well-known formula. Obviously, the frequency of the modulation increases with the interparticle distance.

Aside from explaining the speckled appearance of laser-generated light scattering photographs from collections of spherulites, the present approach is quite useful in understanding effects, such as mutual truncation of spherulites, which are illustrated experimentally in Figure 7, using half sections of tapioca starch granules in two different orientations. Clearly this has the effect of producing considerable scattering on the equator and meridian of the scattering envelopes, whereas the ideal spherulite does not scatter at these positions. When truncation results from impingements of growing spherulites in a volume-filling assembly of spherulites whose full radius is R, and where the distance between nuclei is smaller than $2R$, the above theory predicts the scattering envelope shown in Figure 8.

As could be expected when the separation between nuclei is small in comparison to the spherulite radii, the scattering system tends to behave like a single particle (see Figure 8, $G = 0.125$). The top part of Figure 8 corresponds to the scattering envelope for the systems shown.

An understanding of this general problem of scattering by random or mutually ordered spherulites is pertinent to a full understanding of the factors which influence absolute intensity in volume-filling spherulite systems. Applications to biological systems where spherulites often occur in ordered array, as in the bordered pits of wood tracheids, require an understanding of interspherulitic interference effects.[11]

---

(11) J. Borch, P. R. Sundararajan, and R. H. Marchessault, *J. Polym. Sci., Part A-2*, **9**, 313 (1971).

Diffusion and Solubility of Simple Gases through a Copolymer of Hexafluoropropylene and Tetrafluoroethylene

R. A. Pasternak,* G. L. Burns, and J. Heller

Stanford Research Institute, Menlo Park, California 94025. *Received February 22, 1971*

ABSTRACT: The transport of seven gases, N_2, O_2, CO_2, CH_4, C_2H_6, C_3H_8, and C_2H_4, through FEP, a copolymer of hexafluoropropylene and tetrafluoroethylene, has been studied systematically over a temperature range of about 25–85°. For all the gases studied, linear Arrhenius plots of both permeation and diffusion coefficients were obtained. Empirical linear correlations both between the logarithm of the solubility at 25° and the heat of solution, and the Lennard-Jones force constant of the gases, were found. Furthermore, the standard entropies of solution and of diffusion were linearly dependent on the associated enthalpies. A comparison of the FEP data with those for polyethylene taken from the literature points up the limitations of existing theories of transport through polymers. Finally, the comparison with data on polytetrafluoroethylene (PTFE) indicates that the properties of the latter may be due, at least in part, to micropores or grain boundaries.

In a recent study of gas transport in polytetrafluoroethylene (PTFE) it was found that the activation energies of diffusion of N_2, O_2, and CO_2 were approximately 2 kcal/mol lower than they were in polyethylene (PE).[1] Since complete fluorination of polyolefins leads to considerable stiffening of the carbon backbone, this is an unexpected result which suggests that diffusion progresses partly through micropores in the PTFE. Such an explanation appears reasonable since PTFE of sufficiently high molecular weight to be usable virtually does not flow in the melt above its crystalline melting point of 327° because of its extremely high viscosity; fabrication requires compacting PTFE powder under high pressure near room temperature and then sintering at temperatures around 380°. The final product usually obtained by machining very likely contains micropores.

The present study of diffusion through a copolymer of hexafluoropropylene and tetrafluoroethylene (FEP) was undertaken partly to verify this postulated diffusion mechanism. FEP has a crystalline melting point near 290° and, whereas it retains most of the properties of PTFE, it has a melt viscosity in a range which allows fabrication by conventional techniques. Thus, FEP films can be expected to be free of micropores.

Experimental Section

Measuring Method. The dynamic method for measuring permeation and diffusion rates of gases and vapors in polymer membranes and the evaluation of the permeation and diffusion coefficients from the raw data have been described in detail elsewhere.[2,3] The instrument used here was an engineering model of the polymer permeation analyzer (manufactured by Infotronics Instrument Corp., Mountain View, Calif.). This instrument is equipped with three permeation cells, which can accept membranes of different thickness, and thus it permits a wide choice of measuring conditions. A low-volume valve permits selection of any of the three cells for study.

The instrument is well suited to rapid study of a series of gases over a wide temperature range. In actual operation, a gas at atmospheric pressure is admitted from a manifold to the upstream side of the thermostated cells; after completion of the measurements, the manifold is evacuated with a mechanical pump, another gas is admitted, and the procedure is repeated.

As a test of reproducibility, the permeation rates of CO_2 at 35° through one piece of FEP mounted across all three cells were measured. They were found to agree within 2%, which is equal to the reproducibility of repeat measurements for one cell.

The concentration of permeant gas in the helium carrier gas sweeping past the membrane was measured with a katharometer. The absolute detector sensitivity for CO_2 was determined by means of a CO_2–He mixture of known concentration. The sensitivities

---

* Address correspondence to this author at Pharmetrics, Palo Alto, Calif. 94304.

(1) R. A. Pasternak, M. V. Christensen, and J. Heller, *Macromolecules*, **3**, 366 (1970).

(2) R. A. Pasternak, J. F. Schimscheimer, and J. Heller, *J. Polym. Sci., Part A-2*, **8**, 467 (1970).

(3) R. A. Pasternak and J. McNulty, *Mod. Packag.*, **43**, 89 (1970).

for the other gases studied relative to CO_2 were determined directly by a method which will be described elsewhere.[4]

The measured sensitivities, which compare quite well with those given in the literature,[5] are CO_2, 1; O_2, 1.21; N_2, 1.14; CH_4, 1.32; C_2H_6, 0.97; C_2H_4, 0.98; and C_3H_8, 0.80.

Gases. High-purity bottled gases were used without drying. Ethane and ethylene were better than 99.0%, the other gases were 99.5-99.9% pure. It should be recognized that contamination of a slowly permeating gas with a rapidly permeating gas can greatly influence the data. For example, the permeation coefficient of C_3H_8 at 25° is about 1% of that of CO_2. Thus, a 1% contamination with CO_2 would nominally double the steady-state signal of C_3H_8. However, since a parallelism exists between permeation and diffusion coefficients, CO_2 appears on the downstream side long before C_3H_8, and two well-defined steps would be observed in the dynamic method used here. Indeed, a very low step preceding the main step was occasionally observed and was ascribed to contamination from the manifold.

Membranes. FEP membranes of different thicknesses obtained directly from Du Pont and from local suppliers were compared at 35°. Variations were found in the permeation coefficient for CO_2 of more than 10%, larger than the uncertainty in thickness measurements (0.05 mil). Three membranes were finally selected which had average thicknesses of 1.10, 1.87, and 5.26 mils. The permeation coefficients for the first two membranes were identical within the precision of the measurements, but that for the thick membrane was lower by about 10%. This discrepancy was found at all temperatures and for all gases, whenever a comparison could be made; the diffusion coefficients, however, did not appear to vary for the three membranes. The permeation data reported here are all derived from the 1.10-mil membrane; the diffusion data are combined from all membranes since, depending on the gas and the temperature, steady-state permeation might be reached too fast for the thin membranes and too slow for the thick membranes to determine reliably the diffusion coefficients. In the present instrument, the time to reach half the steady-state signal must be at least 30 sec to allow evaluation of the curves in terms of diffusion coefficients.

The membranes were annealed for 24 hr at 95°. No significant change in thickness was observed; however, both the permeation and diffusion coefficients at 35° had increased by about 10%. Occasional temperature cycling, between higher temperatures and 35°, in the course of the study, did not show further changes in the transport parameters.

Crystallinity. Since no data on the crystallinity of FEP were given by the manufacturer or in the literature, X-ray diffractometer spectra were taken for both FEP and PTFE. A few distinct lines were found superposed on diffuse bands which were identical for the polymers; they are given in Table I. Other lines are indicated but are barely distinguishable from the background.

The first three lines listed fit well a hexagonal lattice with axes of 5.63 and 5.76 Å for PTFE and FEP, respectively. The former value is close to 5.66 Å reported previously.[6,7]

The close agreement in unit cell dimensions and the similar relative intensities of the lines suggest closely similar packing of the chains in the two polymers; apparently the bulky CF_3 groups of FEP can be accommodated in the crystal structure without increasing significantly the unit cell dimensions.

The lines of FEP were found to be significantly wider than those of PTFE. The crystallite sizes (in the *a-b* plane) estimated from the line width were about 200 Å for FEP and at least twice as large for PTFE.

To summarize, the FEP contains a significant fraction of a highly dispersed crystalline phase, though probably less than PTFE. However, the present data are not sufficient to make a quantitative estimate of this fraction.

TABLE I
DIFFRACTION DATA FOR PTFE AND FEP, INDEXED ACCORDING TO A HEXAGONAL LATTICE[a]

	PTFE			FEP		
hkl	Peak heights[b]	*d*, Å	*a* = *b*, Å	Peak heights[b]	*d*, Å	*a* = *b*, Å
100	356	4.90	5.65	208	5.01	5.77
110	16	2.83	5.66	5	2.885	5.77
200	20	2.43	5.58	6	2.49	5.74
	20	2.18				

[a] *hkl* are the indices, *d* represents the spacings, and *a* = *b* refers to the hexagonal axes. [b] Arbitrary units.

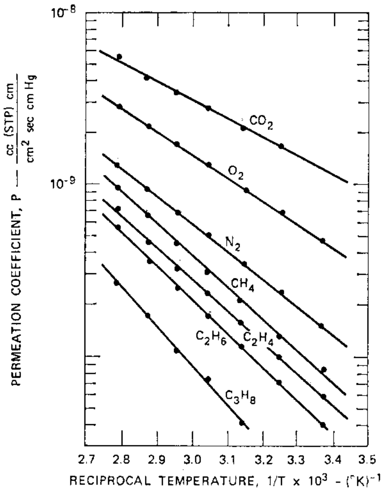


Figure 1. Logarithm of the permeation coefficient *P* of seven gases in FEP, as a function of the reciprocal temperature $1/T$.

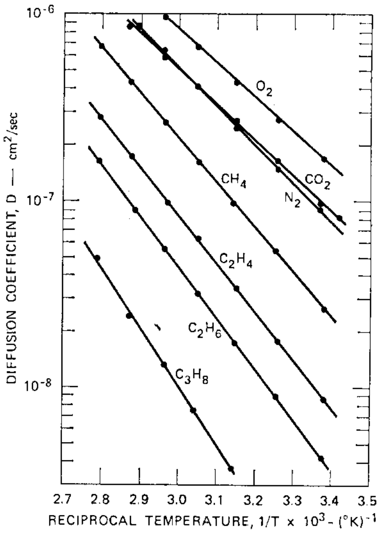


Figure 2. Logarithm of the diffusion coefficient *D* of seven gases in FEP, as a function of the reciprocal temperature $1/T$.

Results

In Figures 1 and 2 the logarithms of the permeation coefficients and of the diffusion coefficients, respectively, are plotted *vs.* the reciprocal absolute temperatures. A temperature range of about 60° is covered by the data, except that the steady-state permeation rates for C_3H_8 at the lowest two temperatures were too small to permit precise measurements. The straight lines drawn were obtained by least-squares treatment of the data. The standard deviation of the data

---

(4) R. A. Pasternak and M. V. Christensen, *J. Appl. Phys.*, in press.

(5) R. Kaiser, "Gas Phase Chromatography," Butterworths, London, 1963, p 92.

(6) C. W. Bunn and E. R. Howells, *Nature (London)*, 174, 549 (1954).

(7) B. Heise, H. G. Killian, and F. H. Müller, *Kolloid-Z. Z. Polym.*, 213, 12 (1966).

TABLE II
DIFFUSION, PERMEATION, AND SOLUBILITY DATA FOR SEVEN GASES IN FEP[a]

Gas	$D_{25} \times 10^8$	D_0	E_D	$P_{25} \times 10^{11}$	$P_0 \times 10^5$	E_P	k_{25}	$k_0 \times 10^3$	ΔH_S
N_2	9.48	0.552	9.20	15.9	3.65	7.31	0.127	5.30	−1.89
O_2	18.4	0.218	8.29	49	1.45	6.09	0.205	5.04	−2.20
CO_2	10.5	0.272	8.75	127	0.59	5.00	0.92	1.64	−3.75
CH_4	2.98	2.92	10.89	8.65	11.00	8.31	0.220	2.86	−2.58
C_2H_6	0.470	5.40	12.35	4.39	11.5	8.74	0.71	1.62	−3.61
C_3H_8	0.077	26.7	14.37	1.42	50.4	10.29	1.40	1.44	−4.08
C_2H_4	0.98	4.13	11.76	6.35	8.35	8.35	0.494	1.53	−3.41

[a] D_{25} and D_0 in cm²/sec; P_{25} and P_0 in (cm³ (STP) cm)/(cm² sec cm); k_{25} and k_0 in cm³ (STP)/(cm³ atm); E and ΔH in kcal/mol.

TABLE III
PERMEATION DATA FOR DIVERSE GASES IN PE, FEP, AND PTFE[a]

	$P_{25} \times 10^8$				E_p			
Gas	PE (22)[b]	PE (59)[c]	FEP	PTFE[d]	PE (22)[b]	PE (59)[c]	FEP	PTFE[d]
N_2	0.11	0.74	1.2	1.1	9.5	11.8	7.3	5.8
O_2	0.31	2.2	3.7	3.2	8.4	10.2	6.1	4.5
CO_2	1.29	9.6	9.7	8.9	7.2	9.3	5.0	3.3
CH_4	0.36	2.2	0.66		9.7	11.3	8.3	
C_2H_6	0.45	5.2	0.33		10.2	11.3	8.7	
C_3H_8	0.44	7.2	0.11		9.3	11.2	10.3	
C_2H_4			0.48				8.4	

[a] P_{25} in (cm³ (STP) cm)/(cm² sec atm); E_P in kcal/mol. [b] PE Grex, 22% amorphous; ref 9. [c] PE Alathon 14, 59% amorphous; ref 9. [d] PTFE, 40% amorphous; ref 1.

points from this line is about 2%, and the uncertainty in the slopes is of about the same magnitude; no systematic deviations are observed. However, both permeation and diffusion coefficients measured at 95° (not shown in the figures) lie significantly above the straight lines; these deviations were shown to be reversible by temperature cycling. We suspect a phase transition, which is also indicated by a discontinuity in the tensile modulus at about 80°.[8]

In Table II the permeation and diffusion coefficients P and D at 25° and the associated preexponential factors and energies are listed; they are derived from the straight-line plots according to the equations

$$\begin{aligned} P &= P_0 \exp(-\Delta E_P/RT) \\ D &= D_0 \exp(-\Delta E_D/RT) \end{aligned} \qquad (1)$$

The solubilities and parameters associated with them, which are also shown, are calculated from the relationship

$$k = P/D = k_0 \exp(-\Delta H_S/RT) \qquad (2)$$

The uncertainties are estimated to be about 0.2 kcal in ΔE_P and ΔE_D and about 0.3 kcal in ΔH_S. Uncertainties in the preexponential factors are quite large because their determination involves a linear extrapolation over a wide interval in $1/T$. For an average temperature of 55° (T = 323°K) (unless otherwise indicated, temperatures are degrees centigrade), an uncertainty of 0.1 kcal in the heats results in an uncertainty of 15% in the preexponential factor.

Discussion

Permeation. In Table III, the experimental permeation coefficients P_{25} at 25° and the heats of permeation E_P of FEP (and PTFE) are compared with those of a linear and of a branched polyethylene, PE Grex (Grace) and Alathon 14 (Du Pont), 22 and 59% amorphous, respectively. The PE data are taken from Michaels and Bixler.[9] N_2 and O_2 permeate faster through the polyfluorocarbons than even through the low-density PE. However, the relative rates shift in favor of PE with increasing boiling temperature (or with increasing molecular size) of the permeant.

In the following discussion of the two basic processes, solubility and diffusion, which together control permeation, only the data for linear PE (Grex) are used for comparison, since the degree of crystallinity of this PE does not change with temperature. We postulate that the crystallinity of the high-melting FEP, after annealing at 95°, is constant also.

Solubility. The solubilities of gases in some nonpolar solvents at 25° and atmospheric pressure have been found to be an exponential function of the Lennard-Jones force constant ϵ/k,[10] or the boiling temperature T_b.[11] The same functional relationship has been observed for the solubilities of gases in PE,[9] natural rubber,[12] and polyethylene terephthalate.[13] The heat of solution in PE is a linear function of ϵ/k also.[9] Since both ϵ/k and T_b are measures of the van der Waals interaction forces of gases and differ only by an approximately constant factor, the discussion will be limited to ϵ/k.

In Figure 3 the logarithms of the observed gas solubilities k_{25} at 25°, and in Figure 4 the heats of solution ΔH_S, are plotted *vs.* ϵ/k for FEP. The values of ϵ/k are those given by Michaels and Bixler,[9] except that for C_2H_4, which is taken from Hildebrand, *et al.*[10] The fit to straight lines is excellent (except for CO_2, which possibly interacts with FEP), but may be somewhat fortuitous since the values of the force constant ϵ/k are not quite certain.[11] The equations of the straight lines are

$$\log k_{25} = 1.38 + 0.0052(\epsilon k) \qquad (3)$$

---

(8) E. I. du Pont de Nemours and Co., Technical Information Bulletin No. T-2C.

(9) A. S. Michaels and H. J. Bixler, *J. Polym. Sci.*, **50**, 393, 413 (1961).

(10) J. E. Jolley and J. H. Hildebrand, *J. Amer. Chem. Soc.*, **80**, 1050 (1958).

(11) J. H. Hildebrand, *Proc. Nat. Acad. Sci. U. S.*, **57**, 542 (1967).

(12) G. J. van Amerongen, *Rubber. Chem. Technol.*, **37**, 1065 (1964).

(13) A. S. Michaels, W. R. Vieth, and J. A. Barrie, *J. Appl. Phys.*, **34**, 1, 13 (1963).

TABLE IV

SOLUBILITY DATA FOR DIVERSE GASES IN PE, FEP, AND PTFE[a]

Gas	ϵ/k	k_{25} PE[b]	k_{25} FEP	k_{25} PTFE[c]	ΔH_S Cond[d]	ΔH_S PE[b]	ΔH_S FEP	ΔH_S PTFE[c]
N_2	95	0.041	0.13	0.30	−1.33	0.5	−1.89	−1.30
O_2	118	0.077	0.21	0.52	−1.63	−0.4	−2.20	−1.73
CO_2	189	0.451	0.92	2.35	−3.46	−1.3	−3.75	−3.50
CH_4	148	0.203	0.22		−1.96	−0.7	−2.58	
C_2H_6	243	1.28	0.71		−3.51	−2.3	−3.61	
C_3H_8	284	3.97	1.40		−4.49	−3.0	−4.08	
C_2H_4	200		0.49		−3.24		−3.41	

[a] ϵ/k in °K; k_{25} in cm^3 (STP)/(cm^3 atm); ΔH_S in kcal/mol. For PE and PTFE k_{25} is the solubility in amorphous phase; for FEP, k_{25} is the experimental solubility. [b] Reference 9. [c] Reference 1. [d] Heat of condensation.

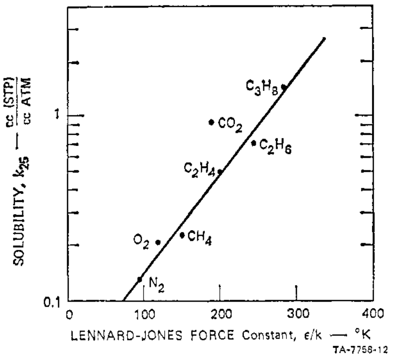


Figure 3. Logarithm of the solubility k_{25} at 25° of seven gases in FEP, as a function of the Lennard-Jones force constant ϵ/k.

$$\Delta H_S \text{ (kcal/mol)} = -0.85 - 0.012(\epsilon/k) \qquad (4)$$

For PE the equivalent log k_{25} and ΔH_S plots have slopes of 0.0095 and 0.0164.[9]

The solubility k and the heat of solution ΔH_S are related by the expression

$$\log k = \log k_0 - (\Delta H_S/2.3RT)$$

If k_0 (or the standard entropy of solution, $\Delta S_0 = 2.3 \log k_0/R$) of the different solutions were the same, the log k *vs.* ΔH_S plot would be linear with a slope of $-1/2.3RT = -0.73$ kcal^{-1} mol at 298°K. The solubilities in PE satisfy this correlation.[9] For FEP (see Table III) the k_0 is, however, not constant; it is within the precision of measurements a linear function of ΔH_S (Figure 5) with a slope of −0.29 kcal mol.

The linear interdependence of the standard entropy and enthalpy of solution appears at least qualitatively plausible, since the higher heats of solution, *i.e.*, stronger interactions, should be associated with reduced degree of freedom of the dissolved molecules.

A theoretical interpretation of the observed empirical correlations involving the Lennard-Jones force constant has been attempted by Michaels and Bixler.[9] It was based on the Hildebrand-Scatchard[14] model for the mixing of two liquids and that model's adaptation for polymers by Flory and Huggins.[15] In addition, the chemical potential of the gases was assumed to obey the simple Clausius–Clapeyron equation. A linear correlation between ΔH_S and ϵ/k was derived with a slope closely matching the experimental one (0.0156 *vs.* 0.0164 for PE).[9] This agreement between observation and model is probably fortuitous because of the rather tenuous assumptions made for the model: (1) the Trouton rule holds, *i.e.*, the entropy of vaporization at the boiling point is equal to 0.020 kcal/deg for all gases studied, (2) the (fictitious) heat of condensation is constant even above the critical point; and (3) the heat of mixing is always small relative to the heat of condensation, or is constant. Postulate 3, made implicitly, conflicts with the theory of mixing of liquids as formulated by Hildebrand and others[14] and with experimental data for such systems. The contradictions with theory are illustrated by the data summarized in Table IV. Indeed, for PE the heats of solution are by an approximately constant amount more positive than the heats of con-

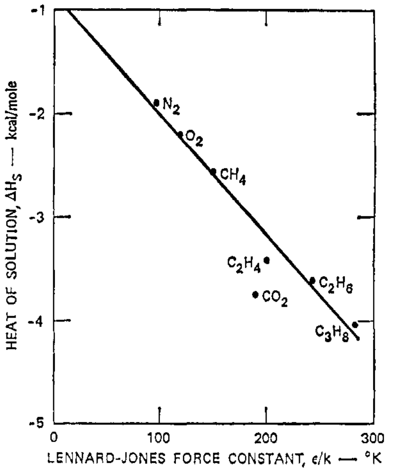


Figure 4. Heat of solution ΔH_S of seven gases in FEP, as a function of the Lennard-Jones force constant ϵ/k.

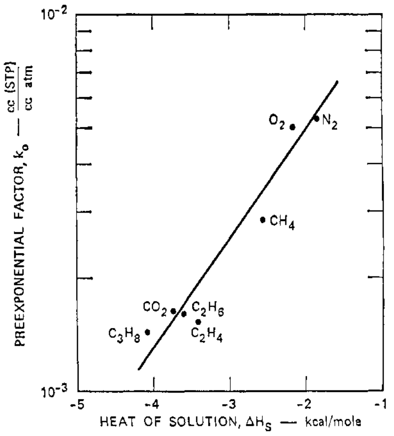


Fig. 5. Logarithm of the preexponential factor k_0 of seven gases in FEP, as a function of heat of solution ΔH_S.

---

(14) J. H. Hildebrand and R. L. Scott, "The Solubility of Non-Electrolytes," 3rd, Reinhold, New York, N. Y., 1950.

(15) P. J. Flory, "The Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953.

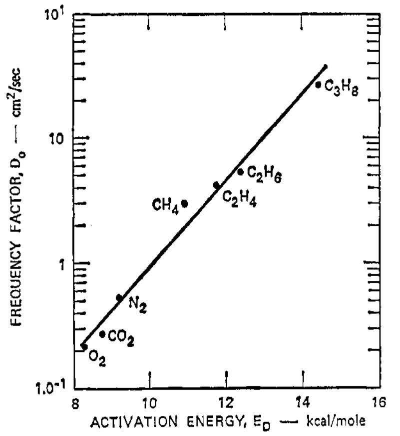


Figure 6. Logarithm of the preexponential factor D_0 of seven gases in FEP, as a function of activation energy of diffusion E_D.

densation; in contrast, for FEP the difference is negative for the low-boiling gases but decreases with increasing boiling point and becomes positive for propane. However, according to the simple theory of solution the heat of mixing can only be positive. Even larger negative heats of solution were found for gases in glassy polyethylene terephthalate;[13] they were ascribed to strong exothermic adsorption of the gases on the walls of internal voids.

The gas solubilities at 25° are listed also in Table IV; for PE and PTFE they are corrected for crystallinity. The uncorrected solubilities in FEP which represent a lower limit are significantly higher than in PE for the low-boiling gases, but the reverse holds for the higher boiling gases.

The solubilities of N_2, O_2, and CO_2 in PTFE appear to be significantly higher than in FEP, but the heats of solution are somewhat less negative. Both these differences may be explained by quasicondensation of the gases in micropores of PTFE.

Diffusion. It is seen from Table II that the preexponential factor D_0 (which is about proportional to the entropy of activation) varies significantly between solutes. In Figure 6 the logarithm of D_0 is plotted *vs.* the activation energy of diffusion E_D of the gases in FEP. The data can be approximated by a linear relationship as has been observed also for other polymers.[16] A theoretical explanation has been given by Lawson.[17]

The activation energies and the diffusion constants at 25° of PE, FEP, and PTFE are listed in Table V. Rather surprisingly, the activation energies for the first two polymers are identical for all gases studied within the precision of the measurements. According to the model by Brandt and Anysas,[18] the activation energy of diffusion has two components; one depends on the cohesive energy of the polymer and is proportional to the molecular diameter of the permeant, the other depends on the chain flexibility and is proportional to the square of the diameter. Michaels and Bixler[9] estimate that for PE the contribution of the flexing energy to the activation energy is small and accordingly find a linear relationship between the activation energies and the molecular diameters. In contrast, the cohesive energy of FEP is smaller than that of PE, but the FEP chain is stiffer. Therefore, the energy associated with chain flexing should be significant in FEP and the activation energies of diffusion should increase more than linearly with the molecular diameter of the permeants.

Table V

Diffusion Data for Diverse Gases in PE, FEP, and PTFE[a]

	$D_{25} \times 10^7$			E_D		
Gas	PE[b]	FEP	PTFE[c]	PE[b]	FEP	PTFE[c]
N_2	0.93	0.95	0.88	9.0	9.20	7.12
O_2	1.70	1.84	1.52	8.8	8.29	6.28
CO_2	1.24	1.05	1.03	8.5	8.75	6.84
CH_4	0.57	0.30		10.4	10.89	
C_2H_6	0.146	0.047		12.5	12.35	
C_3H_8	0.049	0.0077		13.6	14.37	
C_2H_4		0.098			11.76	

[a] D_{25} in cm² sec; E_D in kcal/mol. [b] Reference 9. [c] Reference 1

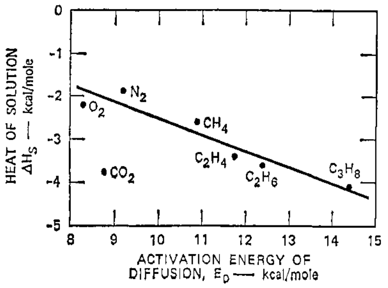


Figure 7. Heat of solution ΔH_S as a function of activation energy of diffusion E_D.

Finally, a comparison between the activation energies of diffusion in FEP and PTFE (Table V) is of considerable interest. Although the cohesive energy of PTFE is certainly quite similar to that of FEP and its chain stiffness is probably higher, the apparent activation energies for all the three gases studied is about 2 kcal lower. Thus, easier diffusion pathways must be available in the sintered PTFE; they very likely are micropores and/or grain boundaries. According to the manufacturer, commercial PTFE has a void volume of about 0.5%; nevertheless, the density of PTFE increases by several per cent if compressed at 4 kbars/in.²,[19] Further study will be needed to show whether this increase is due to the removal of pores or to an increase in crystallinity.

Conclusions

Empirical correlations have been obtained in this and other studies between transport properties and molecular parameters of gases permeating through polymers. However, the apparently specific relationships observed for heat of solution and force constant on the one hand, and activation energy of diffusion and molecular diameter on the other, may well be fortuitous. For the gases studied, the molecular diameters are approximately proportional to the Lennard-Jones force constants (or their boiling temperatures); thus, one could have used either of these parameters and still obtained linear correlations for the heats of solution or of diffusion. Hence, a plot of ΔH_S *vs.* E_D for FEP is approximately linear also (Figure 7); only CO_2 deviates again pronouncedly from the straight line.

In the short discussion of the data we have pointed out the inability of the existing theories of gas-polymer interactions to explain satisfactorily the experimental data for FEP and

---

(16) P. Meares, *J. Amer. Chem. Soc.*, **76**, 3415 (1954); *Trans. Faraday Soc.*, **54**, 40 (1958).

(17) A. W. Lawson, *J. Chem. Phys.*, **32**, 131 (1960).

(18) W. W. Brandt and G. A. Anysas, *J. Appl. Polym. Sci.*, **7**, 1919 (1963).

(19) D. Lawson, private communication.

possibly for PE also. It is beyond the scope of this present study to formulate models more consistent with the observations.

Finally, the conclusion that diffusion through PTFE proceeds at least in part along pores and grain boundaries may have a significance far beyond the diffusion process. Other observed properties of bulk PTFE, which have been ascribed to the dense polymer structure itself, may also be due in part to the physical structure of the sintered material. A reevaluation of PTFE properties on the basis of this model may well be worthwhile.

Acknowledgment. M. Christensen assisted in the experimental work and F. J. Martinelli wrote the computer programs. This work was performed for the Jet Propulsion Laboratory, California Institute of Technology, sponsored by the National Aeronautics and Space Administration under Contract No. NAS 7-698.

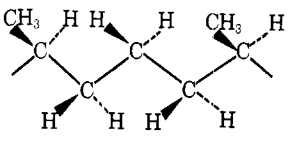
Nuclear Magnetic Resonance Spectroscopy. Steric Control in α-Olefin Polymerization as Determined by ^{13}C Spectra

A. Zambelli,* G. Gatti, C. Sacchi, W. O. Crain, Jr., and John D. Roberts

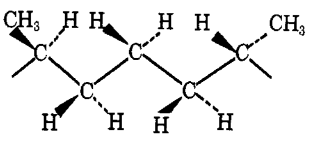
Istituto Chimica delle Macromolecole del C. N. R., Milan, Italy,
and the Gates and Crellin Laboratories of Chemistry,[1a] *California Institute of*
Technology, Pasadena, California 91109.[1b] *Received March 16, 1971*

ABSTRACT: Carbon-13 nmr spectroscopy has been used to elucidate the stereochemistry of ethylene–propylene copolymers prepared from enriched ethylene-*1*-^{13}*C*. The results give useful information on the degree and source of steric control in isospecific and syndiospecific polymerizations of α olefins.

The ^{13}C (cmr) spectra of ethylene–propylene copolymers prepared in the presence of isospecific catalysts appear to show only two resonance peaks for a single ethylene unit flanked by propylene units.[2] The lower field absorption has been ascribed to the lateral CH$_2$ and the higher field absorption to the central CH$_2$ of the (CH$_2$)$_3$ sequences. *A priori*, such (CH$_2$)$_3$ sequences could lie in a meso (m) configuration or in a racemic (r) configuration, depending on the relative stereochemical arrangements of the contiguous propylene units. Thus, if there are only two ethylene resonances for the (CH$_2$)$_3$ sequences, this suggests that for these copolymers only the meso (or only the racemic) situation occurs. Actually, occurrence of only racemic sequences seems quite improbable because of the isospecific nature of the polymerizations. However, it might also be possible that both meso and racemic situations occur, but that the carbon chemical shifts are insensitive to the configurations. We have now clarified this point and reached some conclusions on the mechanism of steric control in α-olefin polymerization by comparing the cmr spectra of copolymers made with ^{13}C-enriched ethylene and isospecific catalysts with those of similar copolymers prepared in the presence of syndiospecific and aspecific catalysts.



meso



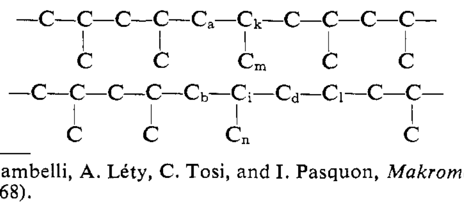
racemic

Results and Discussion

Figures 1a and 1b show the cmr spectra of two samples of 1-^{13}C 60%-enriched ethylene with ordinary propylene. Sample A contains 9 mol % ^{13}C-enriched ethylene and was prepared by the syndiospecific catalyst VCl$_4$–Al(C$_2$H$_5$)$_2$Cl. Sample B contains 9 mol % ^{13}C-enriched ethylene and was prepared by the aspecific catalyst VCl$_4$–Al(C$_2$H$_5$)$_3$. X-Ray and infrared analyses of these samples show that the steric arrangement in propylene blocks is syndiotactic in sample A and atactic in sample B as in the corresponding homopolymers. Therefore, the copolymerization with ethylene does not change the basic stereospecific behavior of the catalysts. In addition, the infrared analysis suggests the presence of –CH(CH$_3$)(CH$_2$)$_2$CH(CH$_3$)– sequences to the extent of 8% (g of CH$_2$/100 g of copolymer) in sample A and 4% in sample B.

The product of the reactivity ratios for both catalyst systems is equal to or less than unity[3] and this fact, along with the low incorporation of C$_2$H$_4$, requires that the greater part of the ethylene units be isolated between propylene units. Comparison of similar nonenriched copolymers permits the assignments, without uncertainty, of the starred peaks of Figures 1a and 1b to carbons in the chain arising from ethylene.

Table I contains the chemical shifts of the resonances detected in samples A and B and in a similar sample (C) prepared in the presence of an isospecific catalyst. The carbons are labeled as in the previous paper, where a partial assignment of the chemical shifts was made.[2b] In addition,



$$\begin{array}{ccccccccccc} — & C — & C — & C — & C — & C_a — & C_k — & C — & C — & C — & C — \\ & & | & & | & & | & & | & & | \\ & & C & & C & & C_m & & C & & C \end{array}$$

$$\begin{array}{ccccccccccc} — & C — & C — & C — & C — & C_b — & C_i — & C_d — & C_l — & C — & C — \\ & & | & & | & & | & & & & | \\ & & C & & C & & C_n & & & & C \end{array}$$

---

(1) (a) Contribution No. 4236. (b) That part of this research carried on at the California Institute of Technology was supported by the National Science Foundation.

(2) (a) A. Zambelli, "NMR Basic Principles and Progress," Vol. 4, Springer-Verlag, Heidelberg, 1971, p 101. (b) W. O. Crain, Jr., A. Zambelli, and J. D. Roberts, *Macromolecules*, **4**, 330 (1971).

(3) A. Zambelli, A. Léty, C. Tosi, and I. Pasquon, *Makromol. Chem.*, **115**, 73 (1968).