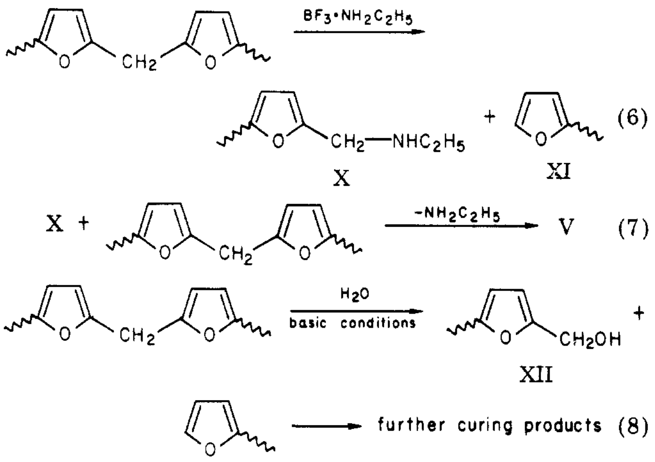
severe conditions employed in curing and neutralization, the most likely possible routes for cross-linking are assumed to be as follows:



These two schemes are supported by the increase in intensity of the peak around 142 ppm, corresponding to the 5-position of terminal furan rings, with increasing cure time.

The ^{13}C NMR spectra show that if amine species (X) or alcohols (XII) are formed during curing, they do not accumulate. If they are formed, they must be consumed by condensing with methylene bridges to form the species V, perhaps a very few of them condensing with the 3- and 4-positions of the furan ring. Another possible way for consuming the alcohol (XII) is elimination of formaldehyde.[14] The fate of the evolving formaldehyde would be either to condense with two methylene bridges to form species IV, as shown in eq 3, or to form paraformaldehyde. The peak around 90 ppm indicates that there is some accumulated paraformaldehyde, which decreases somewhat for longer curing time.

In summary, ^{13}C CP/MAS NMR studies of furfuryl alcohol resins provide no evidence for the existence of appreciable concentrations of formaldehyde, methylol groups, or dimethylene ether linkages in the very early stages of the curing process. The ^{13}C results indicate that the cross-linking process is brought about by cleavage of methylene linkages by the curing agent, $BF_3\cdot NH_2CH_2CH_3$, or by OH^-. Experiments designed to distinguish between these kinds of possibilities are in progress. The ^{13}C CP/MAS NMR studies point to an interesting feature of fixed polymer conformations in these solid resins.

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Registry No. Poly(furfuryl alcohol) (homopolymer), 25212-86-6.

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Comparison of Static with Gas-Chromatographic Solute Infinite-Dilution Activity Coefficients with Poly(dimethylsiloxane) Solvent

A. J. Ashworth,*[†] C.-F. Chien,[‡] D. L. Furio,[‡] D. M. Hooker,[†] M. M. Kopečni,[‡] R. J. Laub,*[‡] and G. J. Price[†]

School of Chemistry, University of Bath, Claverton Down, Bath, England BA2 7AY, and the Department of Chemistry, San Diego State University, San Diego, California 92182. *Received July 20, 1983*

ABSTRACT: Replicate gas–liquid chromatographic based specific retention volumes, activity coefficients, and interaction parameters of ten solutes with poly(dimethylsiloxane) (PDMS) solvent at 303 K are reported. The average relative standard deviation of the former (three GLC columns) is 0.82%. The values moreover compare favorably with those reported previously for four PDMS used commonly as stationary liquids in analytical GLC. Static-determined activity coefficients and interaction parameters are also reported and compared with the GLC results. The internal consistency of the former lies within ±1.2%, while the averages of these agree with the GLC values to within ±0.5%, thus providing validation of the latter. Previously reported discrepancies between static and GLC-based activity coefficients and interaction parameters with PDMS solvents are therefore attributed to experimental artifact rather than fundamental principle.

The potential advantages of gas–liquid chromatography for measurement of physicochemical properties were recognized within 2 years of the inception of the technique.[1,2] There is moreover little question today that, for example, activity and partition coefficient data derived from the GLC method do in fact agree to well within the experimental errors arising with more traditional (static) apparatus of various designs.[3,4]

Application of the GLC technique to polymer solvents

[†] University of Bath.
[‡] San Diego State University.

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Table I
Properties[a] of the Pure Solutes at 303 K

solute	M	T^c/K	V^c/(cm^3 mol^{-1})	n[b]	$\bar{V}_1{}^0$/(cm^3 mol^{-1})	$p_1{}^0$/torr	$-B_{11}$/(cm^3 mol^{-1})
n-pentane	72.146	196.6	311.02	5	117.00	612.39	1147
n-hexane	86.172	234.7	368.04	6	132.51	186.24	1810
n-heptane	100.198	267.0	426.04	7	148.37	58.071	2721
n-octane	114.224	296.2	486.02	8	164.49	18.341	3970
cyclohexane	84.156	281.0	309.63	4.5	109.39	121.15	1702
methylcyclohexane	98.182	299.1	344.62	5	129.06	58.372	2185
benzene	78.108	289.5	260.33	4.5	89.936	118.75	1492
toluene	92.134	320.8	319.98	5	107.423	35.344	2263
dichloromethane	84.940	252.0	150.74	3.5	64.978	527.74	649
chloroform	119.389	271.0	239.00	4	80.855	237.71	1187

[a] Reference 12. [b] References 10 and 11.

represents a quite natural extension of studies of these kinds, as illustrated by the extensive exploitation of the method by Guillet and co-workers.[5] However, there might arise some question regarding GLC-based activity coefficients with solvents of high molecular weight. Summers, Tewari, and Schreiber[6] therefore undertook a comparison of their dynamic-measured activity coefficients and interaction parameters with those reported by Chahal, Kao, and Patterson[7] and found the agreement to be excellent. In contrast, Lichtenthaler, Newman, and Prausnitz,[8a] followed by Lichtenthaler, Prausnitz, Su, Schreiber, and Patterson,[8b] reported notable discrepancies both between static and GLC-based activity coefficients and between (presumed fully corrected) retention volumes determined in intra- and interlaboratory comparisons with independently fabricated as well as identical columns, each containing poly(dimethylsiloxane) (PDMS) solvent. The bulk of GLC data pertaining to polymer solvents was thereby called, in general, into question. Moreover, the implication to be derived is that retentions (hence, separations) are somehow subjectively dependent upon the operator and instrumentation employed. Therefore, and as a result of the serious consequences of the reports by Lichtenthaler et al., we have undertaken in this work an independent reevaluation and comparison of static and GLC-based activity coefficients, interaction parameters, and retentions with PDMS. In addition, the results are used to establish a level of accuracy for the retentions reported by Laub and co-workers[9] for very many solutes with several PDMS utilized commonly in analytical gas–liquid chromatography.

Experimental Section

Solutes and Stationary Phase. The ten solutes *n*-pentane through *n*-octane, cyclohexane and methylcyclohexane, benzene and toluene, and dichloromethane and chloroform, purchased either from Chem Service or from PolyScience Corp., were used in the gas-chromatographic work as received. Those employed in the static studies were high-purity samples from the National Physical Laboratory, England, and were used throughout under vacuum. The properties of the solutes at 303 K, including the second-interaction virial coefficients calculated from the McGlashan–Potter equation,[10,11] are provided in Table I.

PDMS with end groups reacted fully with trimethylsilyl chloride was supplied by Dow Corning Ltd., to one of us for further processing. Fractional precipitation[13] of solutions of 5% w/v in ethyl acetate (methanol precipitant) was utilized to remove low molecular weight material, following which the polymer was recovered and freed from volatile solvent in the usual way. It had an intrinsic viscosity in toluene of 37 cm^3 g^{-1} at 298 K, giving a number-average molecular weight[14] of 89 000. A portion of the PDMS was then forwarded for utilization as a gas-chromatographic stationary phase. The density of the PDMS at 303 K was calculated from the relation of Flory and Shih[13] as 0.9654 g cm^{-3}.

Static Apparatus and Procedures. The Sartorius vacuum microbalance and associated data treatments employed here were as described previously,[15] except that the solute activity coefficients were calculated on a volume- rather than mole-fraction basis in order to avoid uncertainties surrounding the polymer molecular weight. Volume fractions were calculated from the weights of PDMS and absorbed solute by using the known liquid densities. The solvent was as usual dispersed on diatomaceous earth (Celite 545, AW, of 100–120 mesh size) but, in order to ensure that the nominal weight percent coating of PDMS corresponded to that actually present, a second set of measurements ("run A") was carried out. In these, approximately 0.3 g of PDMS was added to a preweighed (ca. 1.5 g) amount of support material already present in the balance pan, and the mixture was slurried with ethyl acetate. The volatile solvent was then left to evaporate until a constant weight was obtained, following which the coated support was heated at 373 K, again to constant weight. The possibility of loss of PDMS upon transfer from a preparation flask to the balance pan was thereby eliminated.

Gas-Chromatographic Apparatus and Procedures. The high-precision GLC apparatus was essentially identical with that which has been described and discussed elsewhere.[4] The carrier throughout was helium at no more than 6 psi above atmospheric pressure (corresponding to ca. 10–50 cm^3 min^{-1} volume flow rate), so that solute–carrier virial corrections were negligible. Three separate columns and packings were used over the temperature range 303–353 K in increments of 10 K with at least three repetitive injections of solutes at each, either neat or in admixture as permitted by the resolution of the system. The amount of column stationary liquid (ca. 4–8% by weight) was determined by washing tared portions of packings held in gooch crucibles with boiling toluene, followed by drying the extracted support (60/80-mesh Chromosorb G; acid washed and treated with dimethylchlorosilane) under vacuum at 385 K for at least 12 h. The procedure required at least two repetitions in order to reach a constant weight for each batch of support.

Solute specific retention volumes were calculated as usual from fully corrected net retention volumes and the column weight of PDMS:

$$V_g{}^0 = 273 V_N / T m_S \tag{1}$$

Mole-, weight-, and volume-fraction-based fugacity-corrected activity coefficients at 303 K were then derived from temperature-smoothed $V_g{}^0$ (ln $V_g{}^0$ against T^{-1}; $r > 0.9995$ in all instances) and the relations[5d,16]

$$\ln {}^x\gamma_1{}^\infty = \ln \frac{273R}{V_g{}^0 P_1{}^0 M_S} - \frac{P_1{}^0(B_{11} - \bar{V}_1{}^0)}{RT} \tag{2}$$

$${}^w\gamma_1{}^\infty = ({}^x\gamma_1{}^\infty) M_S / M_1 \tag{3}$$

$${}^v\gamma_1{}^\infty = ({}^w\gamma_1{}^\infty) \rho_1 / \rho_S \tag{4}$$

where the superscripts x, w, and v represent the respective concentration units for the activity coefficient of solute (species 1) with solvent (species S), and where M_i and ρ_i are molecular weights and densities. Flory-type interaction parameters $\chi_{1(S)}$ were calculated subsequently from the relation[17]

$$\ln {}^{x}\gamma_1^{\infty} = \ln (\bar{V}_1^0/\bar{V}_S) + (1 - \bar{V}_1^0/\bar{V}_S) + \chi_{1(S)} \qquad (5)$$

Results and Discussion

Specific Retention Volumes. The individual and averaged specific retention volumes at 303 K for all solutes are reported in Table II. We provide also the coefficients A and B of the equation (303–353 K)

$$\log V_g^0 = A + B/T \qquad (6)$$

in order to permit comparisons at other temperatures. The precision obtained with PDMS phase is encouraging: the relative deviations amount in nearly all cases to ca. ±1%, which is at the level quoted in previous studies for hydrocarbon phases.[4b] The major source of experimental error remains the determination of m_S, about which Laub and Pecsok (ref 1, pp 34–37) have commented at length. Our experience confirms that the mass of stationary phase can be determined accurately only by reiterative and exhaustive extraction with boiling solvent while the packing is being stirred. In contrast, the process of Soxhlet extraction provides insufficient agitation as well as solution of PDMS and hence yields low m_S with resultant high V_g^0 and low ${}^{x}\gamma_1^{\infty}$. Furthermore, and in contrast, for example, to polyethylene stationary phases which are freely soluble in common solvents,[18] these difficulties are magnified considerably with PDMS of high viscosity with concomitant poor solubility. This accounts at least in part for the observed good agreement between columns 5, 9, and 10 of Table II, namely, the results obtained with PDMS of relatively low viscosity, as opposed to those of column 5 in comparison with those in columns 11 and 12 (the latter two PDMS comprising high molecular weight gums[19]).

We note in passing that there is the additional danger of loss of packing during Soxhlet extraction, as well as the presence of extractable material in thimbles and support materials.[20] Failure to correct for these errors would, of course, lead to erroneously high values of m_S with resultant low V_g^0.

Activity Coefficients and Interaction Parameters. Presented in Table III are the static results reported as absorption isotherms at 303.04 ± 0.01 K. These comprise the volume fractions ϕ_1 of solutes of equilibrium pressure p_1 absorbed by the PDMS. The resultant volume-fraction-based activity coefficients are then given as ${}^{v}\gamma_1$. In order to assess the accuracy of the data of Table II, we compare in Table IV the fugacity-corrrected mole- and weight-fraction-based activity coefficients and interaction parameters derived from the GLC measurements (eq 2, 3, and 5) with those arising from extrapolation to infinite dilution of the two sets of static determinations. The internal agreement of the static experiments is on average ±0.7%, while agreement between the means of these with the GLC-based data is, if anything, a factor of 2 superior. We can only regard these results as confirmation of the accuracy of the GLC technique with PDMS phases in general and, within the stated limits, of the data reported previously in ref 9.

Finally, we note that, based upon the findings of the present work, the results reported by Summers, Tewari, and Schreiber[6] are clearly low by as much as 10%. Although we can only speculate about the matter, we note that errors of this magnitude are due generally to soluble organic or inorganic matter extracted from the support (the latter arising frequently from residual moisture). Moreover, although the data of ref 8b self-evidently are somewhat imprecise, those of columns D and E fall closest to the results of this work.

Table II
Specific Retention Volumes $V_g^0/(\mathrm{cm^3\ g^{-1}})$ with PDMS Solvent at 303 K

	$V_g^0/(\mathrm{cm^3\ g^{-1}})$					eq 6		$V_g^0/(\mathrm{cm^3\ g^{-1}})$			
								ref 9b		ref 9a	
solute	column A	column B	column C	ave	% std dev	$-A$	B	OV-101	SP-2100	OV-1	SE-30
n-pentane	67.05	64.90	66.37	66.11 ± 1.10	1.66	2.60860	1342.12	66.87	67.23	70.00	69.25
n-hexane	181.6	177.9	180.2	179.9 ± 1.8	1.04	2.93901	1573.98	181.1	181.5	184.8	183.4
n-heptane	484.4	480.1	483.1	482.5 ± 2.2	0.46	3.27521	1805.72	490.2	490.0	489.0	486.0
n-octane	1305	1286	1280	1290 ± 13.	1.02	3.63227	2043.33	1327	1323	1296	1290
cyclohexane	316.4	313.8	315.2	315.1 ± 1.3	0.41	2.86707	1625.98	315.2	318.5	328.9	325.2
methylcyclohexane	575.0	566.2	567.7	569.6 ± 4.7	0.83	3.06060	1762.49	564.1			
benzene	291.2	289.7	290.4	290.4 ± 0.7	0.26	2.89128	1622.51	289.6	292.9	304.9	298.5
toluene	797.5	785.0	790.5	791.0 ± 6.2	0.79	3.22531	1855.68	812.4			
dichloromethane	78.89	78.03	79.23	78.72 ± 0.62	0.79	2.66547	1382.32				
chloroform	183.0	179.8	182.2	181.7 ± 1.6	0.92	2.88261	1558.12				

Table III
Static Absorption Results with PDMS Solvent at 303 K

solute	run A ϕ_1	run A p_1/torr	run A ${}^{v}\gamma_1$	run B ϕ_1	run B p_1/torr	run B ${}^{v}\gamma_1$
n-pentane	0.00891	20.07	1.3428	0.01345	29.84	1.3264
	0.02390	52.53	1.3160	0.02741	59.74	1.3069
	0.04164	88.90	1.2843	0.04195	89.36	1.2820
	0.05704	118.95	1.2589	0.05715	118.77	1.2555
	0.07289	148.18	1.2315	0.07322	148.49	1.2291
	0.09072	179.65	1.2031	0.08988	177.78	1.2021
	0.10757	207.66	1.1758	0.10792	207.66	1.1725
	0.12631	236.94	1.1451	0.12704	237.44	1.1414
n-hexane	0.01420	10.22	1.3696	0.01374	9.92	1.3729
	0.02924	20.47	1.3414	0.02820	19.86	1.3473
	0.04396	29.89	1.3113	0.04347	29.74	1.3174
	0.05974	39.66	1.2863	0.05958	39.65	1.2887
	0.07718	49.70	1.2548	0.07696	49.68	1.2572
	0.09517	59.36	1.2219	0.09500	59.43	1.2248
	0.11509	69.40	1.1871	0.11473	69.42	1.1906
	0.13580	79.12	1.1517	0.13590	79.32	1.1535
n-heptane	0.01759	4.19	1.4192	0.01297	3.11	1.4261
	0.02924	6.81	1.3966	0.02587	6.01	1.3940
	0.04371	9.87	1.3653	0.03934	8.91	1.3684
	0.05572	12.31	1.3430	0.05392	11.90	1.3420
	0.07102	15.20	1.3109	0.06919	14.80	1.3103
	0.08769	18.12	1.2751	0.08637	17.89	1.2777
	0.10408	20.95	1.2487	0.10323	20.74	1.2468
	0.12769	24.59	1.2038	0.12214	23.67	1.2103
cyclohexane	0.01166	5.86	1.4338	0.01219	6.09	1.4272
	0.02533	12.44	1.4100	0.02460	11.96	1.4000
	0.03752	17.96	1.3839	0.03797	18.02	1.3752
	0.05136	24.04	1.3608	0.05185	24.04	1.3513
	0.06551	29.87	1.3341	0.06630	29.95	1.3248
	0.08027	35.62	1.3064	0.08133	35.75	1.2969
	0.09931	42.60	1.2718	0.09722	41.59	1.2693
	0.11533	48.07	1.2426	0.11497	47.62	1.2363
benzene	0.01443	9.48	1.7195	0.00948	6.23	1.7198
	0.02636	16.76	1.6860	0.01841	11.86	1.6999
	0.03978	24.52	1.6547	0.02860	17.90	1.6705
	0.05513	32.77	1.6176	0.03881	23.75	1.6474
	0.07013	40.13	1.5790	0.04991	29.67	1.6179
	0.08281	45.94	1.5475	0.06171	35.64	1.5886
	0.09850	52.57	1.5082	0.07423	41.61	1.5582
	0.11410	58.45	1.4667	0.08738	47.40	1.5249

Table IV
Comparison of Static with Gas-Chromatographic Solute Mole- and Weight-Fraction-Based Activity Coefficients and Interaction Parameters at Infinite Dilution with Poly(dimethylsiloxane) Solvent at 303 K

	static					GLC		
	${}^{w}\gamma_1^{\infty}$							
solute	run A	run B	ave	$10^3({}^{x}\gamma_1^{\infty})$	$\chi_{1(S)}$	${}^{w}\gamma_1^{\infty}$	$10^3({}^{x}\gamma_1^{\infty})$	$\chi_{1(S)}$
n-pentane	6.082	6.049	6.066	4.918	0.356	6.092	4.938	0.360
n-hexane	5.991	6.014	6.003	5.812	0.398	6.023	5.832	0.402
n-heptane	6.128	6.090	6.109	6.878	0.454	6.135	6.907	0.458
n-octane						6.342	8.139	0.520
cyclohexane	5.386	5.339	5.363	5.071	0.454	5.378	5.085	0.456
methylcyclohexane						4.712	4.937	0.262
benzene	6.448	6.370	6.409	5.625	0.753	6.404	5.620	0.752
toluene						6.457	6.684	0.748
dichloromethane						4.937	4.712	0.901
chloroform						3.366	4.515	0.640

We conclude that, in the absence (as here) of support or interfacial effects, the GLC method is in fact capable of sufficient precision and accuracy to be of value in the measurement of thermodynamic properties of polymer solutions and that, given the particular ease and simplicity of the technique, it offers considerable advantages as well. In addition, we offer the specific retention volumes of Table II as standards, complementary to those of ref 3, 4, and 9, with which to calibrate GLC instrumentation and techniques with PDMS solvents.

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Registry No. *n*-Pentane, 109-66-0; *n*-hexane, 110-54-3; *n*-heptane, 142-82-5; *n*-octane, 111-65-9; cyclohexane, 110-82-7;

methylcyclohexane, 108-87-2; benzene, 71-43-2; toluene, 108-88-3; dichloromethane, 75-09-2; chloroform, 67-66-3.

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Fate of the Initiator in the Azobis(isobutyronitrile)-Initiated Polymerization of Styrene

Graeme Moad,* David H. Solomon, Stanley R. Johns, and Richard I. Willing

CSIRO, Division of Applied Organic Chemistry, Melbourne, Australia 3001.

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ABSTRACT: The initiator-derived residues in polystyrene prepared by using azobis(isobutyronitrile-α-^{13}C) as the initiator have been identified and quantified by ^{13}C NMR. For low-conversion polymers the only initiator fragments present are those incorporated during the initiation step (i.e., by tail addition to monomer). Contrary to some recent reports, primary radical termination and transfer to initiator were found to be of little importance in AIBN-initiated styrene polymerization. These processes account for less than 2% of end groups in low-conversion (8%) polymers prepared in bulk with initiator concentrations in the range 0.01–0.2 M. In high-conversion (85%) polymers prepared with a high (0.2 M) initiator concentration the copolymerization of methacrylonitrile formed from the initiator can be detected.

Introduction

There is evidence to show that the stabilities of polystyrenes prepared by free radical processes are dependent on the methods used in their preparation and, in particular, the types of initiator used.[1] However, the differences in the polymer structure which might account for the observed variation in properties are unclear.

As a first step toward solving this problem we have investigated the selectivity of the initiation process by examining the interaction of alkoxy, benzoyloxy, and phenyl radicals with styrene by using a radical scavenging technique.[2] The method is, however, not as suitable for looking at the reactions of alkyl radicals (e.g., cyanoisopropyl) and does not give information on the other ways by which initiator fragments can be incorporated into the polymer structure (i.e., primary radical termination and transfer to initiator). To obtain this information we required a method which enables the initiator-derived functionality in the polymer to be determined directly.

A variety of methods (e.g., radiochemical labeling[3-6] and ^{1}H NMR[7]) have been used for determining the initiator residues incorporated into vinyl polymers during their preparation. These methods, however, only give information as regards the number of such groups. They are, in general, not sufficiently sensitive to the environment of the initiator-derived functionality for one to be able to say, with any degree of certainty, how it was incorporated into the polymer.

Recently, we demonstrated a ^{13}C NMR technique by which the nature of the benzoyloxy groups in polystyrene prepared with benzoyl-*carbonyl*-^{13}C peroxide as the initiator could be evaluated.[8] Thus, the benzoate end groups

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