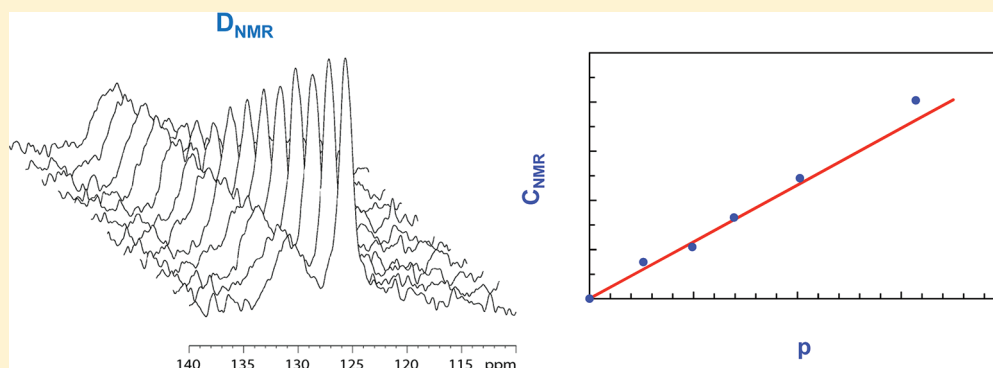# Determination of Carbon Dioxide Transport Coefficients in Liquids and Polymers by NMR Spectroscopy

Julio Guzmán and Leoncio Garrido*

Departamento de Química-Física, Instituto de Ciencia y Tecnología de Polímeros, Consejo Superior de Investigaciones Científicas (ICTP-CSIC), Juan de la Cierva 3, 28006 Madrid, Spain

ABSTRACT: In liquids and in polymeric membranes, a precise determination of their transport properties is of paramount importance. In this work, an NMR method to measure sequentially the solubility and diffusion coefficients of carbon dioxide in liquids (n-alkanes and 1-alkanols) and in polymer membranes (polyethylene, polybutadiene, and polycarbonate) is described. The results show that NMR measurements are very reproducible and in good agreement with those determined by other methods. Considering that the gas permeability is defined as the product of the solubility and diffusion coefficients, the method allows the determination of all transport parameters in an accurate manner. The influence of chain length, viscosity, and solubility parameters on the transport coefficients of $[^{13}C]O_2$ in alkanes and 1-alkanols was also analyzed and compared to those measured in polyethylene.

INTRODUCTION

The determination of transport coefficients in liquids and polymer membranes is of high interest in the field of gas and vapor separation and purification processes. The availability of precise values of these coefficients and their relationship with the chemical structure could lead to the development of new materials with outstanding gas transport properties, especially in the field of polymer membrane science. Although over the last two decades significant advances have been made,[1−4] the synthesis of new polymers and design of membranes that fulfill the requirements for these applications are needed to overcome present limitations and realize the full potential of the polymer materials.

In this context, the measurement of molecular transport parameters in polymer membranes can assist in the design of new polymeric materials for this application, since they could provide essential information to aid molecular simulation methods and attain a better understanding of transport phenomena in these systems. One of the most studied polymers is polyethylene in combination with its homologous n-alkane series. Thus, theoretical and experimental procedures for the determination of the transport coefficients of gases in alkanes and polyethylene have been widely described in the literature.[5−7] In the case of alkanes, numerous researchers have carried out solubility measurements of different gases, focusing the attention on the influence of the number of methylene groups in the hydrocarbon chain, in order to extrapolate the results to the case of amorphous polyethylene.[8−10] Moreover, considering the broad use of polyethylene in many applications where gas permeability is a very important property, gas transport studies in this polymer are commonly found in the scientific literature devoted to analyze the influence of crystallinity on the permeability, diffusion, and solubility coefficients.[11−14]

In liquid and solid compounds, the measurements of gas solubility require pressure apparatuses with very accurate detection of changes in pressure due to the dissolution of the gas in the studied liquid but often without determination of the other transport coefficients (permeability and diffusion). In polymer membranes, the widely used pressure method permits the simultaneous determination of the three transport coefficients, although for highly permeable membranes, the errors involved in the transport parameters could be significant.

NMR is a powerful tool to investigate chemical structure and molecular dynamics due to its excellent sensitivity to the environment of the observed nuclei. NMR techniques allow the

simultaneous detection of the various chemical moieties present in a sample and probe their surroundings at molecular level. Thus, it is feasible to identify and assess the concentration of a given functional group in a sample. C-13 NMR has been used to determine the solubility of CO_2 in aqueous solutions.[15,16] Moreover, pulsed-field gradient (PFG) NMR methods have been extensively used to investigate molecular diffusion in a wide variety of systems[17−20] and, in particular, in polymer membranes.[21−25] Therefore, NMR permits the direct determination of gas solubility and diffusion coefficients in different media, and since the permeability is defined as the product between both coefficients, then all transport coefficients could be determined from NMR measurements, as it has been shown in a recently published work.[26]

The main goal of this work is to determine by means of NMR spectroscopy the transport coefficients of $[^{13}C]O_2$ in alkanes (from hexane to heptadecane), 1-alkanols (from methanol to undecanol), polyethylene, and two other polymers, polybutadiene and polycarbonate, chosen as representative of rubbery and glassy polymers, and propose the NMR method as a universal procedure for the determination of diffusion and solubility coefficients of some gases and vapors in liquids and polymer membranes. The comparison of the obtained transport coefficients with the experimental results provided by others, as well as its critical analysis in light of common solution and diffusion models, constitutes part of the work.

■ EXPERIMENTAL SECTION

Materials. The n-alkanes and 1-alkanols were from Aldrich (Steinheim, Germany) with a purity degree higher than 99.9%. The $[^{13}C(1)]$ labeled 99% acetic acid was of Euriso-top, Gif-sur-Yvette, France; the $[^{13}C]O_2$ labeled 99% was of Cambridge Isotopes Laboratories, Andover, MA, and nonlabeled CO_2 99.998% from Praxair (Madrid, Spain). Glycerol was of Aldrich (Steinheim, Germany) and tricresyl phosphate was of Bayer (Germany). All the materials were used as received.

The polymer samples used in this work were a copolymer of 1-octene-co-ethylene (Dow LLDPE, ρ = 902 kg m^{-3}), poly[bisphenol A carbonate-co-4,4′-(3,3,5-trimethylcyclohexyli-dene) diphenol carbonate]carbonate (Aldrich, Steinheim, Germany) and poly(cis-1,4-butadiene) with 50% cis content (Polimeri Europe).

Polymer Sample Preparation. Films of poly[bisphenol A carbonate-co-4,4′-(3,3,5-trimethylcyclohexylidene) diphenol carbonate] were prepared from pellets by compression molding at 573 K and kept under compression at this temperature for 15 min. Then they were quenched at room temperature. Pellets of a copolymer of 1-octene-co-ethylene with roughly 8% content of 1-octene were pressed between two hot plates at 463 K during 10 min to form films and quenched at room temperature. The degree of crystallinity of these films was 0.26, obtained from DSC by assuming that the melting enthalpy of 100% crystalline polyethylene is 290 J g^{-1}. Samples of polybutadiene rubber were prepared by vulcanization with sulfur, obtaining a cross-link density of 127 mol m^{-3}.

NMR Gas Solubility Measurements. To perform the NMR measurements of carbon dioxide solubility, an amount (0.7−1.5 g) of the liquid or polymer membrane strips less than 2 mm wide and approximately 2 cm long were placed inside a 10 mm o.d. NMR tube designed for NMR studies of moderately pressurized gases. In addition, a standard consisting of a sealed glass capillary with a known amount of labeled $[^{13}C(1)]$ acetic acid was placed in the tube.

Prior to filling the tube at a given pressure with $[^{13}C]O_2$, the air was removed by vacuum. Unless indicated otherwise, the gas pressure used in these experiments was in the range of 0.1 to 0.65 MPa to facilitate the measurements with adequate signal-to-noise ratio in a reasonable amount of time. The gas pressure was monitored with a transducer working in the range 0−1 MPa.

In the case of the n-alkanes and 1-alkanols, the samples were cooled to approximately 200 K and degassed, and the temperature was raised to 298 K prior to filling with the gas. For comparative purposes, the solubility of nonlabeled CO_2 in n-tetradecane was also measured at a gas pressure of 0.265 MPa.

The NMR measurements were performed in a Bruker Avance 400 spectrometer (Bruker BioSpin GmbH, Rheinstet-ten, Germany) equipped with a 89 mm wide bore, 9.4 T superconducting magnet (^{13}C Larmor frequency at 100.61 MHz). The reported data were acquired at 298 ± 0.2 K with a Bruker diffusion probehead Diff60 using 90° ^{13}C radio-frequency (rf) pulse lengths of 12.5 μs. An inversion−recovery pulse sequence was used to estimate the ^{13}C longitudinal relaxation times, T_1, of sorbed gas. Solubility measurements were performed by acquiring ^{13}C NMR spectra of samples using a single pulse excitation sequence with a repetition rate $\geq 5 \times T_1$. All FIDs (free induction decays) were subjected to 1 Hz line broadening, Fourier transformation, and baseline correction. All ^{13}C NMR spectra were referenced to ^{13}C(1) acetic acid (178.1 ppm), secondary to tetramethylsilane (0.0 ppm).

To calibrate the standard, the peak area corresponding to ^{13}C(1) acetic acid was normalized to the area associated to all tetradecane peaks, and a ^{13}C natural abundance in the alkane sample of 1.07% was assumed. To estimate the amount of sorbed $[^{13}C]O_2$ in n-alkanes, 1-alkanols, and polymer samples, the peak area corresponding to the sorbed gas was normalized to the peak area of ^{13}C(1) acetic acid. When a spectrum showed significant peak overlap in the region of interest, spectral deconvolution was used to determine the individual peak areas.

PFG NMR Measurements. The samples prepared as described above were also used to determine the diffusion coefficients of sorbed $[^{13}C]O_2$. For these measurements, a pulsed field gradient stimulated spin echo pulse sequence was used, as shown by Stejskal et al.[27] The echo time between the first two 90° rf pulses, τ_1, was 3.11 ms. The apparent diffusion coefficient of $[^{13}C]O_2$, D, was measured at diffusion times, t_D, of 20 or 120 ms. The length of the field gradient pulses, t_g, was 2 ms. For these experiments, the amplitude of the gradient pulses varied from 0 up to a maximum value of 20 T m^{-1}. The repetition rate was $\geq 5 \times T_1$, and the total acquisition time ranged from about 4 to 15 h. The diffusion coefficients were calculated by fitting the experimental data to the corresponding exponential function.

Previous to these measurements, the temperature at the sample volume in the probehead was determined by measuring the difference between the proton chemical shifts of a solution of ethylene glycol at 80% v/v in deuterated dimethyl sulfoxide. Also, the field gradient was calibrated as described previously.[24]

■ RESULTS AND DISCUSSION

Solubility of Carbon Dioxide. The suitability of NMR to determine the solubility of $[^{13}C]O_2$ in liquids and polymer membranes was assessed first on n-tetradecane. Thus, Figure 1
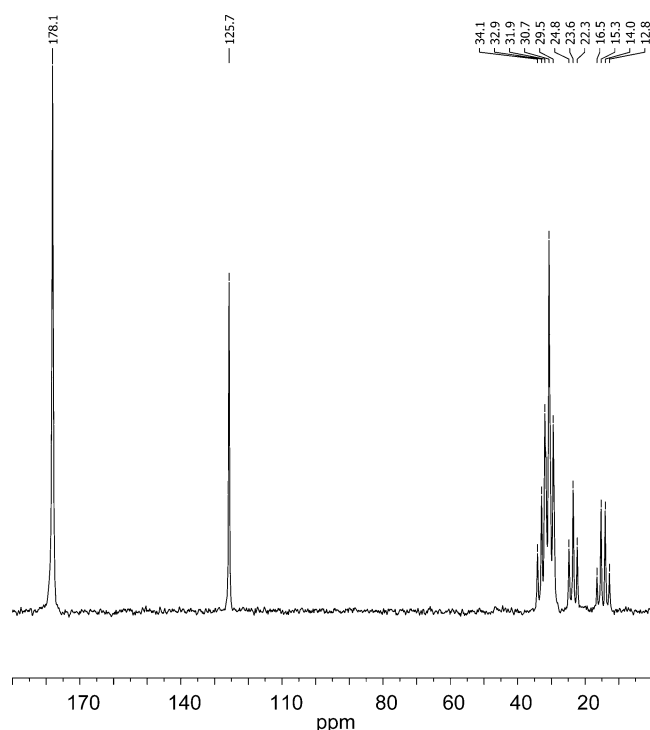
Figure 1. ^{13}C NMR spectrum corresponding to a sample of *n*-tetradecane in the presence of $[^{13}C]O_2$ at 0.198 MPa and 298 K, and with a standard of $CH_3[^{13}C]OOH$ 99% labeled. The peaks in the region between 10 and 35 ppm correspond to the carbons of the alkane, and the peaks at 178.1 and 125.7 ppm are associated with the standard and the sorbed gas, respectively.

shows the ^{13}C NMR spectrum corresponding to a sample of *n*-tetradecane loaded with $[^{13}C]O_2$ at a pressure of 0.198 MPa and the acetic acid standard. The peaks in the region between 10 and 35 ppm correspond to the alkane carbons, and those at 125.7 and 178.1 ppm are associated to the sorbed gas and the carboxyl carbon of acetic acid, respectively. The free gas does not contribute to the NMR signal significantly because the active volume of the radiofrequency coil is occupied mainly by the liquid sample, and consequently a peak is not observed. ^{13}C T_1 relaxation measurements showed the largest value for the carbon of sorbed gas, ~15 s, and the rest exhibited values of relaxation times of less than 9 s. Thus, the repetition rates were set to 75 s in order to minimize saturation effects in the solubility measurements.

To determine the amount gas sorbed in the alkane and hence its solubility coefficient at 298 K, the peak area associated to $[^{13}C]O_2$ was normalized to the peak area of *n*-tetradecane, assuming a ^{13}C natural abundance in the alkane sample of 1.07%. In Figure 2, the variation of the concentration of $[^{13}C]O_2$ with pressure is illustrated. In the case of liquids, alkanes, and alkanols, the solubility coefficient is equivalent to Henry's solubility coefficient (k_d) that is determined from the slope of the curve at different pressures. As could be expected, within the range of pressures studied, a small increase in the value of the solubility coefficient is observed. These values varied between 1.16×10^{-2} in the limit of zero pressure and 1.28×10^{-2} $m^3(STP)$ m^{-3} kPa^{-1} at a gas pressure of 0.628 MPa, in good agreement with those measured by other methods.[28] The solubility coefficient (k_d) of nonlabeled carbon dioxide in *n*-tetradecane was also measured at a pressure of
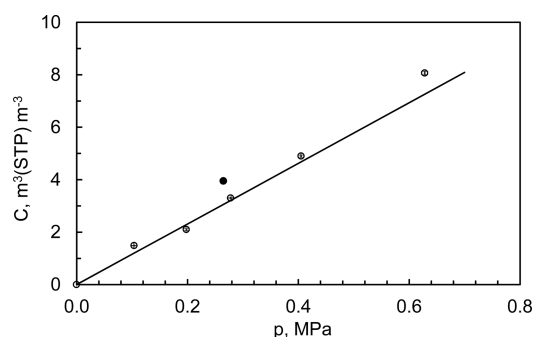

Figure 2. Variation of the concentration of $[^{13}C]O_2$ (open circles) and nonlabeled carbon dioxide (closed circle) in *n*-tetradecane with gas pressure at 298 K.

0.265 MPa, and a value slightly higher than that of $[^{13}C]O_2$ was obtained (see Figure 2).

The same set of experiments was also used to calibrate the sample of acetic acid. The area of the peak at 178.1 ppm, corresponding to $CH_3[^{13}C]OOH$, was normalized with respect to the alkane signal. Thus, the number of moles of acetic acid in the capillary was determined, and subsequently it was used as a standard for all measurements of carbon dioxide solubility in liquid samples and polymer membranes.

The ^{13}C NMR spectra of the other liquid samples (*n*-alkanes and 1-alkanols) with the standard and under $[^{13}C]O_2$ pressure also showed different signals belonging to the hydrocarbon chain and two single peaks corresponding to the ^{13}C signal of the carboxyl group of acetic acid at 178.1 ppm and to the $[^{13}C]O_2$ sorbed in the liquid at ~125 ppm. For illustrative purposes in Figure 3, the spectra corresponding to the sorption equilibrium of $[^{13}C]O_2$ in several hydrocarbons and alcohols are shown.

After equilibrium conditions at 298 K were reached, the solubility of $[^{13}C]O_2$ in the liquid hydrocarbons and alcohols was determined by comparing the areas of the peaks associated to the reference compound ($^{13}C(1)$ labeled acetic acid) and the sorbed gas in the corresponding ^{13}C NMR spectra. Similar results are obtained by using as reference the resonance signals corresponding to the carbons belonging to the hydrocarbon or alcohol whose $[^{13}C]O_2$ sorption is being analyzed. The results are summarized in Tables 1 and 2 (column 5) for alkanes and alcohols, respectively. These results show good agreement with reported values (see Table 3).[28,29]

The initial pressure of almost all the experiments was in the range between 0.22 and 0.25 MPa, though in some cases different pressures varying from 0.1 to 0.7 MPa were used. Negligible differences were found, indicating that k_d is practically constant for the liquids analyzed at these low pressures.

In addition, the solubility coefficient of $[^{13}C]O_2$ in polymer membranes (S) was studied. In this case, the use of Henry's solubility coefficients k_d is not strictly appropriate, except in the case of amorphous polymers above the glass transition temperature, such as polybutadiene, but not in the other cases where adsorption phenomena can occur. The polymer samples used in this work were selected to (i) include the morphologies generally found in polymers [i.e., amorphous (rubbery and glassy) and semicrystalline], (ii) cover a wide range of values for the transport parameters of interest, namely solubility, diffusion, and permeability coefficients, and (iii) be able to compare the NMR results with those obtained by other
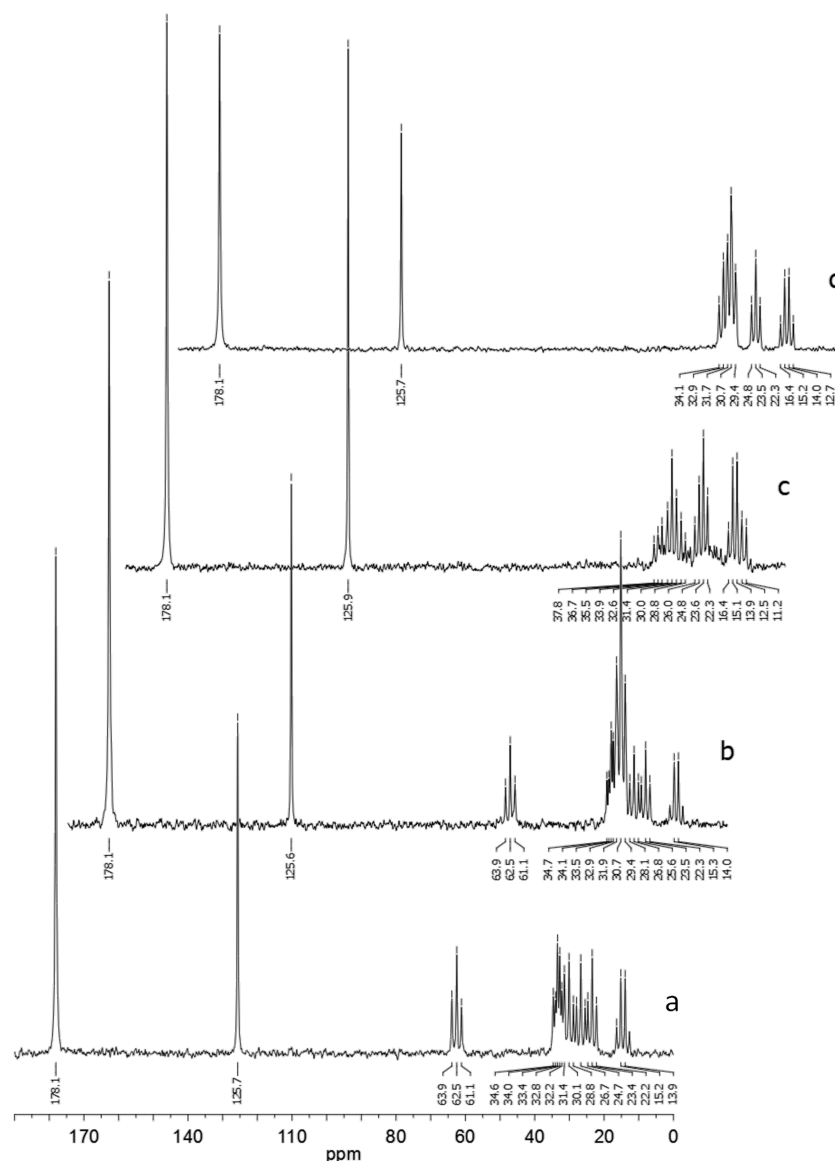
Figure 3. ^{13}C NMR spectra corresponding to samples of (a) 1-heptanol, (b) 1-undecanol, (c) n-hexane, and (d) n-undecane in the presence of $[^{13}C]O_2$ at 298 K, and with a standard of $CH_3[^{13}C]OOH$ 99% labeled. The peaks in the region between 10 and 64 ppm correspond to the carbons of the alkane or alkanol, and the peaks at 178.1 and 125.7 ppm are associated with the standard and the sorbed gas, respectively.

Table 1. Transport Coefficients of $[^{13}C]O_2$ at 298 K in n-Alkanes As Determined by NMR Spectroscopy (standard deviations are shown in parentheses)[a]

n-alkane	$\delta,$[b] MPa$^{1/2}$	$\rho,$[d] kg m^{-3}	$\eta,$[f] mPa s	$k_d \times 10^2$, m^3(STP) m^{-3} kPa^{-1}	$D \times 10^9$, m^2 s^{-1}	$P \times 10^{14}$, m^3(STP) m m^{-2} s^{-1} kPa^{-1}
hexane	14.87	660	0.300	1.76 (0.02)	8.50 (0.05)	14960 (280)
heptane	15.21	684	0.387	1.68 (0.02)	7.21 (0.08)	12110 (370)
octane	15.47	703	0.508	1.43 (0.05)	6.07 (0.05)	8680 (380)
nonane	15.67	718	0.665	1.36 (0.04)	5.44 (0.03)	7400 (260)
decane	15.83	730	0.838	1.43 (0.03)	4.67 (0.02)	6680 (190)
undecane	15.96	740	1.098	1.29 (0.02)	3.97 (0.04)	5120 (140)
dodecane	16.06	749	1.383	1.20 (0.03)	3.52 (0.03)	4220 (130)
tridecane	16.14	756[f]	1.724	1.22 (0.02)	3.15 (0.03)	3840 (100)
tetradecane	16.21	760[f]	2.128	1.15 (0.02)	2.71 (0.03)	3120 (90)
pentadecane	16.28	769[f]	2.534[g]	1.14 (0.04)	2.53 (0.03)	2880 (140)
hexadecane	16.33	773	3.032	0.90 (0.02)	2.44 (0.02)	2200 (70)
heptadecane	16.43[c]	778[f]	3.183[h]	1.09 (0.03)	2.19 (0.02)	2390 (90)
polyethylene amorphous	17.30[e]	855[e]				

[a]The solubility parameter, density, and viscosity data taken from the literature are included. [b]Reference 40. [c]Calculated from vaporization enthalpy data; ref 41. [d]Reference 42. [e]Reference 6. [f]Reference 43. [g]Reference 44. [h]Reference 45.

Table 2. Transport Coefficients of $[^{13}C]O_2$ at 298 K in 1-Alkanols As Determined by NMR Spectroscopy (standard deviations are shown in parentheses)[a]

1-alkanol	δ,[b] MPa$^{1/2}$	ρ,[e] kg m^{-3}	η,[f] mPa s	$k_d \times 10^2$, m^3(STP) m^{-3} kPa^{-1}	$D \times 10^9$, m^2 s^{-1}	$P \times 10^{14}$, m^3(STP) m m^{-2} s^{-1} kPa^{-1}
methanol	29.7	787	0.544	3.50 (0.02)	5.34 (0.03)	18690 (230)
ethanol	26.6	785	1.074	2.29 (0.04)	4.21 (0.04)	9640 (260)
propanol	24.6	800	1.945	1.74 (0.01)	3.02 (0.03)	5250 (80)
butanol	23.1	806	2.544	1.66 (0.03)	2.59 (0.02)	4300 (100)
pentanol	21.7	811[f]	3.619	1.48 (0.03)	2.23 (0.03)	3300 (100)
hexanol	21.6[d]	815	4.578	1.4 (0.1)	1.92 (0.02)	2690 (230)
heptanol	21.3[d]	822[f]	5.810	1.51 (0.03)	1.70 (0.02)	2570 (80)
octanol	20.9[c]	822	7.288	1.10 (0.03)	1.42 (0.02)	1560 (70)
nonanol	20.7[d]	828[f]	9.123	0.98 (0.03)	1.34 (0.01)	1310 (50)
decanol	20.5[c]	826	10.9	1.01 (0.01)	1.21 (0.02)	1220 (36)
undecanol	19.9[d]	830[f]	13.72[g]	1.16 (0.02)	1.15 (0.02)	1330 (50)
glycerol	36.2	1,261[f]	934	0.070 (0.003)	0.0094 (0.0005)	0.66 (0.05)

[a]The solubility parameter, density, and viscosity data taken from the literature are included. [b]Reference 46. [c]Reference 47. [d]Calculated from vaporization enthalpy data; ref 48. [e]Reference 29. [f]Reference 43. [g]Reference 49.

Table 3. Values of the Solubility Coefficients of $[^{13}C]O_2$ in Different Liquids at 298 K Obtained by NMR Spectroscopy and Comparison with Those Reported in the Literature for Unlabeled Carbon Dioxide (standard deviations are shown in parentheses)

liquid	$k_d \times 10^2$, m^3(STP) m^{-3} kPa^{-1}	(lit.) $k_d \times 10^{2}$,[b] m^3(STP) m^{-3} kPa^{-1}
hexane	1.76 (0.02)	2.01[a], 2.01
heptane	1.68 (0.02)	1.79[a], 1.78
octane	1.43 (0.05)	1.65[a], 1.65
decane	1.43 (0.03)	1.42[a], 1.41
dodecane	1.20 (0.03)	1.25[a]
tetradecane	1.15 (0.02)	1.16[a]
hexadecane	0.90 (0.02)	1.08[a], 1.07
metanol	5.34 (0.03)	3.56
etanol	4.21 (0.04)	2.75
propanol	3.02 (0.03)	2.01
butanol	2.59 (0.02)	1.74
octanol	1.42 (0.02)	1.32
decanol	1.21 (0.02)	1.14

[a]Reference 28. [b]Reference 29.

methods. As in the case of liquids, the measurements were performed at equilibrium conditions and 298 K. Thus, prior to initiation of the NMR measurements, 2 to 18 h elapsed after loading the sample tube with C-13 labeled gas. For the rubbery samples, the equilibrium was reached relatively fast while for glassy polymers longer waiting times were required.

The C-13 NMR spectra of the polymer samples with the standard exhibited several peaks, as illustrated in Figure 4. Three peaks were identified in all samples. One peak corresponding to the C-13 signal of the carboxyl group of acetic acid at 178.1 ppm, and two peaks associated with the $[^{13}C]O_2$ in the membranes, centered at 128.8 and 125.3 ppm. These two peaks reflect the existence of two populations of $[^{13}C]O_2$ corresponding, respectively, to the nonsorbed (free) and sorbed (in the membrane) gas fractions, in a slow exchange regime. Unlike in the case of a liquid, there is enough free gas between the polymer strips and within the active volume of the radiofrequency coil to contribute to the NMR signal, and a peak is observed. The free gas can be easily identified because the value of its T_1 relaxation time is about 60 ms, compared with the value of T_1 of sorbed gas in the polymers studied, i.e., 2
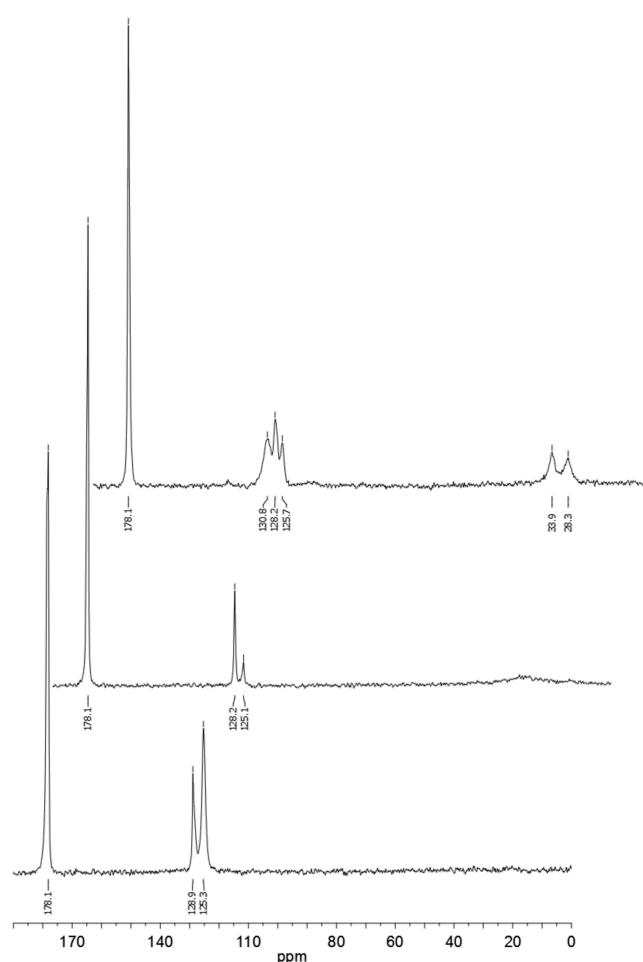

Figure 4. ^{13}C NMR spectra corresponding to samples of vulcanized polybutadiene (top trace), polyethylene (middle trace), and polycarbonate (bottom trace) in the presence of $[^{13}C]O_2$ at 298 K. In addition to the resonances associated to $[^{13}C(1)]$ of acetic acid (178.1 ppm), and free (128.2 ppm) and sorbed (125.4 ppm) $[^{13}C]O_2$, additional peaks are observed in the spectra of the polymers with low T_g (polybutadiene and polyethylene).

to 5 s. In addition, the spectra corresponding to the polymers with a glass transition temperature, T_g, well below the temperature at which these measurements were performed

(298 K), showed additional peaks associated to carbons in macromolecular segments with high mobility. Thus, the C-13 spectrum corresponding to polybutadiene (top trace, Figure 4) exhibits peaks in the aliphatic region centered at 28.3 and 33.9 ppm and the unsaturated region at 130.8 ppm. The C-13 spectrum of polyethylene (middle trace, Figure 4) shows a peak in the aliphatic region at about 30 ppm, attributed to the amorphous fraction. In Table 4, the results of the solubility

Table 4. Solubility Coefficient of $[^{13}C]O_2$ in Several Polymers at 298 K (standard deviations are shown in parentheses)

sample	p, MPa	$S \times 10^2$, m³(STP) m⁻³ kPa⁻¹	(lit.) $S \times 10^2$, m³(STP) m⁻³ kPa⁻¹	ref
polyethylene (26% crystallinity)	0.238 (0.001)	0.278 (0.008)	0.3	31
polyethylene amorphous (calc.)		0.38	0.44	32, 33
polybutadiene	0.233 (0.001)	0.68 (0.02)	0.98	30
polycarbonate	0.243 (0.001)	3.94 (0.06)	5.55^a	24

^{a}Value calculated at 298 K and 0.243 MPa by interpolation of data at different temperatures and pressures from ref 24.

measurements in the three types of polymers studied, rubbery (polybutadiene), semicrystalline (polyethylene), and glassy (polycarbonate), are shown. For comparison, results of carbon dioxide solubility in these polymers by sorption measurements are also included.[24,30,31] A good agreement between the values obtained from the NMR measurements and those determined by other methods is observed.

Concerning the solubility coefficients of $[^{13}C]O_2$ in alkanes and amorphous polyethylene, it is of interest to analyze the influence on the carbon chain length and assess the contribution of the polymer phases (crystalline and amorphous) to the solubility of carbon dioxide. In Figure 5 the solubility coefficient of $[^{13}C]O_2$ determined experimentally in several alkanes is shown as a function of the number of carbons in the chain, as well as the results obtained by other researchers.[28] It can be seen that a good agreement is attained, indicating again the reliability of the NMR method in the
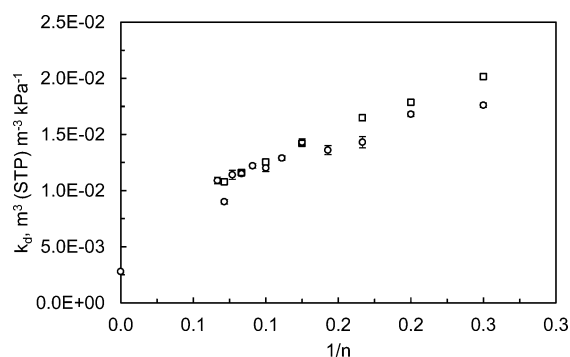

Figure 5. Values of the solubility coefficient of $[^{13}C]O_2$ at 298 K determined with NMR spectroscopy for alkanes and polyethylene as a function of the inverse of the number of carbons in the chain. The circles represent the experimental results of this work, and the squares correspond to data in ref 28.

determination of transport coefficients of carbon dioxide in liquids and polymers.

The solubility coefficient of carbon dioxide in 100% amorphous polyethylene, associated in this case to the Henry solubility coefficient (k_{dam}), cannot be determined experimentally, but it may be estimated by considering that only the amorphous regions contribute to the gas sorption. Thus, the value found is in good agreement with the results reported by Michaels et al.[32−34] (Table 4) determined in the same manner. However, at first sight, the solubility data of $[^{13}C]O_2$ in alkanes shown in Figure 5 suggest that the result of any extrapolation would be associated to a very high uncertainty in the value k_{dam}, given the enormous difference between the number of methylene groups in the liquid alkanes and the polymer chains.

Alternatively, k_{dam} could be determined from the solubility results of alkanes and alkanols with the modified Flory−Huggins theory for solutions. Although the approach also implies extrapolations of limited experimental data, we could evaluate the convergence of the two independent data sets and assess the goodness of the result. Considering the work of Budzien et al.[6] and Lin and Freeman,[35] the value of k_d (in m³(STP)/m³ MPa) can be expressed by the following equation:

$$k_d = \frac{22.414 \times 10^{-3}}{p_s V_1} \exp\left[-\left(\left(1 - \frac{1}{N}\right)\phi_2 + \chi\phi_2^2\right)\right] \quad (1)$$

where V_1 (m³/mol) is the molar volume of the solute (the gas in our case) in the pure liquid state, χ the gas−solvent interaction parameter, p_s (in MPa) is the saturation vapor pressure at the experimental temperature, N is the ratio of the molar volume of the solvent (or polymer) to that of the gas, V_2/V_1, and ϕ_2 is the volume fraction of the solvent.

Knowing k_d of carbon dioxide in the hydrocarbons and alcohols, we obtained the corresponding values of χ using eq 1, where V_1 was taken as the partial molar volume for CO_2, $\overline{V}_1 = 46 \times 10^{-6}$ m³/mol[36,37], and $p_s = 6.48$ MPa at 298 K was obtained directly from the carbon dioxide phase diagram.

On the other hand, values of the interaction parameter χ could be calculated using the equation[38]

$$\chi = \frac{V_1}{RT}(\delta_1 - \delta_2)^2 \quad (2)$$

where δ_1 and δ_2 are the corresponding solubility parameters of the gas and of the solvent. However, other authors[6] have pointed out that both the regular solution and Flory−Huggins theories suggest the calculation of χ with:

$$\chi = \frac{V_1}{RT}[(\delta_1 - \delta_2)^2 + 2I_{12}\delta_1\delta_2] \quad (3)$$

where I_{12} is an additional mixing parameter that must be taken into account for each gas−solvent pair. Thus, the values of χ for hydrocarbons and alcohols determined with eq 1 were used in eq 3 to calculate their corresponding values of I_{12}. The solubility parameter for CO_2 (12.32 MPa$^{1/2}$ at 298 K) was calculated using the expression[39] $\delta_{CO_2} = -0.0535T$ (K) + 28.26, and the values of δ for hydrocarbons and alcohols shown in Tables 1 and 2 (column 2), respectively, taken from the literature[40,41,46−48] were used.

In the same manner to the method reported by Budzien et al.,[6] all values of I_{12} were plotted vs the inverse of the molecular weight, as shown in Figure 6. An estimation of the value of I_{12} for completely amorphous polyethylene was obtained by
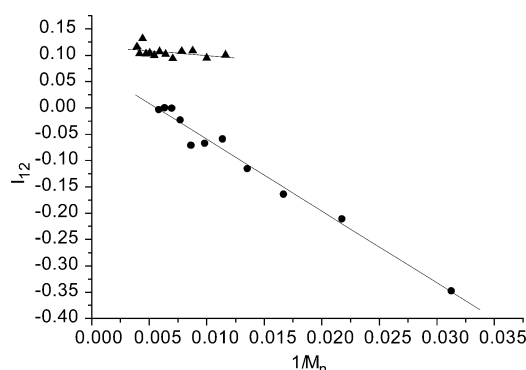
Figure 6. Plot of the variation of the parameter I_{12} vs the inverse of the molecular weight for the absorption of carbon dioxide in n-alkanes (triangles) and 1-alkanols (circles).

extrapolation to zero abscissa, and then the value of its interaction parameter, χ_{am}, was calculated using eq 3. The corresponding Henry solubility coefficient for amorphous polyethylene was calculated with eq 1, $k_{dam} = 0.008 \pm 0.001$ m³(STP) m⁻³ kPa⁻¹. This value is in disagreement with the value calculated directly from measurements of solubility of CO_2 in semicrystalline polyethylene, assuming that only the amorphous fraction contributes to the gas sorption.[32,33]

Diffusion of Carbon Dioxide. The diffusion coefficient of $[^{13}C]O_2$ in n-alkanes, 1-alkanols, and polymer membranes was determined with a PFG NMR stimulated spin echo sequence.[27] In this type of NMR measurement, the magnetic labeling of nuclei is accomplished by applying two field gradient pulses spaced by the so-called diffusion time. In the absence of motion, the loss of phase coherence of the NMR signal caused by the first gradient pulse would be compensated by the second gradient pulse, but this would not be the case if molecular diffusion occurs during the diffusion time. For illustrative purposes, ^{13}C PFG NMR spectra corresponding to $[^{13}C]O_2$ sorbed in polybutadiene are shown as a function of the amplitude of the field gradient in Figure 7.
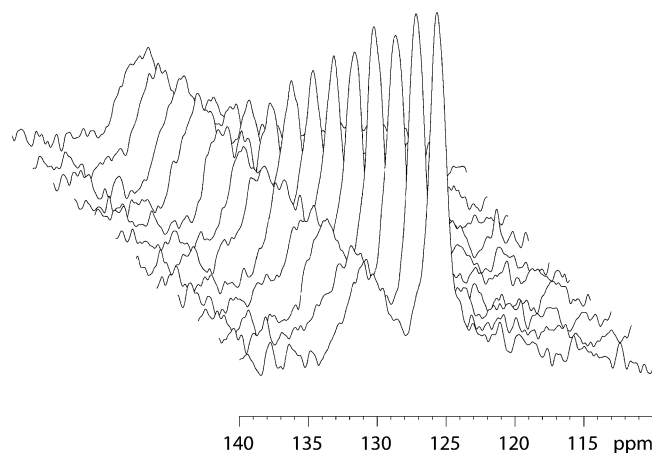
The echo attenuation can be written as[27]

Figure 7. ^{13}C PFG NMR spectra corresponding to $[^{13}C]O_2$ sorbed in vulcanized polybutadiene, at 298 K and 0.233 MPa, obtained with a diffusion time, t_D, equal to 20 ms. The duration of the gradient pulse, t_g, was 2 ms, and the amplitude of the field gradient, g, in T m⁻¹, was varied between 0.46 and 5.52. The peak at 130.7 ppm corresponds to the unsaturated carbons in polybutadiene; its intensity is not attenuated by the increasing value of g.

$$A(g) = A(0) \exp[-(bD)] \quad (4)$$

where $A(g)$ and $A(0)$ are the amplitude of the echo in the presence of a gradient pulse with amplitude g and 0, respectively, $b = (\gamma g t_g)^2 (t_D - t_g/3)$ where γ is the gyromagnetic ratio of the nucleus being observed, t_D and D are, respectively, the diffusion time and the diffusion coefficient of the sorbed gas, and t_g is the duration of the gradient pulse. Figure 8
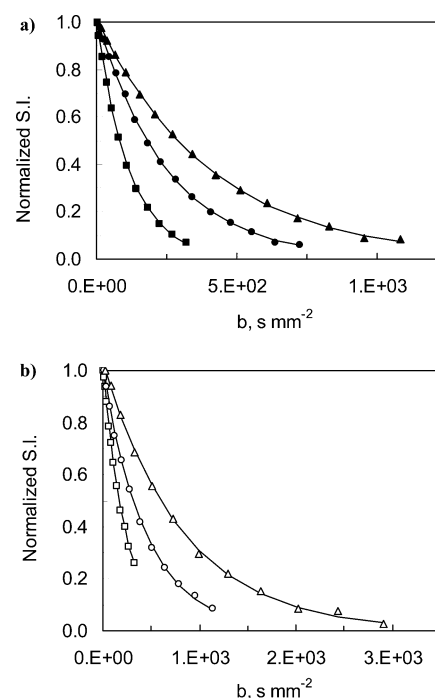

Figure 8. Plot of normalized peak intensity vs b corresponding to $[^{13}C]O_2$ sorbed in (a) alkanes (■ n-hexane, ● n-undecane, ▲ n-hexadecane) and (b) alkanols (□ ethanol, ○ 1-pentanol, and △ 1-decanol) obtained with the diffusion time, t_D, equal to 20 ms. The duration of the gradient pulse, t_g, was 2 ms and the amplitude of the field gradient, g, in T m⁻¹, was varied between 0.08 and 2.88.

illustrates the attenuation of normalized signal intensity in several samples of n-alkanes (Figure 8a) and 1-alkanols (Figure 8b). In all cases, the monoexponential function (eq 4) provides a very good fit for the data obtained, and the results are summarized in Tables 1 and 2 (column 6). These results have been analyzed according to the fractional Stokes–Einstein equation for Brownian particles in a liquid,[50]

$$D = k_b T / n \pi \eta r \quad (5)$$

where k_b is the Boltzmann constant, η the viscosity of the medium, r is the radius of the particle considered spherical, n is a viscosity-dependent parameter $n = n_0 \eta^{(\alpha-1)}$, n_0 being the value of n at unit viscosity and α a coefficient that indicates the deviation of the pure Stokes–Einstein law ($\alpha = 1$), variable for each solute and very dependent on its size. The double logarithm plot of D vs η illustrated in Figure 9 for n-alkanes and 1-alkanols shows a straight line with a slope equal to -0.52 ± 0.01, valid for both kinds of liquids, up to viscosity values of about 10^{-2} Pa s and with a significant deviation for liquids with high viscosity, such as tricresyl phosphate and glycerol. The results of this work for the diffusion coefficients are in excellent agreement with those reported by Sovova et al.,[51] where an empirical equation is proposed for determining D as a function
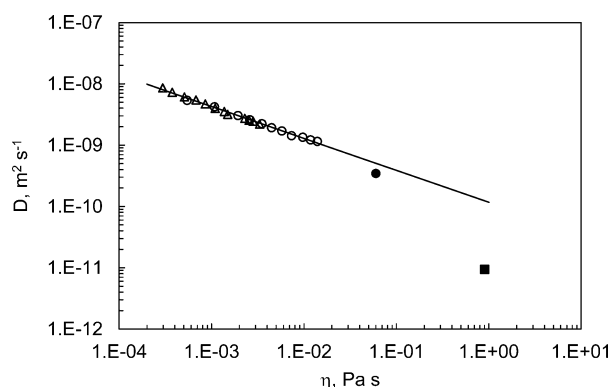
6056

dx.doi.org/10.1021/jp302037w | J. Phys. Chem. B 2012, 116, 6050–6058

Figure 9. Double logarithmic plot of the variation of $[^{13}C]O_2$ diffusion coefficient with viscosity as determined by NMR spectroscopy at 298 K for *n*-alkanes (triangles) and 1-alkanols (circles). Values for two higher viscosity liquids are also included (● tricresyl phosphate, ■ glycerol).

of the viscosity η and of the molar volume of the solute V_G with exponents −0.5 and −0.6, respectively.

The echo attenuation plot for $[^{13}C]O_2$ in cross-linked polybutadiene is shown in Figure 10, and the results of the diffusion measurements of $[^{13}C]O_2$ in samples of polymers are summarized in Table 5.
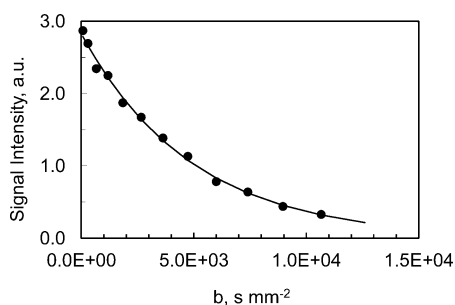

Figure 10. Plot of the peak intensity *vs b* corresponding to $[^{13}C]O_2$ sorbed in vulcanized polybutadiene obtained with the experimental parameters indicated in Figure 7. The solid line represents the fit using eq. 4.

Once Henry's solubility coefficient (k_d) and diffusion coefficients (D) were obtained, the corresponding permeability coefficients (P) were directly calculated from $P = k_d D$, and the NMR results for the *n*-alkanes and *n*-alkanols analyzed in this study, expressed in m^3(STP) m m^{-2} s^{-1} kPa^{-1}, are shown in the seventh column of Tables 1 and 2, respectively. Similarly, the permeability coefficients determined for the polymers ($P = SD$) are shown in the fourth column of Table 5.

After determination of all the transport coefficients, it was of interest to compare the results with those determined by other

procedures. Table 6 shows some values of the diffusion coefficients for several liquids found in the literature[52−54] and

Table 6. Values of the Diffusion Coefficients of $[^{13}C]O_2$ in Different Liquids at 298 K Obtained by NMR Spectroscopy and Comparison with Those Reported in the Literature for Unlabeled Carbon Dioxide (standard deviations are shown in parentheses)

liquid	(lit.) $\eta^d \times 10^3$, Pa s	(lit.) $D \times 10^9$, m^2 s^{-1}	$D \times 10^9$, m^2 s^{-1}
hexane	0.300	7.05, 8.2[a]	8.50 (0.05)
heptane	0.387	6.03, 6.89, 5.88[a]	7.21 (0.08)
tetradecane	2.128	2.95, 2.13[a]	2.71 (0.03)
hexadecane	3.032	2.20, 1.65[a]	2.44 (0.02)
water	1	1.97[b]	2.03 (0.04)
methanol	0.544	5.55, 8.37, 4.54, 4.95, 8.02, 5.13[b]	5.34 (0.03)
ethanol	1.074	3.42[c], 3.17[a]	4.21 (0.04)

[a]Reference 52 and references a−e, g therein. [b]Reference 53 and references a, c−f therein. [c]Reference 54. [d]Reference 43.

those obtained in the present work by NMR methods. A good agreement is obtained, demonstrating the reliability of the NMR method for the determination of all transport coefficients of $[^{13}C]O_2$ in the compounds analyzed. In the case of the polymers studied, the comparative analysis of the solubility, diffusion, and permeability coefficients obtained by NMR and those reported in the literature,[24,30,31,55] determined by other methods, shows that a reasonable agreement is also attained, as illustrated in Tables 4 and 5. Overall, these results highlight the value of the NMR procedure to determine all gas transport coefficients, either in liquids or in polymers at temperatures above and below the glass transition.

■ CONCLUSIONS

An NMR-based method is described that allows the sequential measurement of the solubility and diffusion coefficients of C-13-labeled carbon dioxide in liquids and polymer membranes with high accuracy and reproducibility. With these results, the gas permeability coefficient could also be calculated, and therefore all transport parameters for the material of interest are determined. The NMR method could also be applied to the measurement of these parameters with different gases labeled by C-13 or other suitable nucleus (e.g., H-1, F-19, N-15, etc.).

■ AUTHOR INFORMATION

Corresponding Author
*Tel: +34 91 5622900. Fax: +34 91 5644853. E-mail: lgarrido@cetef.csic.es.

Notes
The authors declare no competing financial interest.

Table 5. Diffusion and Permeability Coefficients of $[^{13}C]O_2$ in Several Polymers at 298 K (standard deviations are shown in parentheses)

sample	$D \times 10^{11}$ m^2 s^{-1}	(lit.) $D \times 10^{11}$, m^2 s^{-1}	$P \times 10^{14}$, m^3(STP) m m^{-2} s^{-1} kPa^{-1}	(lit.) $P \times 10^{14}$, m^3(STP) m m^{-2} s^{-1} kPa^{-1}	ref
polyethylene (26% crystallinity)	5.8 (0.3)	5.0	17 (2)	15	31
polybutadiene	20.4 (0.6)	10.5−33	138 (8)	104[a]−323	30, 55
polycarbonate	0.26 (0.01)	0.24[a]	11 (2)	12.3[a]	24

[a]Values at 303 K.

REFERENCES

(1) Bernardo, P.; Drioli, E.; Golemme, G. *Ind. Eng. Chem. Res.* **2009**, *48*, 4638.

(2) Aroon, M. A.; Ismail, A. F.; Matsuura, T.; Montazer-Rahmati, M. M. *Sep. Purif. Technol.* **2010**, *75*, 229.

(3) Abetz, V.; Brinkmann, T.; Dijkstra, M.; Ebert, K.; Fritsch, D.; Ohlrogge, K.; Paul, D.; Peinemann, K. V.; Nunes, S. P.; Scharnall, N.; Schossia, M. *Adv. Eng. Mater.* **2006**, *8*, 328.

(4) Lin, H.; Freeman, B. D. *J. Mol. Struct.* **2005**, *739*, 57.

(5) Budzien, J. L.; McCoy, J. D.; Curro, J. G.; LaViolette, R. A.; Peterson, E. S. *Macromolecules* **1998**, *31*, 6669.

(6) Budzien, J. L.; McCoy, J. D.; Weinkauf, D. H.; LaViolette, R. A.; Peterson, E. S. *Macromolecules* **1998**, *31*, 3368.

(7) Compañ, V.; del Castillo, L. F.; Hernández, S. I.; López-González, M. M.; Riande, E. *J. Polym. Sci., Part B: Polym. Phys.* **2007**, *45*, 1798.

(8) van der Vegt, N. F. A.; Briels, W. J.; Wessling, M.; Strathmann, H. *J. Chem. Phys.* **1996**, *105*, 8849.

(9) Tamai, Y.; Tanaka, H.; Nakanishi, K. *Macromolecules* **1995**, *28*, 2544.

(10) Curro, J. G.; Honnell, K. G.; McCoy, J. D. *Macromolecules* **1997**, *40*, 1145.

(11) Koros, W. J.; Paul, D. R.; Rocha, A. A. *J. Polym. Sci.: Polym. Phys. Ed.* **1976**, *14*, 687.

(12) Michaels, A. S.; Bixler, H. J.; Fein, H. L. *J. Appl. Phys.* **1964**, *35*, 3165.

(13) Compañ, V.; López, M. L.; Andrio, A.; Riande, E. *Macromolecules* **1998**, *31*, 6984.

(14) Compañ, V.; Andrio, A.; López, M. L.; Riande, E. *Polymer* **1996**, *37*, 5831.

(15) Tomizaki, K.; Kanakubo, M.; Nanjo, H.; Shimizu, S.; Onoda, M.; Fujioka, Y. *Ind. Eng. Chem. Res.* **2010**, *49*, 1222.

(16) Böttinger, W.; Mainwald, M.; Hasse, H. *Fluid Phase Equilib.* **2008**, *263*, 131.

(17) Callaghan, P. T. *Principles of nuclear magnetic resonance microscopy*; Oxford University Press: New York, 1991.

(18) Price, W. S. *Concepts Magn. Reson.* **1997**, *9*, 299.

(19) Matsukawa, S.; Yasunaga, H.; Zhao, C.; Kuroki, S.; Kurosu, H.; Ando, I. *Prog. Polym. Sci.* **1999**, *24*, 995.

(20) Sen, P. N. *Concepts Magn. Reson.* **2004**, *23A*, 1.

(21) Wen, W. Y. *Chem. Soc. Rev.* **1993**, *22*, 117.

(22) Meresi, G.; Wang, Y.; Cardoza, J.; Wen, W. Y.; Jones, A. A.; Gosselin, J.; Azar, D.; Inglefield, P. T. *Macromolecules* **2001**, *34*, 4852.

(23) Matsui, M.; Yamane, Y.; Kuroki, S.; Ando, I.; Fu, K.; J. Watanabe, J. *J. Mol. Struct.* **2005**, *739*, 131.

(24) Garrido, L.; López-González, M.; Sainz, E.; Riande, E. *J. Phys. Chem. B* **2008**, *112*, 4253.

(25) Díaz, K.; Garrido, L.; López-González, M.; Del Castillo, L. F.; Riande, E. *Macromolecules* **2010**, *43*, 316.

(26) García, C.; López-González, M.; de Abajo, J.; Garrido, L.; Guzmán, J. *Macromolecules* **2011**, *44*, 3862.

(27) Stejskal, E. O.; Tanner, J. E. *J. Chem. Phys.* **1965**, *42*, 288.

(28) King, M. B.; Kassim, K.; Al-Najjar, H. *Chem. Eng. Sci.* **1977**, *32*, 1241.

(29) Cibulka, I.; Heintz, A. *Fluid Phase Equilib.* **1995**, *107*, 235.

(30) Krykin, M. A.; Bondar, V. I.; Kukharsky, Y. M.; Tarasov, A. V. *J. Polym. Sci., Part B: Polym. Phys.* **1997**, *35*, 1339.

(31) Laguna, M. F.; Guzmán, J.; Riande, E. *Polymer* **2001**, *42*, 4321.

(32) Michaels, A. S.; Parker, R. B. *J. Polym. Sci.* **1959**, *41*, 53.

(33) Michaels, A. S.; Bixler, H. J. *J. Polym. Sci.* **1961**, *50*, 393.

(34) Michaels, A. S.; Bixler, H. J. *J. Polym. Sci.* **1961**, *50*, 413.

(35) Lin, H.; Freeman, B. D. *J. Membr. Sci.* **2004**, *239*, 105.

(36) Fleming, G. K.; Koros, W. J. *Macromolecules* **1986**, *19*, 2285.

(37) Merkel, T. C.; Bondar, V. I.; Nagai, K.; Freeman, B. D.; Pinnau, I. *J. Polym. Sci., Part B: Polym. Phys.* **2000**, *38*, 415.

(38) Di Paola-Baranyi, G.; Guillet, J. E. *Macromolecules* **1978**, *11*, 228.

(39) Camper, D.; Scovazzo, P.; Koval, C.; Noble, R. *Ind. Eng. Chem. Res.* **2004**, *43*, 3049.

(40) Wingefors, S.; Liljenzin, J.-O. *J. Chem. Technol. Biotechnol.* **1981**, *31*, 523.

(41) Morawetz, E. *J. Chem. Thermodyn.* **1972**, *4*, 139.

(42) Aucejo, A.; Burguet, M. C.; Muñoz, R.; Marques, J. L. *J. Chem. Eng. Data* **1995**, *40*, 141.

(43) Lide, D. R., Ed. *Handbook of Chemistry and Physics*, 89th ed.; CRC Press: Boca Raton, FL, 2008.

(44) Wu, J.; Nhaesi, A. H.; Asfour, A-F.A. *J. Chem. Eng. Data* **1999**, *44*, 990.

(45) Yoshida, N.; Hamada, S. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 351.

(46) Brandrup, J.; Immergut, E. H.; Grulke, E. A., Eds. *Polymer Handbook*, 4th ed.; John Wiley & Sons: New York, 1999; p 700.

(47) Zeng, W.; Du, Y.; Xue, Y.; Frisch, H. L. *Physical Properties of Polymers Handbook*, 2nd ed.; Mark, J. E., Ed.; Springer: New York, 2007; Ch. 16, pp 289−303.

(48) Kulikov, D.; Verevkin, S. P.; Heintz, A. *Fluid Phase Equilib.* **2001**, *192*, 187.

(49) Faria, M. A. F.; de Sá, C. F.; Lima, G. R.; Filho, J. I. B. C.; Martins, R.; Cardoso, M. J. E. M.; Barcia, O. E. *J. Chem. Eng. Data* **2005**, *50*, 1938.

(50) Kenneth, R. H. *J. Chem. Phys.* **2009**, *131*, 054503 and references therein.

(51) Sovova, H. *Collect. Czech. Chem. Commun.* **1976**, *41*, 3715.

(52) Luthjens, L. H.; De Leng, H. C.; Warman, J. M.; Hummel, A. *Radiat. Phys. Chem.* **1990**, *36*, 779 and references a−e, g therein.

(53) Frank, M. J. W.; Kuipers, J. A. M.; van Swaaij, W. P. M. *J. Chem. Eng. Data* **1996**, *41*, 297.

(54) Akerman, A.; Gainer, J. L. *J. Chem. Eng. Data* **1972**, *17*, 372.

(55) Crank, J.; Park, G. S. *Diffusion in Polymers*; Academic Press: New York, 1968; pp 50−69.