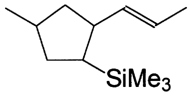
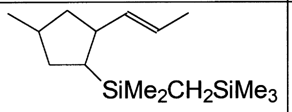
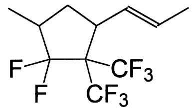
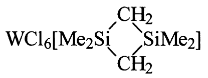
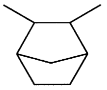
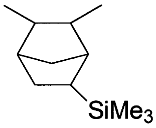
The structures, catalytic systems used, and glass transition temperatures of the norbornene polymers are given in Table 2. Depending upon the type of catalyst used, norbornene derivatives can experience ring opening metathesis polymerization (ROMP) which gives a cyclolinear structure of the resulting polymers or they can undergo addition polymerization with opening of double bonds that leads to the polymers having an entirely different structure. As shown in Table 2, both types of norbornene polymers were investigated.

A stable nitroxyl radical, 2,2,6,6-tetramethylpyperidine-1-oxyl (TEMPO), was used as the spin probe. It was introduced into the polymers from the vapour phase at ambient temperature. Samples of the solid spin probe and polymers were kept together in a closed vessel long enough for uniform sorption of TEMPO into the polymer. Exposure times were selected to obtain a strong ESR spectrum of the sorbed free radical. In some cases the samples were heated to 50°C–80°C in order to achieve a more uniform distribution of TEMPO in the sample. The criterion for uniform distribution of the probe molecules in the sample was the absence of spectral distortion caused by dipole–dipole and exchange interactions of the sorbed free radicals. Some of the polyacetylenes show their own ESR signal, i.e. in absence of added TEMPO. Polyacetylene III (see Table 1) had the most intensive probe-free ESR signal with the following parameters: g-factor $= 2.0023$ and line width,

Table 1
Polyacetylenes -$CR_1{=}CR_2$- and catalytic systems used

N	R_1	R_2	Catalytic system	Ref.
III	H	$Si(CH_3)_3$	$VOCl_3$ $Al(i\text{-}Bu)_3$	[12]
IV	CH_3	$Si(CH_3)_3$	$TaCl_5$ $Al(i\text{-}Bu)_3$	[13]
V	Ph	$p\text{-}C_6H_4Si(CH_3)_3$	$TaCl_5$ $Sn(n\text{-}Bu)_4$	[14]
VI	Ph	$p\text{-}C_6H_4C(CH_3)_3$	$TaCl_5$ $Sn(n\text{-}Bu)_4$	[15]
VII	Cl	Ph	$Mo(CO)_6CCl_4$	[16]
VIII	Cl	$n\text{-}C_6H_{13}$	$MoCl_5Sn(n\text{-}Bu)_4$	[16]

Table 2
Norbornene polymers and catalytic systems used

N	Repeat unit	Catalytic system	T_g °C	$\nu \bullet 10^{-9}$, s^{-1}	$P(O_2)$, Barrer[a]	Ref.
IX		$WCl_6[PhC_2H]$	31	0.1	2.8	17
X		$WCl_6[PhC_2H]$	-	0.1	-	18
XI		$WCl_6[Si(C_3H_5)_4]$	-	0.1	2.3	18
XII		$RuCl_3\ 3H_2O$	-	0.3	0.46	18
XIII		$Re_2O_7/Al_2O_3\ PbEt_4$	-	0.5	1.0	18
XIV		$WCl_6[PhC_2H]$	113	0.5	30	17
XV		$WCl_6[PhC_2H]$	24	0.8	16	17
XVI		 $WCl_6[Me_2Si(CH_2)_2SiMe_2]$	169	1.0	50	19
XVII		Pentenyl nickel chloride ethylaluminum sesquichloride	>390	0.6	2.5	20
XVIII		Idem	>370	1.0	-	20

[a] 1 Barrer = 10^{-10} cm^3 (STP).cm.cm^{-2}.s^{-1}.(cmHg)$^{-1}$

$\Delta H = 3.95$ G. The signals of the other polyacetylenes were much less intense. In every case, the intensity of the ESR signals ascribed to TEMPO was much larger than that of the ESR signals of the polymers themselves. Hence, the polymer signal offered no practical interference with TEMPO ESR signal and did not prevent meaningful analysis of the ESR spectrum of the spin probe. ESR spectra were recorded at temperatures ranging from 14°C to 105°C using an X-band ESR-spectrometer (Radiopan, Poland) under conditions which were far from saturation. Spin probe rotation correlation times τ_c (or frequencies of rotation of the spin probe $\nu = 1/\tau_c$) were calculated using traditional methods [5,21]. Fig. 1 presents some examples of the ESR signals of the spin probe in polymers.

Gas permeability and diffusion coefficients were determined by a mass spectrometric technique described in detail elsewhere [22].

3. Results and discussion

During the last decades, interesting novel membrane materials, distinguished by unusually loose chain packing and, consequently, extremely high values of gas permeability and difflision coefficients attracted much attention. These materials such as Teflon AF, PTMSP, and other substituted polyacetylenes exhibit extraordinary high free volume as determined by the Bondi method or by positron annihilation lifetimes spectroscopy (PALS). Accordingly,

Table 3
Mobility of TEMPO ν and gas permeability–diffusivity of high free volume and conventional polymers at ambient temperatures

N	Polymer	$\nu \times 10^{-9}$ (s^{-1})	$P(O_2)$ Barrer	$D(CO_2)10^7$ ($cm^2\,s^{-1}$)
Perfluorodioxole copolymers				
I	AF2400	1.2	1140	—
II	AF1600	0.8	170	7.0
Polyacetylenes				
III	-CH=C($SiMe_3$)-	0.7		
IV	-C(Me)=C($SiMe_3$)-	0.8	2600	250
V	-CPh=C(*p*-$C_6H_4SiMe_3$)-	0.7	1100	
VI	-CPh=C(*p*-C_6CMe_3)-	0.6	1100	
VIII	-C(Cl)=C(*n*-C_6H_{13})-	1.5	32	14
VII	-C(Cl)=C(Ph)-	0.4	5.1	1.7
Conventional polymers[a]				
Glassy				
	PS	0.25	1–2	0.8
	PMMA	0.1	0.09	0.07
	PVC	0.08	0.045	0.025
	PVAc	0.01	0.45	
Rubbery				
	NR	2.3	23	12.5
	PIB	0.5	1.3	0.58
	PDMS	90	600	110

[a] PS, polystyrene; PMMA, poly(methyl methacrylate); PVC, poly(vinylchloride); PVAc, poly(vinyl acetate); NR, natural rubber; PIB, poly(isobutylene); PDMS, polydimethylsiloxane

one of the aims of this work is to investigate the behaviour of the TEMPO spin probe in such materials and to compare the parameters of its rotational mobility with those of conventional, more densely packed glassy and rubbery polymers. Another objective is to record the variation of spin probe mobility in a series of structurally related polymers. Such systematic studies of the effect of polymer structure on gas permeability (*P*) and diffusion (*D*) coefficients has provided many useful insights [10]. At last, it is interesting to test, using a wider set of polymers, the correlations of transport parameters, such as *D* and *P*, with the rotation frequency of TEMPO. Our earlier studies revealed systematic and interesting correlations between these variables [7].

Table 3 presents the mobility of TEMPO (as characterized by the rotation frequency ν) at ambient temperature (25°C) in high free volume polymers. The rotation frequencies for conventional polymers are also provided for comparison. From these results, both glassy AF2400, AF1600 and the majority of the amorphous polyacetylenes are characterized by ν values significantly higher than those of conventional polymers. The polymers with larger free volume permit higher TEMPO mobility. Thus AF2400 copolymer, which contains more perfluorodioxole than AF1600 has higher TEMPO mobility than AF1600. PTMSP (IV), the polymer with the highest free volume among all glassy polymers, as estimated e.g by positron annihilation [10] or Bondi's [23] methods, also has rather high rotation frequency of $0.8 \times 10^9\,s^{-1}$ much larger than the rotational frequency values for conventional glassy polymers. Most other polyacetylenes are characterized by somewhat lower frequencies of TEMPO rotation.

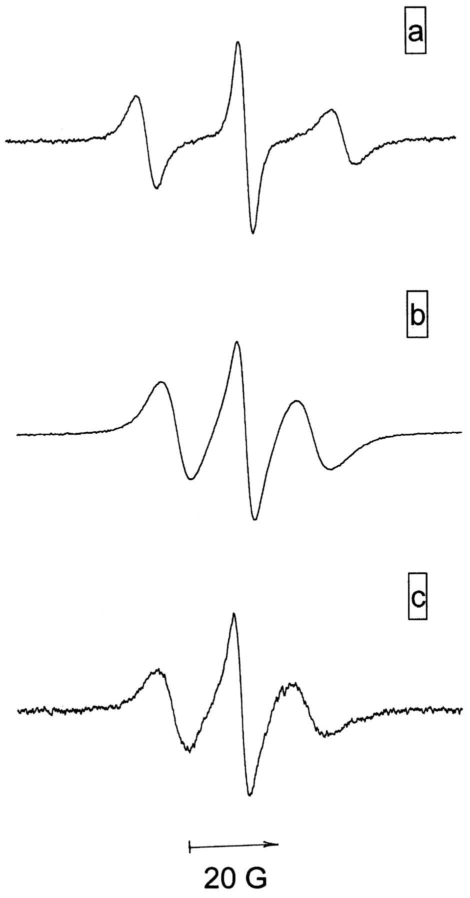


Fig. 1. ESR spectra of the spin probe TEMPO in: (a) polyacetylene VII; (b) teflons AF2400 or I; and (c) AF 1600 or II.

While the probe mobility is extraordinarily higher in the large free volume perfluorocopolymers and polyacetylenes, it is importanbt to recall that the methodology of determining probe mobility in large free volume and conventional polymers is somewhat different. The ν values recorded in Table 3 for conventional glassy polymers were obtained using the 'traditional' method of ESR spectroscopy, which corresponds to the region of so-called 'slow' movement of a spin probe (4×10^{-9}–$10^{-7}\ s^{-1}$) [5,21]. A comparison of rotational frequencies of spin probes measured by the 'traditional' ESR method and the method of ESR spectroscopy with saturation transfer showed [24,25] that the correlation times (or rotation frequencies) determined by the 'traditional' method characterize not the average value, but the upper limit of the spectrum of rotation frequencies of the spin probe in the polymer. This upper limit corresponds to the fastest rotational movements of the probe in the polymer. As a rule, the average value of the rotational frequency of TEMPO is smaller at least an order of magnitude than the value measured by the 'traditional' ESR method. Thus, in polystyrene, this average value is about $0.01 \times 10^{9}\ s^{-1}$ at room temperature. On the other hand, frequency measured by the 'traditional' method in the region of 'fast' movements (i.e. in the range of 2×10^{10}–$3 \times 10^{8}\ s^{-1}$), which is characteristic of TEMPO probe rotation in rubbers and the high free volumes polymers studied in this work, as a rule, characterize namely the average value of the rotation frequency distribution of the spin probe [24,25]. Therefore, the difference between the average rotation frequencies in the two groups of polymers compared in Table 3 is even more dramatic than the values in the table may suggest.

Gas permeability and diffusion coefficients in Table 3 can be compared with spin probe mobility to identify correlations between spin probe mobility and small molecule transport properties in a polymer matrix. Based on this comparison there is an approximate correlation between rotation frequency and the D and P values. Indeed, the copolymer AF1600 is distinguished by lower ν values and permeability coefficients than AF2400. Polymer VII, which has the lowest mobility of the spin probe among the polyacetylenes, is the least permeable. However, the correlation of ν versus P and D is fairly poor and can hardly be used, for example, for a prediction of the gas transport parameters based on the ESR spectra of sorbed spin probe molecules. For example, in fluoropolymer AF1600 and PTMSP, TEMPO rotates with same frequency whereas P and D values differ significantly. TEMPO rotational frequency ν is higher in AF2400 than in PTMSP, though the relation between gas permeability of these polymer is opposite. It seems that there are other factors that influence ν and P values independenly in addition to the effects of free volume in glassy polymers.

An interesting case for comparison is polyacetylene VIII, which contains a long alkyl side group. This polymer has the highest rotation frequency $1.5 \times 10^{9}\ s^{-1}$ of all the polyacetylenes. Meanwhile, its diffusivity is lower than that of PTMSP (IV) by an order of magnitude and its permeability is lower than that of PTMSP by two orders of magnitude. A common structural feature of polyacetylenes is a very rigid main-chain. Hence the introduction of a side-chain alkyl group which is very flexible relative to the main-chain can increase local mobility in the vicinity of the spin probe molecule. The same effect is observed if one compares gas permeability and difflisivity of PTMSP and polydimethylsiloxane (PDMS), the most permeable rubber. PTMSP is, of course, much more permeable than PDMS. However, the mobility of TEMPO is much higher in PDMS than in PTMSP. This result is ascribed to the extremely high mobility of the main-chains in PDMS.

An analysis of the data in Table 2 for norbornene polymers leads to similar conclusions. This table presents a long series of norbornene polymers prepared via ring opening metathesis polymerization and two addition type norbornene polymers XVII and XVII. Again only a rough correlation of spin probe mobility and gas permeability is observed.

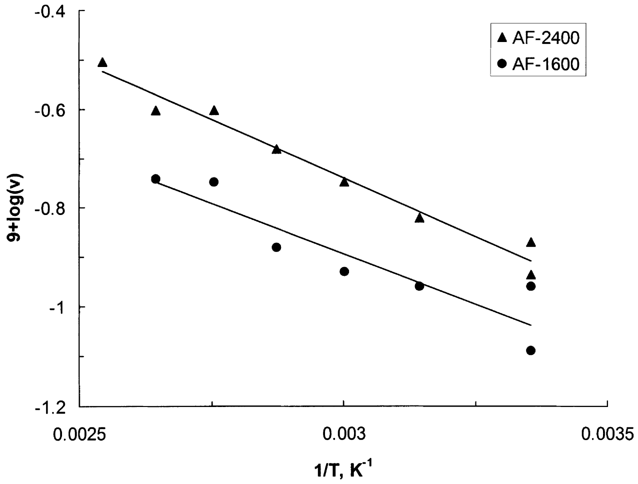


Fig. 2. Temperature dependence of rotational frequency of TEMPO in: (1) AF2400; and (2) AF1600.

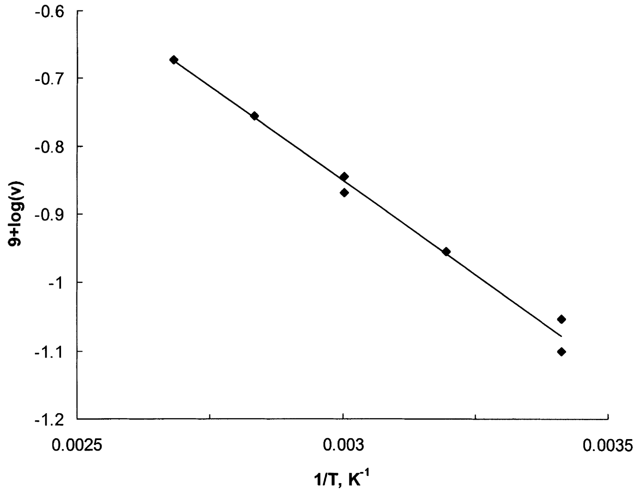


Fig. 3. Temperature dependence of rotational frequency of TEMPO in PTMSP (IV).

Table 4
Parameters of Arrhenius dependence of TEMPO mobility[a]

N	Polymer	$\nu_0 \times 10^{-10}$ (s^{-1})	E (kcal mol^{-1})
I	AF2400	4.8	2.2 ± 0.2
II	AF1600	2.15	1.9 ± 0.3
IV	-C(Me)=C($SiMe_3$)-	6.3	2.5 ± 0.1
V	-CPh=C(p-$C_6H_4SiMe_3$)-	6.6	2.5 ± 0.3
VI	-CPh=C(p-$C_6H_4CMe_3$)-	4.5	2.8 ± 0.3
VII	-C(Cl)=C(n-C_6H_{13})-	1.2	2.7 ± 0.6
VIII	-C(Cl)=C(Ph)-	303	4.4 ± 0.4
XVIII	PTMSNB(add)	7.1	2.6 ± 0.2
	PS[b]	0.62	1.9
	PMMA[b]	0.05	1.0
	PVC[b]	0.24	2.1
	PVAc[b]	0.012	1.2
	NR	1.8×10^4	6.7
	PIB	4×10^6	10.8

[a] These parameters were obtained by fitting data of type shown in Figs 2 and 3 to the Arrhenius type equation: $\nu = \nu_0 \exp(-E/RT)$. The lines in Figs 2 and 3 represent the best fit of the data to this model.

[b] The value obtained by the 'traditional' method of ESR spectroscopy

The most permeable polymer of this group, the fluorine containing polymer XVI, has the highest frequency, 1×10^9 s^{-1}. On the other hand, the mobility of the spin probe is small in polynorbornenes with low gas permeability (IX, XI).Analogous to the substituted polyacetylenes, an introduction of groups which provide more flexible side-chains is accompanied by a noticeable growth of the TEMPO rotation frequency. For example, the introduction of a methylene spacer between the chlorine and cyclopentane ring in XII results in a marked decrease in permeability, in comparison with polymer XI, but an increase in ν.

It is also interesting to compare the silicon-containing polynorbornenes XIV and XV. It is well known that the $Si(CH_3)_3$ groups impart high gas permeability, large free volume, and elevated T_g in glassy polymers [10]. Indeed, poly(trimethylsilyl norbornene) (XIV) exhibits a rather high oxygen permeability coefficient and high spin probe mobility. However, the introduction of longer silicon-containing side-chains, like in polymer XV, results in a substantial decrease in the glass transition temperature that is caused by a self-plasticization effect. As Table 2 shows the T_g value of polymer XV is even lower that that of nonsubstituted polynorbornene IX. A large local mobility that makes the chains of XV more flexible induces also relatively large rotational mobility of TEMPO spin probe. Meanwhile the permeability of polymer XV is lower than those in polynorbornenes containing bulky groups attached directly, that is without spacers, to the main-chain (XIV, XVI). These results can again be interpreted as an indication that spin probe rotational frequency is much more sensitive to local (small scale) mobility in glassy polymers than gas permeability.

Table 5
Parameters of temperature dependence of TEMPO mobility and thermal expansion coefficients α_g

Polymer	$(\Delta\nu/\nu_{av}\Delta T) \times 10^4$ (K^{-1})	$\alpha_g \times 10^4$ (K^{-1})
AF2400	96	1.37
AF1600	96	1.22
PS	83	2
PMMA	44	2
PVC	91	3.5

Two addition type norbornene polymers form a group of another molecular design. Both polymers have relatively high TEMPO mobility. The silicon-containing norbornene polymer XVIII, in spite of its rather large molecular mass (ca. 200 000), has poor film forming properties, so its gas permeability could not be determined. However, the high rotational mobility of TEMPO implies that it should exhibit rather high permeability coefficients.

The temperature dependence of the TEMPO rotation frequency was determined for several polymers in the range of 14°C to 105°C. The rotation frequency exhibited an Arrhenius temperature dependence in every case. Examples of these results for AF2400, AF1600 and PTMSP are shown in Figs 2 and 3, respectively. The mobility of the spin probe in AF2400 is higher than in AI1600 at all temperatures. The mobility of PTMSP (IV) is higher than in other polyacetylenes at all temperatures too.

The Arrhenius parameters for several high free volume polymers are shown in Table 4. They are compared with those characteristic for conventional glassy and rubbery polymers. The apparent activation energies for the spin probe mobility in most polyacetylenes as well as AF2400 and AF1600 do not differ substantially from the values observed for conventional glassy polymers. However, pre-exponential factors are larger by approximately an order of magnitude. Again a noticeable exception is polyacetylene VIII, which contains a flexible side-chain. Its activation energy is twice as large as that for the other high free volume glassy polymers, and its pre-exponential factor is larger by two orders of magnitude. Thus, the difference in TEMPO rotational frequencies between PTMSP and polymer VIII increases with temperature, and at 100°C it amounts to a factor of about 4. Bearing in mind the Arrhenius parameters of spin probe rotation, the rotational frequency of TEMPO in polyacetylene VIII is intermediate between the TEMPO rotational frequencies in glassy and rubbery polymers. We will consider this result in more detail below.

An important difference between rubber and glassy polymers is the much steeper temperature dependence of specific volume of the former as expressed by the inequality $\alpha_1 > \alpha_g$., where α_1 and α_g are the slopes of the temperature dependences of the specific volume of a polymer $V_g(T)$ above and below the glass transition temperature, respectively. In other words, the variation of free volume with temperature is stronger above the glass transition temperature than below T_g. In the rubbery state, free volume is determined predominantly by segmental motion or larger scale chain mobility. This notion is consistent with the observation that larger apparent activation energies of rotation of spin probes are typical for rubbers than for glassy polymers [5]. Therefore, the higher activation energy and pre-exponential factor observed for polyacetylene VIII confirms the assumption that the high rotational frequency of TEMPO in this material is determined basically by the local mobility of its flexible side group.

The mobility of spin probes should be sensitive to the size of free volume, but probably does not depend solely on this factor. If one approximates the Arrhenius temperature dependence of spin probe mobility by a linear function $\nu(T)$, then the slope $\beta = \Delta\nu/\nu_{av}\Delta T$, where $\Delta\nu$ is the difference between $\nu(T_{max})$ and $\nu(T_{min})$, can be compared with α_g in the polymers studied. Here T_{max} and T_{min} are the maximum and minimum temperatures in the temperature range studied. It is seen from Table 5 that the rotational frequency of TEMPO in different glassy polymers is much more strongly dependent on temperature than specific volume and, hence, free volume. Therefore, the rotational mobility of spin probes is not determined exclusively by the size of a cavity in which they are located, but also by activation of rotational diffusion. This phenomenon is equally true for rotation of spin probes in rubbers because there the difference in activation energies is much bigger than the difference between α_1 and α_g.

4. Conclusions

The mobility of the TEMPO spin probe in a big group of high permeability glassy polymers belonging to various classes (random copolymers of 2,2-bistrifluoromethyl-4,5-difluoro-1,3-dioxole and tetrafluoroethylene, substituted polyacetylenes and polynorbornenes) revealed a common feature of all these materials: the rotation frequencies ν of TEMPO are much larger (or equivalently, the correlation times, τ_c, are much smaller) than in ordinary glassy polymers. Therefore, the rotation of the spin probe is facilitated in high free volume media. In the many cases but not everywhere, there is a reasonable correlation between ν values and gas permeability and diffusion coefficients. However, the spin probe frequency is sensitive to the presence of flexible side groups, which are responsible for enhanced local mobility of side-chains in the vicinity of sorbed TEMPO molecules. This mobility does not affect the translational diffusion of small gas molecules and, hence, is not manifested in D and P values. The temperature dependence of the rotation frequency of TEMPO in high free volume and conventional glassy polymers is characterized by similar apparent activation energies. Therefore, the main difference between the temperature dependence of TEMPO mobility in these qualitatively different types of polymeric material is reflected in the preexponential factors.

The faster rotation rate of TEMPO in high permeability glassy polymers, if compared with that in conventional glassy polymers, is interpreted as follows. For the polymers for which the frequency of TEMPO rotation is higher than $0.5 \times 10^9\ s^{-1}$, the size of free volume elements is larger than or comparable with the size of TEMPO, i.e. 100 A [3].

Thus the study of a wide range of glassy polymers which have large free volume and high gas permeability allows one to conclude that large mobility of sorbed spin probes is typical for these materials.These results suggest that further studies of the effects of spin probes size and symmetry on their behaviour in different membrane materials are needed. Further, application of the spin probe technique to characterize free volume in advanced membrane materials may provide useful information and more insight into the complex connection between free volume, free volume size distribution, localized long range segmental dynamics, and small molecules diffusion and transport properties.

Acknowledgements

The authors are grateful to Professors K.L. Makovetskii and E.Sh. Finkelshtein who kindly provided norbornene polymers for this study. The research described in this publication was made possible in part by Award no. RC2-347 of the US Civilian Research and Development Foundation for the Independent States of the Former Soviet Union (CRDF).

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