Notes

Specific Retention Volumes from Gas-Liquid Chromatography for Poly(dimethylsiloxane)-Hydrocarbon Systems

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Gas-liquid chromatography shows much promise as a technique for rapid measurement of polymer-solvent interactions in highly concentrated polymer solutions. Several recent articles have discussed application of the method.[1-3] As part of a more extensive study of polymer-solvent interactions we have obtained new results for several poly(dimethylsiloxane)-hydrocarbon systems. In this note we compare our results with those reported by Summers *et al.*[4] Our purpose here is to call attention to a systematic discrepancy between the two sets of results, which apparently cannot be explained by experimental errors. The results illustrate some unsolved problems and difficulties in this particular technique for measuring activity coefficients in polymer solutions.

Table I
Chromatographic Columns

Column No. and Polymer Source	Wt of PDMS (g)	Support (g)	Coverage Ratio	Support	Solvent	Length (*m*)	I.d. (cm)
1, Cellomer Corp.	1.7998	12.9948	0.139	Chrom P	*n*-Hexane	1.5	0.635
2, Cellomer Corp.	1.9810	12.7800	0.155	Chrom P	*n*-Hexane	1.5	0.635
3, Cellomer Corp.	3.1810	12.6853	0.251	Chrom P	Toluene	1.5	0.635
4, Cellomer Corp.	1.0096	8.0130	0.126	Chrom W	*n*-Hexane	1.5	0.635
5, Summers	0.8761	8.4557	0.104	Chrom W	Toluene	1.5	0.635

Table II
Specific Retention Volumes for Poly(dimethylsiloxane)-Hydrocarbon Systems at 25°

	$V_g°$ (cm^3/g)				
	Column				
	1	5	Av	Summers	Dev (%)
n-Pentane	81.01	80.31	80.66	74.76	7.7
n-Hexane	230.4	225.0	227.7	211.1	7.8
Benzene	380.0	370.2	375.1	340.4	10.2
Toluene		1032	1032	959.6	7.5

Experimental Section

The apparatus used has been described previously.[5] The carrier gas was helium. Measurements were made at 25, 40, and 55°. Special care was exercised to control and determine the system temperature accurately.

Column Preparation. Poly(dimethylsiloxane) was coated onto Chromosorb P, AW-DMCS, or Chromosorb W, AW-DMCS, from solution in *n*-hexane or toluene. Details of column preparation are shown in Table I.

Materials. In columns 1-4 we used poly(dimethylsiloxane) obtained from Cellomer Corp., Webster, N. Y. As reported by Cellomer, average molecular weight, $\bar{M}_w$, for this polymer is 609,000 by light scattering and $\bar{M}_n$ is 150,000 by gpc. In column 5 we used the same poly(dimethylsiloxane) as that used by Summers *et al.* ($\bar{M}_v$ = 500,000). Before use the polymer was dried to constant weight in a vacuum oven at 90°. Reagent grade hydrocarbons were obtained from standard laboratory supply sources.

Data Reduction. The specific retention volume, corrected to 0°, is given by

$$V_g° = Q(t_r - t_g)\frac{273.15}{T}\frac{f_p}{W_2} \qquad (1)$$

where Q = volumetric carrier gas flow rate at column outlet temperature and pressure, cm^3/min; $t_r - t_g$ = retention time, *i.e.*, the time difference between air and solvent peaks, min; T = column temperature, °K; W_2 = weight of polymer in the column, g; f_p = pressure correction term[6]

$$f_p = \frac{3}{2}\frac{\left[\left(\frac{P_i}{P_o}\right)^2 - 1\right]}{\left[\left(\frac{P_i}{P_o}\right)^3 - 1\right]} \qquad (2)$$

where P_i = inlet pressure and P_o = outlet pressure.

Results and Discussion

Tables II-IV show experimental specific retention volumes at 25, 40, and 55°. The carrier gas flow rate varied from 18 to 120 cm^3 per min and at least ten runs were made with each of the columns. No effect of flow rate was detected. The overall variation of $V_g°$ for any particular column was at most ±1.25%, the same as that in $V_g°$ for all five columns.

In all cases we find a discrepancy of the order of 10% between our retention volumes and those of Summers *et al.*[4] Summers' results are consistently lower than ours. This cannot be explained by dissimilarity of the poly(dimethylsiloxane) received from different manufacturers, as we have used in column 5 the same polymer used by Summers *et al.* It does not appear to be reasonable to ascribe this discrepancy to experimental conditions since we found excellent agreement for polyethylene-hydrocarbon systems[7] between our work and that of Schreiber whose apparatus, support and procedure are the same as those of Summers.[4]

The reliability and accuracy of the chromatographic

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(1) O. Smidsrød and J. E. Guillet, *Macromolecules*, **2**, 272 (1969).

(2) D. Patterson, Y. B. Tewari, H. P. Schreiber, and J. E. Guillet, *Macromolecules*, **4**, 356 (1971).

(3) Y. B. Tewari and H. P. Schreiber, *Macromolecules*, **5**, 329 (1972).

(4) W. R. Summers, Y. B. Tewari, and H. P. Schreiber, *Macromolecules*, **5**, 12 (1972).

(5) R. D. Newman and J. M. Prausnitz, *J. Phys. Chem.*, **76**, 1492 (1972).

(6) J. H. Purnell, "Gas Chromatography," Wiley, New York, N. Y., 1962.

(7) H. P. Schreiber, Y. B. Tewari, and D. Patterson, *J. Polym. Sci., Part A-2*, in press.

Table III
Specific Retention Volumes for Poly(dimethylsiloxane)-Hydrocarbon Systems at 40°

	V_g° (cm³/mole)							
	Column							
	1	2	3	4	5	Av	Summers	Dev (%)
n-Pentane	48.20	48.60	47.10	47.30	46.79	47.60	43.65	9.0
n-Hexane	124.2	126.8	123.0	124.5	122.5	124.2	114.8	8.2
Benzene	201.3	203.3	196.2	199.0	198.9	199.7	181.2	10.2
Toluene	520.3	525.1	504.8	517.0	515.8	516.6	463.7	11.40

Table IV
Specific Retention Volumes for Poly(dimethylsiloxane)-Hydrocarbon Systems at 55°

	V_g° (cm³/g)		
	Column 5	Summers	Dev (%)
n-Pentane	29.80	27.43	8.6
n-Hexane	70.50	66.45	6.1
Benzene	112.5	105.4	6.7
Toluene	269.2	251.4	7.1

technique for measuring polymer-solvent interaction is still open to question.

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Communications to the Editor

A New Catalyst for the Living Polymerization of Lactones to Polyesters

The mechanism of ring-opening coordination polymerization of heterocyclic monomers such as oxiranes and lactones to high polymers has been thoroughly investigated in the presence of several types of catalysts; however, clear experimental evidence on the reaction mechanism are usually difficult to obtain, owing often to the poor knowledge of the structure of the actual catalytic species.

Table I
Characterization of the Main Products from the First and Second Steps of CL Polymerization

	Mol Wt[a]		Calcd (%)			Found (%)			
Esters	Calcd	Found	C	H	O	C	H	O	Spectroscopic Analysis
From [CL]/[Zn] = 1[b]	188	200	63.79	10.71		64.38	10.77	25.46	Ir and nmr spectra are
$HO(CH_2)_5COO$-n-C_4H_9[c]	188	198			25.50				identical (as well as glc)
From [CL]/[Zn] = 2[d]	344	340	62.76	9.36	27.87	63.29	9.71	27.00[e]	Nmr spectrum corresponds to $CH_3CO[-O(CH_2)_5CO-]_2O$-n-C_4H_9

[a] Obtained in toluene solution by vapor pressure depression method. [b] Isolated by distillation after hydrolysis. [c] Synthetized by refluxing CL in an excess of n-C_4H_9OH in the presence of p-toluenesulfonic acid. [d] Isolated by molecular distillation after hydrolysis and acetylation. [e] Calculated by difference.

A recent publication[1] prompts us to report here a new and rather clear-cut example of ring-opening polymerization of lactones to the corresponding polyesters. The catalyst used is a well-characterized aluminum-zinc oxoalkoxide, $(n\text{-}C_4H_9O)_2AlOZnOAl(n\text{-}C_4H_9O)_2$, obtained by an improvement[2] of the condensation method described earlier.[3]

This catalyst is a highly active one for some oxirane and lactone polymerizations. ε-Caprolactone (CL) is a particularly interesting monomer. Under mild conditions (10°, $[CL] = 1.0\ M$, $[Zn] = 1.83 \times 10^{-2}\ M$, in toluene solution) the half-polymerization time is only 23 min, and at 30° the reaction is already extremely rapid and difficult to control.

The characteristic feature of this polymerization reaction is the lack of chain termination or transfer, as indicated by the accurate correspondence between the mean degree of polymerization (DP, obtained from $\bar{M}_n$ determinations) and the monomer over catalyst molar ratio ($[M]/[C] = [CL]/[Zn]$, at total conversion (Figure 1).

The "living" character of the propagation is also demonstrated by polymerization resumption experiments, involving the addition of a new and equal amount of monomer to a completely polymerized system. The viscosity-

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(2) T. Ouhadi, A. J. Hubert, and Ph. Teyssié, in preparation.

(3) M. Osgan and Ph. Teyssié, *J. Polym. Sci., Part B*, **5**, 789 (1967).