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Thermodynamic Characterization by Inverse Gas Chromatography of a 50% Methyl,50% Trifluoropropyl Polysiloxane

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ABSTRACT: Poly[methyl(3,3,3-trifluoropropyl)siloxane] with a 50% substitution of trifluoropropyl radical has been studied by inverse gas chromatography (IGC) between 90 and 180 °C. Both packed and capillary columns have been used, the latter prepared with and without cross-linking of the polymer. Flory-Huggins solute-polymer interaction parameters and partial molar enthalpies and free energies of solution and mixing were calculated for 21 substances (ketones, alcohols, aromatic and saturated hydrocarbons, nitriles, esters, and dimethylaniline). Nitriles, tertiary amines, and ketones behave as good solvents. Aromatic hydrocarbons are moderate solvents if a hydrocarbon chain is not attached to the aromatic ring, while alcohols and alkanes are nonsolvents in the temperature range considered, although solubility increases slightly with temperature. The thermodynamic functions vary linearly with the number of carbon atoms of the alkyl chain in homologous series. The solubility parameter of the polymer varies linearly with temperature from about 7.9 (cal cm^{-3})$^{1/2}$ at 90 °C to 7.4 (cal cm^{-3})$^{1/2}$ at 180 °C. A value of 8.2 (cal cm^{-3})$^{1/2}$ may be deduced for δ_2 at 25 °C. No meaningful difference was found between values deduced from V_g data obtained on packed or capillary columns, cross-linked or not.

Introduction

Gas chromatography (GC) is a useful technique in the study of some of the thermodynamic characteristics of polymers.[1-10]

(Trifluoroalkyl)siloxanes are interesting stationary phases (SP's) for use in GC, due to the special selectivity that the trifluoropropyl (TFP) group shows toward carbonyl compounds, based on the special interaction between the fluorine atoms and the free electrons of the oxygen atom. The only commercially available SP of this type is the 50% methyl,50% 3,3,3-trifluoropropyl polysiloxane, hereafter referred to as MTFPS50, with very little variation in composition when different commercial brands are considered.[11] The particular behavior of carbonyl compounds in this SP has led to its consideration as a preferred SP for GC.[12,13] The MTFPS50 is often used in the analysis of chlorinated pesticides, sometimes in mixed stationary phase columns, and of biological metabolites which include the keto group.[14-16]

We present here results of the thermodynamic characterization of the polymer by IGC and its interactions with 21 solutes, most of which belong to the general type R-Y, where R is a linear alkyl radical and Y represents a chemical function (methyl, hydroxyl, acetyl, and phenyl). Results are also presented on the differences of interactions of the chemical function Y with the polymers MTFPS50 and PS-255, the latter an apolar dimethylsilicone (2% vinyl content), used as a reference.

Experimental Section

Seven chromatographic columns have been used. Two packed columns were prepared with QF-1 (a MTFPS50) on Chromosorb W AW DMCS 80/100 mesh. This polymer has the consistency of an oil. One packed column of PS-255 (a poly(dimethylsiloxane)) on the same support was also prepared. The percentage of SP in the packings was determined by an extraction method.[17] Two capillary columns were prepared on borosilicate glass, using OV-215 (a TFPS50, with 1% vinyl group) as SP. This polymer has the consistency of a gum. The column walls were leached and washed following the method described by Grob.[18] The tube was then silanized with (3,3,3-trifluoropropyl)methylcyclosiloxane (TFPMCS) at high temperature, according to the procedure described by Blomberg.[19,20] The SP of one of these capillary columns was immobilized with dicumyl peroxide. Two other capillary columns were prepared with the same type of glass, leached and washed in the same way. The tube walls were silanized with hexamethyldisilizane (HMDS), and the SP PS-255 was deposited by the static method. One of the columns was immobilized with dicumyl peroxide. Further details appear in Table I. Densities of the polymers at different temperatures were determined by pycnometry.

Two Hewlett-Packard Model HP-5890A gas chromatographs were used for the capillary columns, and a Varian 3300 gas chromatograph was used for the work with packed columns. In all cases the carrier gas head pressure was measured with pressure transducers (capillary columns) or a precision mechanical manometer (packed columns). Oven temperatures were monitored with independent thermocouples, and the uniformity of the temperature distribution in the column oven was found to be better than ±0.3 °C.

Chromatograms were obtained at 90, 120, 150, and 180 °C. Injections were in all cases of about 0.01 μL, representing an amount of each component of the mixture of the order of 100 ng. The split ratio in the case of the capillary columns was of the order of 1:20. All samples injected contained a minimum of five *n*-alkanes, with the total number of substances varying from six to twelve. A mathematical dead time method was used to calculate correct retention times.[21]

Data Reduction. Specific retention volumes (V_g) were calculated in the usual manner.[22] Activity coefficients at infinite dilution based on weight fraction, Ω^∞_1, were calculated according to the expression of Guillet et al.[23,24] Vapor pressures were deduced using Antoine coefficients from various sources.[25,26] Second virial coefficients of *n*-alkanes were calculated by the method of O'Connell and Prausnitz;[27] for other substances, values were interpolated or extrapolated from literature values corresponding to other temperatures.[28] Densities were calculated according to the pertinent equation.[29,30] Molar volumes were deduced from molecular weight and density values.

Flory-Huggins interaction parameters $\chi^\infty_{1,2}$ were calculated from the known expression.[23,24,31] Partial molar enthalpies of solution (ΔH_s), mixing (ΔH_m), and vaporization (ΔH_v) were deduced in each case from experimental results.[32] Partial molar free energies of mixing were calculated from activity coefficients at infinite dilution.[6,31] Partial molar free energies of solution at infinite dilution were calculated from experimental values of V_g.[6]

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Table I
Characteristics of the Chromatographic Columns[a]

	column						
	1	2	3	4	5	6	7
stationary phase	OV-215	OV-215	QF-1	QF-1	PS-255	PS-255	PS-255
type	WCOT	WCOT	packed	packed	WCOT	WCOT	packed
length, m	23.49	22.00	2.00	2.00	23.84	20.73	2.00
internal diameter, mm	0.230	0.259	2.2	2.2	0.253	0.248	2.2
percentage of stationary phase			17.69	18.05			12.18
mass of stationary phase, mg	5.26	5.10	360	370	5.094	4.199	257
film thickness, μm	0.309	0.286			0.269	0.261	
deactivation agent	TFPMCS	TFPMCS	none	none	HMDS	HMDS	none
immobilization agent	none	DCP	none	none	none	DCP	none

[a] WCOT, wall-coated open-tubular column; TFPMCS, (3,3,3-trifluoropropyl)methylcyclosiloxane; HMDS, hexamethyldisilizane; DCP, dicumyl peroxide.

Table II
Specific Retention Volumes on OV-215 (mL/g)[a]

	temp, °C			
	90	120	150	180
n-hexane	8.69	4.87	2.87	2.04
n-heptane	15.23	7.69	4.27	2.57
n-octane	26.91	12.54	6.26	3.79
n-nonane	47.51	19.91	9.73	5.22
n-decane	83.47	31.56	14.16	7.53
n-undecane	147.68	50.50	20.70	10.42
n-dodecane	259.31	80.99	30.95	14.40
n-butyl alcohol	31.78	14.90	8.01	4.75
n-pentyl alcohol	56.19	23.89	12.51	6.73
n-octyl alcohol	328.61	102.81	39.21	18.22
acetone	29.53	13.48	6.98	3.90
2-butanone	47.20	20.15	9.73	5.16
2-pentanone	78.78	32.62	15.20	8.45
2-octanone	441.69	135.64	49.19	20.42
benzene	26.63	12.66	7.03	4.15
toluene	49.11	21.21	10.54	5.84
propylbenzene	129.10	49.21	21.92	10.73
pentylbenzene	388.04	118.96	47.66	20.16
pyridine	83.46	35.33	17.35	9.82
ethyl acetate	35.96	16.60	8.55	4.99
dimethylaniline	529.65	159.70	59.77	26.33
butyronitrile	113.13	46.31	21.92	11.72
valeronitrile	206.57	76.22	33.30	16.90

[a] Capillary column without immobilization.

Solubility parameters of the solutes were deduced from the experimentally determined enthalpies of vaporization. Solubility parameters of the polymers used as stationary phases were deduced from a plot based on the expression of Guillet et al.[24,33] The FORTRAN programs necessary to obtain the values of the different parameters were run on a personal computer.

Results and Discussion

The experimental determination of specific retention volumes must be carried out under conditions that minimize the effect of any adsorption phenomenon. The capillary columns prepared for this work have film thicknesses of the order of 0.3 μm, and the packed columns have SP percentages of the order of 18% w/w (MTFPS50) and 12% (PS-255). It has been shown that under these conditions adsorption contribution to retention is negligible.[34] Independent experiments carried out in our laboratories with these and other SP's using different film thicknesses confirm this. Plots of log V_g versus the inverse of the absolute temperature were drawn for each solute on all columns. Correlation coefficients were in all cases better than 0.99. Values of V_g obtained in equivalent SP's for the same substance and the same temperature on different columns (capillary and packed) were not significantly different. In view of the reproducibility of results, values used hereafter for the polymer MTFPS50 will correspond to the capillary nonimmobilized column. Table II presents values of V_g obtained with this column at four temperatures. No significant difference was found when values obtained on any of the other polar columns were used for the calculations involved in the deduction of the results. It may be concluded that both OV-215 and QF-1 have similar thermodynamic parameters, which are not affected by the degree of cross-linking of the polymer. The purpose of this work concerns MTFPS50, so in the case of PS-255, only the thermodynamic parameters used as reference for comparison of the interactions of the different chemical functions (see later) will be presented.

Solute–Polymer Interaction Parameters. Table III shows values of the Flory–Huggins interaction parameter, $\chi^{\infty}_{1,2}$, for the different temperatures studied. According to the values shown, dimethylaniline, ketones, benzene, toluene, pyridine, the ester, and the nitriles are good solvents of MTFPS50, while the rest of the substances, are nonsolvents. For hydrocarbons, alcohols, ethyl acetate, and aromatics the interaction parameter decreases with increasing temperature; butyronitrile, propylbenzene, and pentylbenzene show a group of little or no variation of $\chi^{\infty}_{1,2}$, whereas for dimethylaniline, ketones, and valeronitrile the interaction parameter increases as the temperature rises.

The shape of the plots just discussed indicates the relative position of the different solute–polymer systems in their solubility diagram. It is known[35,36] that these systems show both an upper critical solution temperature (UCST) and a lower critical solution temperature (LCST). The solute–polymer interaction parameter $\chi^{\infty}_{1,2}$ represents an excess free energy, with a parabolic dependence on temperature.[8] The plots just presented may be considered as part of the corresponding curves.

The dependence of $\chi^{\infty}_{1,2}$ on the number of carbon atoms of a homologous series is linear in all cases and all temperatures. Table IV shows the values of the different slopes of the equations obtained with data at 150 °C. The slope of the line represents in each case the contribution of the methylene group of the homologous series to the value of $\chi^{\infty}_{1,2}$. The fact that values are slightly different indicates that the function Y attached to the alkyl chain modifies the contribution of the methylene group differently. Thus, the loss of solubility due to the increase in the number of carbon atoms diminishes in the order *n*-alkanes > aromatics > ketones > alcohols.

Considerations on the Solute–Polymer Interaction Parameters. Values of χ from IGC are an average of all possible interactions encountered in the solute–polymer system, which, depending on the nature of its components, could be (a) systems where both are apolar, in which case

Table III
Solute–Polymer Interaction Parameters, $\chi^{\infty}_{1,2}$, at Different Temperatures

	temp, °C			
	90	120	150	180
n-hexane	1.11	0.93	0.81	0.61
n-heptane	1.34	1.18	1.07	0.95
n-octane	1.55	1.37	1.29	1.12
n-nonane	1.74	1.58	1.44	1.34
n-decane	1.92	1.77	1.64	1.49
n-undecane	2.10	1.94	1.82	1.67
n-dodecane	2.28	2.10	1.97	1.83
n-butyl alcohol	1.96	1.58	1.28	1.04
n-pentyl alcohol	1.99	1.67	1.38	1.25
n-octyl alcohol	2.27	1.90	1.67	1.49
acetone	0.02	0.03	0.05	0.10
2-butanone	0.17	0.25	0.34	0.44
2-pentanone	0.15	0.15	0.19	0.17
2-octanone	0.79	0.72	0.70	0.72
benzene	0.74	0.70	0.64	0.60
toluene	0.90	0.88	0.86	0.83
propylbenzene	1.25	1.20	1.17	1.20
pentylbenzene	1.55	1.53	1.46	1.51
pyridine	0.82	0.78	0.75	0.70
ethyl acetate	0.20	0.15	0.12	0.09
dimethylaniline	−0.82	−0.61	−0.44	−0.29
butyronitrile	0.50	0.50	0.50	0.50
valeronitrile	0.49	0.53	0.56	0.57

Table IV
Slopes and Correlation Coefficients of the Plots of the Solute–Polymer Interaction Parameters ($\chi^{\infty}_{1,2}$) versus Number of Carbon Atoms of the Alkyl Side Chain at 150 °C

family	slope	correl coeff
hydrocarbons	0.190	1.00
aromatics	0.162	1.00
ketones	0.119	0.92
alcohols	0.097	1.00

interactions would be due to dispersion forces and the lowest values of χ would correspond to the highest similarity between the two substances, or (b) systems where one or both components are polar or polarizable, in which case specific interactions would be produced and, generally speaking, the lowest values of χ should be expected. Both the value of the interaction parameter and a consideration of the chemical nature of the components of the system should indicate the type of interactions involved, although, ideally, this should be confirmed by spectroscopic evidence or other means.

It is known that halocarbons tend to form hydrogen bonds with electron donors, with the accepting capacity diminishing in the order of diminishing atomic diameter. The ability to act as electron donors decreases in the sense N > O > S. Spectroscopic evidence has shown that complexes between substances containing these atoms and those with halocarbons are due to hydrogen bonding and charge transfer. The polymer MTFPS50, with its CF_3 groups, is a potential electron acceptor and has a strong dipolar moment. Therefore, dimethylaniline, ketones, and esters show strong interactions while hydrocarbons have poor interactions with this polymer. Alcohols should interact fairly strongly, but their strong autoassociation competes with the association with MTFPS50, making them poor solvents of the polymer. Nitriles, with a strong dipolar moment, have a low value of χ, as expected. Aromatic hydrocarbons exhibit the dipole–induced dipole type of interaction as well as charge transfer; therefore values of χ are lower than 1, except when a hydrocarbon chain is attached to the aromatic ring, in which case solubility deteriorates.

Table V
Partial Molar Enthalpies and Free Energies of Mixing on MTFPS50 (kcal/mol)

		ΔG_m			
	ΔH_m	90 °C	120 °C	150 °C	180 °C
n-hexane	1.97	1.96	1.97	2.00	1.94
n-heptane	1.70	2.10	2.12	2.16	2.19
n-octane	1.83	2.22	2.24	2.31	2.30
n-nonane	1.88	2.34	2.37	2.41	2.45
n-decane	2.02	2.45	2.50	2.55	2.55
n-undecane	2.04	2.57	2.62	2.68	2.69
n-dodecane	2.14	2.69	2.74	2.80	2.82
n-butyl alcohol	3.86	2.40	2.26	2.14	2.04
n-pentyl alcohol	3.33	2.41	2.33	2.22	2.20
n-octyl alcohol	3.35	2.61	2.50	2.45	2.42
acetone	0.06	1.04	1.12	1.19	1.29
2-butanone	−0.57	1.14	1.26	1.40	1.56
2-pentanone	0.23	1.11	1.18	1.28	1.32
2-octanone	0.79	1.56	1.60	1.66	1.75
benzene	0.87	1.48	1.54	1.58	1.63
toluene	0.73	1.59	1.67	1.74	1.80
propylbenzene	0.71	1.84	1.92	2.01	2.12
pentylbenzene	0.79	2.07	2.18	2.25	2.40
pyridine	0.98	1.44	1.50	1.54	1.55
ethyl acetate	0.78	1.08	1.10	1.13	1.15
dimethylaniline	−1.35	0.27	0.42	0.55	0.67
butyronitrile	0.48	1.38	1.46	1.54	1.60
valeronitrile	0.20	1.36	1.47	1.57	1.64

Thermodynamic Parameters of Mixing. Table V shows the values of ΔH_m and ΔG_m found for MTFPS50. The values of Table V show the same tendency as do the values of the solute–polymer interaction parameters of Table III. Thus, those of the hydrocarbons and alcohols are high, indicating poor solubility, while the rest are lower, particularly those of dimethylaniline, the ketones, and the nitriles, indicating good solubility.

Thermodynamic Solution Parameters. Table VI lists values of ΔH_s, ΔG_s, and $T\Delta S_s$ at all temperatures. For homologous series, the partial molar enthalpy of solution becomes more negative as the chain length increases. Values now do not follow the tendency of Tables III and V. The partial molar enthalpies of solution ΔH_s refer to the mixing of a vapor (the solute) and a liquid and will differ by the partial molar enthalpy of vaporization ΔH_v from ΔH_m, referring to the mixing of two liquids. Thus, alcohols show partial molar enthalpies of mixing which are high (poor solubility of MTFPS50), but their strong intermolecular interactions produce high values of ΔH_v and therefore low values of ΔH_s. Figures 1–4 present the solution parameters of the four homologous series versus the number of carbon atoms at 150 °C. The plots are linear. The corresponding slopes are shown in Table VII. Similar representations are obtained at other temperatures. Accepting the additivity principle, the slope of the lines will represent the contribution of the methylene group to the corresponding thermodynamic parameter in the series. The value deduced from the plots of the hydrocarbons may be considered as the real contribution of the methylene group. For other homologous series, the chemical function Y will interact with the adjacent methylene groups, modifying them. The effect of this interaction may be deduced from the differences in the slopes.

Interactions of the Chemical Functions. An approximate estimation of the interaction of the chemical functions Y with MTFPS50 when used as a stationary phase in a chromatographic system may be obtained from

Table VI
Solution Parameters on MTFPS50 (kcal/mol)

		90 °C		120 °C		150 °C		180 °C	
	ΔH_s	ΔG_s	$T\Delta S_s$	ΔG_s	$T\Delta S_s$	ΔG_s	$T\Delta S_s$	ΔG_s	$T\Delta S_s$
n-hexane	-5.34	-0.23	-5.10	0.20	-5.54	0.66	-6.00	1.02	-6.35
n-heptane	-6.47	-0.75	-5.73	-0.27	-6.20	0.20	-6.67	0.67	-7.14
n-octane	-7.19	-1.25	-5.94	-0.76	-6.43	-0.23	-6.96	0.20	-7.39
n-nonane	-8.02	-1.75	-6.27	-1.21	-6.81	-0.70	-7.32	-0.19	-7.83
n-decane	-8.77	-2.23	-6.54	-1.65	-7.12	-1.10	-7.66	-0.61	-8.15
n-undecane	-9.67	-2.71	-6.97	-2.09	-7.58	-1.50	-8.17	-0.99	-8.68
n-dodecane	-10.53	-3.17	-7.36	-2.53	-8.00	-1.91	-8.62	-1.36	-9.17
n-butyl alcohol	-6.91	-1.06	-5.85	-0.55	-6.35	-0.08	-6.83	0.39	-7.30
n-pentyl alcohol	-7.66	-1.59	-6.06	-1.06	-6.60	-0.60	-7.06	-0.08	-7.58
n-octyl alcohol	-10.54	-3.15	-7.39	-2.50	-8.03	-1.88	-8.65	-1.33	-9.21
acetone	-7.35	-0.83	-6.52	-0.29	-7.06	0.25	-7.59	0.79	-8.13
2-butanone	-8.04	-1.32	-6.72	-0.77	-7.27	-0.22	-7.82	0.34	-8.38
2-pentanone	-8.15	-1.82	-6.33	-1.28	-6.87	-0.74	-7.41	-0.26	-7.88
2-octanone	-11.17	-3.35	-7.82	-2.71	-8.46	-2.06	-9.11	-1.42	-9.75
benzene	-6.73	-0.97	-5.76	-0.47	-6.26	-0.01	-6.72	0.46	-7.19
toluene	-7.74	-1.53	-6.21	-1.00	-6.74	-0.50	-7.25	0.01	-7.15
propylbenzene	-9.03	-2.41	-6.61	-1.87	-7.16	-1.33	-7.69	-0.78	-8.25
pentylbenzene	-10.69	-3.37	-7.32	-2.72	-9.40	-2.16	-8.53	-1.54	-9.15
pyridine	-7.79	-1.80	-5.99	-1.28	-6.51	-0.78	-7.01	-0.32	-7.47
ethyl acetate	-7.19	-1.27	-5.92	-0.77	-6.42	-0.28	-6.91	0.19	-7.38
dimethylaniline	-10.91	-3.44	-7.47	-2.79	-8.12	-2.18	-8.73	-1.60	-9.32
butyronitrile	-8.25	-1.92	-6.32	-1.39	-6.86	-0.86	-7.38	-0.36	-7.89

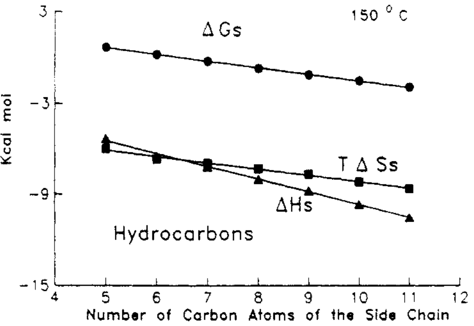

Figure 1. Dependence of the thermodynamic parameters of solution of the size of the *n*-alkane. The *x* axis represents the length of the chain attached to a methyl group.

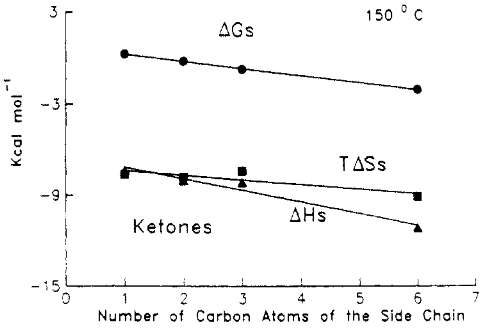

Figure 2. Dependence of the thermodynamic parameters of solution on the size of the alkane chain attached to an acetyl group.

a comparison of the values of the partial molar enthalpies of mixing and solution for a substance R–Y and for a hydrocarbon of the same number of carbon atoms. Results may be presented as the difference between the interaction of the radical Y with a reference apolar polymer and with MTFPS50, in a way similar to the presentation of Rohrschneider's constants[37] used to characterize stationary phases by their chromatographic behavior.

The notation used to refer to a particular solute–polymer pair will be $\Delta H_{\mathrm{m}}{}^{\mathrm{solute}}{}_{\mathrm{polymer}}$.

From

$$\Delta H_{\mathrm{m}}{}^{i}{}_{j} = {}^{1}/_{2}c_i(\epsilon_{ii} + \epsilon_{jj} - 2\epsilon_{ij}) \tag{1}$$

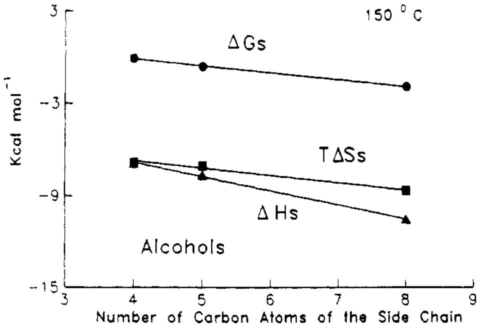

Figure 3. Dependence of the thermodynamic parameters of solution on the size of the alkane chain attached to a hydroxyl group.

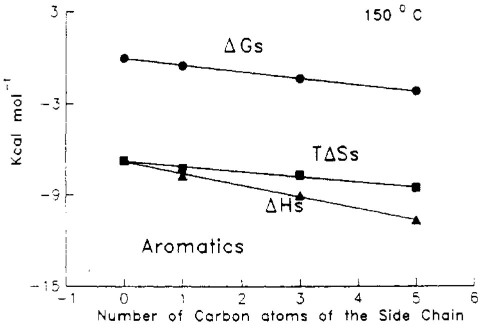

Figure 4. Dependence of the thermodynamic parameters of solution on the size of the alkane chain attached to a phenyl ring.

$$\Delta H_{\mathrm{s}}{}^{i}{}_{j} = {}^{1}/_{2}c_i(\epsilon_{jj} - 2\epsilon_{ij}) \tag{2}$$

where i refers to the solute, j refers to the polymer, c_i is a constant related to the size of the solute molecule, and ϵ_{ii}, ϵ_{jj}, and ϵ_{ij} are segmental attractive interaction energies,[38] we obtain for two solutes (1 = hydrocarbon, 2 = R–Y) and two polymers (3 = PS-255, 4 = MTFPS50)

$$\Delta H_{\mathrm{m}}{}^{1}{}_{3} - \Delta H_{\mathrm{m}}{}^{1}{}_{4} = {}^{1}/_{2}c_1(\epsilon_{33} + \epsilon_{44} - 2(\epsilon_{13} - \epsilon_{14})) \tag{3}$$

$$\Delta H_{\mathrm{m}}{}^{2}{}_{3} - \Delta H_{\mathrm{m}}{}^{2}{}_{4} = {}^{1}/_{2}c_2(\epsilon_{33} + \epsilon_{44} - 2(\epsilon_{23} - \epsilon_{24})) \tag{4}$$

making $\Delta\Delta H_{\mathrm{m}}{}^{12}{}_{j} = \Delta H_{\mathrm{m}}{}^{1}{}_{j} - \Delta H_{\mathrm{m}}{}^{2}{}_{j}$. Assuming that c_1 and

Table VII
Slopes of the Plots of the Thermodynamic Parameters of Solution versus Carbon Number of the Alkyl Side Chain at 150 °C

	ΔH_s	ΔG_s	$T\Delta S_s$
hydrocarbons	−0.841	−0.428	−0.414
aromatics	−0.770	−0.426	−0.342
ketones	−0.769	−0.390	−0.309
alcohols	−0.920	−0.445	−0.472

Table VIII
Enthalpies of Solution and Mixing on PS-255 at 150 °C (kcal/mol)

substance	ΔH_s	ΔH_m
n-pentane	−5.30	1.07
n-hexane	−6.16	1.15
n-heptane	−7.10	1.08
n-octane	−8.17	0.83
n-nonane	−9.13	0.77
n-decane	−10.07	0.72
n-undecane	−11.02	0.69
n-dodecane	−11.96	0.70
n-butyl alcohol	−6.54	4.23
n-pentyl alcohol	−7.79	3.20
n-octyl alcohol	−10.34	3.56
acetone	−5.85	1.55
2-butanone	−6.43	1.05
2-pentanone	−7.02	1.36
2-octanone	−10.28	1.68
benzene	−6.42	1.18
toluene	−7.31	1.16
propylbenzene	−9.44	0.30
pentylbenzene	−11.28	0.25

Table IX
Interactions of the Acetyl, Hydroxyl, Phenyl, and Methyl Groups with MTFPS50, Taking PS-255 as an Apolar Reference (kcal/mol)

	thermodynamic magnitude used	
chemical function	ΔH_s	ΔH_m
acetyl	−1.81 ± 0.17	−1.97 ± 0.27
hydroxyl	−0.75 ± 0.23	−0.93 ± 0.16
phenyl	0.01 ± 0.13	−0.19 ± 0.22
methyl	0.13 ± 0.27	0.11 ± 0.21

c_2 are not very different for two substances which have a similar structure,[38-40] we arrive at

$$\Delta\Delta H_m{}^{12}{}_3 - \Delta\Delta H_m{}^{12}{}_4 = c_1(\epsilon_{23} - \epsilon_{24}) - c_1(\epsilon_{13} - \epsilon_{14}) \quad (5)$$

The second term of expression 5 is related to the difference in the interactions with the polar and apolar polymers, between the substance R–Y and the corresponding hydrocarbon, i.e., to the difference of the interaction of the chemical function Y with the two polymers. Similar results should be expected if in eqs 1–5 $\Delta H_s{}^i{}_j$ is used instead of $\Delta H_m{}^i{}_j$. The necessary enthalpies of solution and mixing, on PS-255, obtained from experimental values of V_g and the value of the activity coefficient $\Omega^\infty{}_1$ are presented in Table VIII. Values corresponding to the first member of eq 5 (using either magnitude) are presented in Table IX.

Enthalpies of solution are somewhat more reliable because the plots used to obtain them have better correlation coefficients than those used to obtain enthalpies of mixing. The value obtained for the phenyl group should be considered with caution because only two substances were used, and the values of V_g of the corresponding hydrocarbons (propane and pentane) have been deduced by extrapolation, which might not be reliable for the lighter *n*-alkane.

Table X
Solubility Parameters of MTFPS50 (cal cm^{-3})$^{1/2}$

polymer	90 °C	120 °C	150 °C	180 °C
OV-215 (as such)	7.84	7.72	7.58	7.37
OV-215 (cross-linked)	7.89	7.74	7.54	7.37
QF-1 (packed column)	7.91	7.71	7.56	7.40

An examination of Table IX indicates that the interaction of the function Y with MTFPS50 is much stronger than that with an apolar polymer in the case of the acetyl group. The tendency is similar in the case of the primary alcohols, although now differences are smaller, and little or no difference can be observed with hydrocarbons.

Solubility Parameters of MTFPS50. Table X shows that the solubility parameters of all the stationary phases are very similar, with small differences probably due to the different number and type of solutes being used in the appropriate representation.[24,33] Plots against temperature are linear with correlation coefficients better than 0.98. The value of δ_2, expressed in (cal cm^{-3})$^{1/2}$, decreases from about 7.9 to 90 °C to about 7.4 at 180 °C. Assuming that linearity extends to lower temperatures, the value of δ_2 at 25 °C becomes 8.20 (cal cm^{-3})$^{1/2}$ for MTFPS50 (8.25 if all data are included). The similarity of both values suggests that the degree of cross-linking of the capillary column does not modify the value of the solubility parameter, which is equal to that obtained with a packed column of QF-1.

Conclusions

Results presented in this paper show that IGC is appropriate for the thermodynamic characterization of polymers usable as stationary phases in chromatographic systems and confirm that there is no significant difference in the results if a packed or a capillary column is used for the purpose, provided that the tube walls are previously cleaned and deactivated. Under the conditions used here, with a sufficient film thickness, no adsorption phenomena are present.

MTFPS50 has been characterized between 90 and 180 °C by the Flory–Huggins interaction parameter and the thermodynamic functions of mixing and solution. It was found that the compounds that act as the best solvents of the polymer are electron donors such as nitriles, tertiary amines, and ketones. Aromatic hydrocarbons act as moderate solvents, while alcohols and *n*-alkanes are nonsolvents of MTFPS50. Using an apolar polymer as reference (PS-255), the interactions between the trifluoropropyl group and a series of chemical functions has been evaluated and found to decrease in the order acetyl > hydroxyl > methyl. Neither the solubility parameter of MTFPS50 nor the thermodynamic functions evaluated seem to depend on the degree of cross-linking of the polymer used in the capillary columns, the former decreasing linearly with increasing temperature.

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Registry No. $H(CH_2)_6H$, 110-54-3; $H(CH_2)_7H$, 142-82-5; $H(CH_2)_8H$, 111-65-9; $H(CH_2)_9H$, 111-84-2; $H(CH_2)_{10}H$, 124-18-5; $H(CH_2)_{11}H$, 1120-21-4; $H(CH_2)_{12}H$, 112-40-3; BuOH, 71-36-3; $H(CH_2)_5OH$, 71-41-0; $H(CH_2)_8OH$, 111-87-5; H_3CCOCH_3, 67-64-1; $H_3CCO(CH_2)_2H$, 78-93-3; $H_3CCO(CH_2)_3H$, 107-87-9; $H_3CCO(CH_2)_6H$, 111-13-7; PhH, 71-43-2; MePh, 108-88-3; PrPh, 103-65-1; $H(CH_2)_5Ph$, 538-68-1; pyridine, 110-86-1; ethyl acetate, 141-78-6; dimethylaniline, 121-69-7; butyronitrile, 109-74-0; valeronitrile, 110-59-8.