Eur. Polym. J. Vol. 28, No. 12, pp. 1597–1600, 1992
Printed in Great Britain. All rights reserved

0014-3057/92 $5.00 + 0.00

CHARACTERIZATION OF POLYETHERPOLYURETHANE BY INVERSE GAS CHROMATOGRAPHY

A. Mohammed Farooque and Dinkar D. Deshpande*
Department of Chemistry, Indian Institute of Technology, Powai, Bombay 400076, India

(Received 4 March 1992)

Abstract—Inverse gas chromatography has been used to characterize the interaction of polyetherpolyurethane with 17 solvents of various polarities at 100–150°C. The specific retention volume (V_g^0) measured for each probe was used to calculate various thermodynamic parameters and properties at infinite dilution, viz. χ, χ^*, X_{12}, ΔH_1^s, ΔH_1^∞, ΔG_1^∞ and $T\Delta S_1^\infty$. The dependencies on temperature and nature of the solvent are discussed. Also we have calculated the solubility parameter of the polymer using the method of Guillet and Dipaola–Baranyi at the above temperatures and also at 25°C.

INTRODUCTION

The application of polyurethane (PU) under aggressive conditions of temperature and solvent contact necessitates study of its solvent resistance over a range of temperatures. Also, we need to know suitable solvents which easily dissolve PU to help other techniques based on solution methods for elucidation of structure. There are not many techniques available which can be used to study these polymer–solvent interactions over wide ranges of solvents and temperatures; the techniques that are available involve difficult and time-consuming experiments and are usually confined to relatively dilute solutions. Inverse gas chromatography (IGC) is a method that overcomes these limitations and is particularly applicable to concentrated solutions, which are of considerable industrial interest. IGC, which is conventional gas chromatography where the stationary phase is of interest, is widely used for the characterization of many polymer systems [1–4]. Added advantages of this technique are simplicity, accuracy, precision, rapid data collection and low cost. Since the early work of Smidsrod and Guillet [5], numerous systems have been studied by this method and good agreement with more traditional static equilibrium measurements has been demonstrated.

Here we have used IGC to evaluate various thermodynamic quantities such as polymer–solvent interaction parameters, enthalpy of mixing and solubility parameter. The partial molar enthalpy of mixing at infinite dilution of solvent with polymer, ΔH_1^∞, is a most important thermodynamic parameter for the description of the solubilization process of low molecular weight species in a liquid polymeric phase.

The concept of solubility parameter is useful for many practical applications such as solvent selection and prediction of phase equilibrium. The solubility parameter of a polymer can be determined either by swelling experiments or group contribution methods. We use here the chromatographic method developed by Dipaola–Baranyi and Guillet [6] for the evaluation of the solubility parameter of a polymeric stationary phase, from measurements of interaction parameters. A frequent use of solubility parameters is the prediction of compatibility of blends of polymers with additives, such as plasticizers, used to modify the polymer properties.

EXPERIMENTAL PROCEDURES

Materials

Polyurethane was a commercial polyetherpolyurethane sample obtained from QUIMAL International, U.S.A. (product No. PE 88-200). It was purified by dissolving in tetrahydrofuran (THF) and reprecipitating with methanol [average molecular weight = 54,000 from GPC (polystyrene calibration) and density = 0.95478 g/cm^3 (from dilatometry)]. The chromatographic support was 60–80 mesh Chromasorb W, acid washed and treated with dimethyldichlorosilane (DMCS). Packed columns were prepared from 150 cm long annealed copper tubing having 0.635 cm o.d. The tubing was rinsed with acetone, followed by petroleum ether. It was then dried by passing through dry N_2 gas. Seventeen probes of various polarities were of analytical grade.

Columns

Weighed amounts of each of the polymer samples were dissolved in about 50 ml of THF. The support, which was kept under vacuum for 6 hr, was coated using the soaking method of Al-Saigh and Munk [7]. The percentage coating of the polymer on the support was determined by calcination of the coated support in duplicate. A correction was made for the loss of volatile matter from the uncoated support. It was found that the amount determined by calcination closely matched the amount of polymer taken. Prior to any retention measurements, each new column was conditioned in the chromatograph at 150°C for 8 hr, for attainment of equilibrium at the experimental temperature.

Data acquisition

Retention times were measured using a dual column gas chromatograph fabricated by us with a thermal conductivity detector. Analytical reagent grade H_2 was used as carrier gas. The gas flow rate was measured using a soap bubble flow meter. The inlet pressure was measured using a U-tube Hg manometer and outlet pressure by a barometer. Less

---

*To whom all correspondence should be addressed.

than 0.1 μl of probe (together with marker, air) was injected manually with a 10 μl Hamilton syringe in order to approach infinite dilution condition for the probe. The retention time was taken as the difference of retention time of the probe and the air peak, measured using a Hewlett–Packard integrator (HP 3396A). For each probe, the average of triplicate readings of retention time was taken for a given flow rate of the carrier gas.

Data reduction

The standard specific retention volumes (V_g^0) were calculated in the usual manner [8], using:

$$V_g^0 = \frac{F(P_0 - P_w)}{P_0} \frac{273.16}{T_a} \frac{3}{2} \frac{(P_i/P_0)^2 - 1}{(P_i/P_0)^3 - 1} \frac{t_r}{W_L} \qquad (1)$$

where t_r is the retention time for the probe, W_L is the weight of the stationary phase, F is the carrier gas flow rate measured at room temperature T_a, P_0 is atmospheric pressure, P_i is the inlet pressure and P_w is the water vapour pressure at temperature T_a.

The polymer–solvent interaction parameters χ_{12} were calculated from the relation [9] applicable for polymers having high molecular weight.

$$\chi_{12} = \ln\left(\frac{273.16 R v_2}{P_1^0 V_1 V_g^0}\right) - 1 - \frac{P_1^0}{RT}(B_{11} - V_1) \qquad (2)$$

where subscripts 1 and 2 refer to probe and polymer respectively. v_2 is the specific volume of polymer and V_1, B_{11} and P_1^0 are molar volume, second virial coefficient and vapour pressure respectively of the probes at the temperature of experiment T. Values of these parameters were obtained from various sources [10, 11].

The corresponding equation of state parameter, χ_{12}^*, can be obtained easily by replacing in equation (2) the specific volume by core specific volume v_2^*. The Flory–Prigogine exchange interaction parameter, X_{12}, was calculated using the relationship [12]

$$RT\chi_{12}^* = \frac{V_1^* X_{12}}{\tilde{V}_2} + P_1^* V_1^* \left[\frac{1}{\tilde{V}_1} - \frac{1}{\tilde{V}_2} + 3\tilde{T}_1 \ln \frac{\tilde{V}_1^{1/3} - 1}{\tilde{V}_2^{1/3} - 1}\right] \qquad (3)$$

where the first term is the interaction term and the second is the free volume term. P^* and V^* are the pressure and volume reduction parameters (Table 1) and

$$\tilde{V} = \frac{V}{V^*} = \left(1 + \frac{\alpha T}{3(1 + \alpha T)}\right)^{1/3} \qquad (4)$$

$$\tilde{T} = \frac{T}{T^*} = \frac{\tilde{V}^{1/3} - 1}{\tilde{V}^{4/3}} \qquad (5)$$

$$P^* = \left(\frac{\alpha}{\beta}\right)\tilde{V}^2 T \qquad (6)$$

where α is the thermal expansion coefficient and β is the isothermal compressibility.

The partial heats of solution ΔH_1^S are obtained by

$$\Delta H_1^S = -R\frac{\partial(\ln V_g^0)}{\partial(1/T)}. \qquad (7)$$

The partial molar heats of mixing, ΔH_1^∞ are obtained using the relation

$$\Delta H_1^\infty = R\frac{\partial \ln \Omega_1^\infty}{\partial(1/T)} \qquad (8)$$

where the weight fraction activity coefficient, Ω_1^∞ is related to the χ parameter by

$$\ln \Omega_1^\infty = \chi - \ln\frac{v_2}{v_1} + 1. \qquad (9)$$

The free energy of mixing ΔG_1^∞ is given by

$$\Delta G_1^\infty = RT \ln \Omega_1^\infty. \qquad (10)$$

The entropy term of mixing $T\Delta S_1^\infty$ is given by

$$\Delta G_1^\infty = \Delta H_1^\infty - T\Delta S_1^\infty. \qquad (11)$$

Table 1. Equation of state parameters of probes and polymer at 20°C

Probe No.	Probe	V^* (cm^3/mol)	P^* (J/cm^3)	T^* (K)
1	n-Octane	127.74	437.23	4825
2	n-Nonane	142.01	437.57	5003
3	n-Decane	156.16	437.17	5134
4	Methyl cyclohexane	100.96	474.77	4929
5	*trans*-Decalin	130.93	504.60	5683
6	*cis*-Decalin	127.30	542.60	5739
7	Toluene	84.58	560.12	4941
8	*p*-Xylene	99.10	530.86	5112
9	*o*-Xylene	97.59	544.66	5313
10	Chlorobenzene	82.62	586.81	5550
11	n-Butyl acetate	104.13	538.70	4901
12	iso Amyl acetate	116.51	552.60	4734
13	iso Butyl methyl ketone	98.13	501.24	4795
14	Cyclohexanone	84.46	624.20	5444
15	*p*-Dioxane	71.02	334.61	5730
16	Butanol	74.44	459.17	5411
17	Pentanol	88.06	461.31	5476
—	PU	0.7712 cm^3/g	—	6839

The interpretation of the Flory–Huggins interaction parameter χ as a residual free energy function rather than the original enthalpy parameter allows separation into enthalpic and entropic contributions:

$$\chi = \chi_H + \chi_S. \qquad (12)$$

The method of DiPaola–Baranyi and Guillet [6] is an extension of the work of Bristow and Watson [13] who calculated solubility parameters for a series of network polymers from swelling equilibria. The basis is that the solubility parameters of solvent, δ_1, and polymer, δ_2, are introduced in the form of Regular Solution theory to account for enthalpic effects:

$$\chi^\infty = \frac{V_1}{RT}(\delta_1 - \delta_2) + \chi_S^\infty \qquad (13)$$

where the superscript ∞ indicates that IGC data are obtained at infinite dilution of solvent in the polymer. Expansion of the terms in parentheses and rearrangement yields

$$\left(\frac{\delta_1^2}{RT} - \frac{\chi^\infty}{V_1}\right) = \left(\frac{2\delta_2}{RT}\right)\delta_1 - \left(\frac{\delta_2^2}{RT} - \frac{\chi_S^\infty}{V_1}\right). \qquad (14)$$

A plot of the function on the left hand side of equation (14) vs δ_1 should give a linear graph with the δ_2 value being calculated from the slope. Values of δ_1 for the various probes were obtained at experimental temperatures from the corresponding enthalpies of vaporization ΔH_v

$$\delta_1 = \left(\frac{\Delta H_v - RT}{V_1}\right)^{1/2} \qquad (15)$$

where ΔH_v was obtained using the relation [14]

$$-\Delta H_v = \frac{\partial \ln P}{\partial(1/T)}. \qquad (16)$$

RESULTS AND DISCUSSION

The PU was found to be soluble in a limited number of common solvents. NMR (both ^{1}H— and ^{13}C—) studies in pyridine as solvent and i.r. studies of a thin film cast from THF reveal that the basic structural unit consists of diphenyl methane 4,4′-diisocyanate (MDI) and butanediol [or polymer of it i.e. polytetramethyleneglycol (PTMG)]. Since the DSC studies show the presence of two distinct glass transition temperatures (T_g), one below room temperature, it can be concluded that the polymer is a block copolymer with phase separation. So the present polymer could be a segmented PU with MDI and PTMG, with butanediol as chain extender. From

Table 2. Specific retention volume (V_g^0) and χ_{12} of PU at various temperatures

Probe No.	V_g^0 (ml/g)					χ_{12}				
	100°C	120°C	130°C	140°C	150°C	100°C	120°C	130°C	140°C	150°C
1	24.57	14.70	11.83	9.71	7.85	1.37	1.28	1.22	1.16	1.13
2	46.34	26.01	20.34	16.22	12.66	1.47	1.35	1.28	1.22	1.19
3	87.54	46.00	34.78	26.60	20.45	1.50	1.39	1.33	1.27	1.24
4	21.66	13.88	11.48	9.63	7.94	1.01	0.93	0.88	0.83	0.81
5	235.79	124.06	94.69	72.74	56.12	0.98	0.90	0.84	0.80	0.77
6	330.20	171.32	128.73	98.45	74.77	0.97	0.87	0.82	0.77	0.74
7	60.64	35.78	28.57	23.17	18.73	0.44	0.40	0.37	0.34	0.32
8	113.25	62.72	48.78	38.61	30.46	0.51	0.46	0.43	0.39	0.37
9	145.64	79.48	61.17	48.09	37.70	0.47	0.43	0.39	0.36	0.34
10	138.17	76.57	59.59	47.20	37.25	0.29	0.27	0.24	0.21	0.20
11	71.26	39.66	30.61	24.18	19.20	0.56	0.51	0.48	0.44	0.41
12	71.14	39.56	30.60	24.16	19.26	0.86	0.75	0.69	0.63	0.57
13	55.18	32.08	25.27	20.30	16.53	0.55	0.49	0.46	0.42	0.38
14	296.14	156.45	119.00	91.75	71.29	0.28	0.24	0.20	0.17	0.15
15	62.23	37.27	29.87	24.05	19.66	0.37	0.31	0.27	0.24	0.21
16	75.32	39.84	30.44	23.80	18.51	0.73	0.62	0.55	0.48	0.44
17	148.12	73.12	54.25	41.03	31.04	0.66	0.56	0.49	0.44	0.40

the elemental analyses, it was found that the MDI content is about 31.53%.

T_gs were measured using a thermomechanical analyzer, dilatometry and differential scanning calorimetry and were found to be 65.5, 58.5 and 61°C respectively. DSC showed an additional T_g below room temperature at −52.3°C. Also, x-ray diffraction and DSC studies revealed the amorphous nature of the polymer.

Inverse gas chromatography

The specific retention volume, V_g^0, was measured for 17 probes of various chemical types at five temperatures viz. 100, 120, 130, 140 and 150°C each at two different flow rates. These measurements have been performed on two columns having different loadings. The V_g^0 values were found to agree within 2% for each measurement. It was found that V_g^0 values do not depend on the flow rate or on the amount of polymer loading. The linear relation found in the plot of ln V_g^0 vs $1/T$ indicates that equilibrium is achieved even at 100°C, which is only 40°C above T_g of the polymer. It is also confirmed by the symmetrical nature of the elution peaks of all the probes. The V_g^0 values are qualitatively in good agreement with those of Newman and Prausnitz [15], where a PU of unknown chemical structure was used.

The polymer–solvent interaction parameter χ_{12} was calculated for all the probes, and values are given in Table 2 along with V_g^0. The aliphatic and cycloaliphatic hydrocarbons gave highly positive values indicating that these are nonsolvents for the PU. The value becomes more positive with increase in chain length of hydrocarbons indicating less solubility of the solvents. The aromatic hydrocarbons and isobutylmethyl ketone gave less positive values. Chlorobenzene, cyclohexanone and *p*-dioxane gave small positive values, indicating that these are good solvents for the PU. It is also observed that the interaction parameter of all the probes decrease with increase in temperature. This dependence is obvious from the fact that the χ_{12} value is inversely proportional to the vapour pressure and the molar volume of the probe and it can be said that there exists no specific interaction between any of the probes and the polymer.

By introducing the equation of state term, we have also calculated χ_{12}^*, and contact interaction parameter, X_{12}, the more representative parameter for measuring specifically the interaction energy between the components of a mixture (Table 3). χ_{12}^* calculated for all the probes shows similar behaviour as that of χ_{12} but it is found to be slightly higher than χ_{12}. The contact interaction parameter, X_{12}, is also found to be

Table 3. χ_{12}^* and X_{12} (J/cm^3) of PU at various temperatures

Probe No.	χ_{12}^*					X_{12}(J/cm^3)				
	100°C	120°C	130°C	140°C	150°C	100°C	120°C	130°C	140°C	150°C
1	1.51	1.43	1.38	1.33	1.31	34.69	33.90	32.90	31.68	31.60
2	1.59	1.47	1.42	1.36	1.35	34.49	33.11	32.10	31.10	31.10
3	1.60	1.51	1.46	1.40	1.38	32.52	31.81	31.10	30.31	30.31
4	1.14	1.07	1.03	0.99	0.98	33.31	32.19	31.02	29.80	29.72
5	1.04	0.96	0.91	0.87	0.84	27.21	26.50	25.50	24.79	24.41
6	1.02	0.93	0.88	0.83	0.81	27.71	26.50	25.50	24.49	24.20
7	0.56	0.53	0.51	0.48	0.47	14.00	12.92	11.62	10.20	9.45
8	0.60	0.57	0.54	0.51	0.50	14.88	14.09	13.00	11.70	11.12
9	0.56	0.52	0.49	0.46	0.45	15.38	14.59	13.59	12.41	11.79
10	0.38	0.36	0.34	0.32	0.31	17.39	17.89	17.31	16.59	16.80
11	0.70	0.66	0.63	0.61	0.59	14.00	12.58	11.70	10.41	9.45
12	0.99	0.89	0.84	0.79	0.74	17.68	14.71	12.79	10.62	8.53
13	0.68	0.64	0.62	0.59	0.56	14.09	12.71	11.62	10.12	8.61
14	0.36	0.33	0.30	0.27	0.25	10.41	9.15	7.61	6.10	4.93
15	0.44	0.39	0.36	0.34	0.32	21.82	20.48	19.19	18.60	17.81
16	0.82	0.72	0.66	0.60	0.57	37.49	34.40	31.89	29.30	28.00
17	0.74	0.65	0.59	0.55	0.52	27.88	25.41	23.41	21.49	20.69

Table 4. ΔH_1^S, ΔH_1^∞, ΔG_1^∞ and $T\Delta S_1^\infty$ of PU with various solvents at 130°C

Probe No.	ΔH_1^S	ΔH_1^∞	ΔG_1^∞	$T\Delta S_1^\infty$
		(kJ/mol)		
1	−29.84	5.52	9.20	−3.68
2	−33.77	6.56	9.32	−2.76
3	−37.95	6.02	9.41	−3.39
4	−26.13	4.51	7.77	−3.26
5	−37.54	5.31	7.06	−1.76
6	−38.79	5.73	6.90	−1.17
7	−30.68	2.42	5.64	−3.22
8	−34.32	2.84	5.81	−2.97
9	−35.32	2.88	5.60	−2.72
10	−34.23	1.88	4.31	−2.42
11	−34.36	2.80	5.98	−3.18
12	−34.28	6.52	6.65	−0.13
13	−31.64	3.09	6.23	−3.14
14	−37.29	3.01	4.72	−1.71
15	−30.22	3.14	4.72	−1.59
16	−36.66	6.69	6.44	0.25
17	−40.88	5.89	6.19	−0.29

Table 5. Solubility parameter δ_2 of PU at various temperatures

Temperature (°C)	$\delta_2(\mathrm{J/cm^3})^{1/2}$
100	17.38 ± 0.16
120	17.20 ± 0.15
130	17.14 ± 0.14
140	17.06 ± 0.15
150	16.96 ± 0.15
25	17.99 ± 0.02

positive for all the probes, indicating the absence of any specific interaction between PU and probes. The trend with temperature is also quite similar to that for χ_{12}.

The partial molar heats of solution ΔH_1^S, partial molar heats of mixing ΔH_1^∞, partial molar free energy of mixing ΔG_1^∞ and the entropy of mixing term $T\Delta S_1^\infty$ calculated for all the probes are given in Table 4. The positive values of ΔH_1^∞ and ΔG_1^∞ confirm the absence of any specific interaction between probe and polymers. The entropy term is found to contribute a negative value to the mixing process which is unfavourable.

Solubility parameter

The solubility parameter calculated using equation (14) by plotting

$$\left(\frac{\delta_1^2}{RT} - \frac{\chi^\infty}{V_1}\right)$$

against the solubility parameter of probe, δ_1, gave an excellent linear fit at all temperatures. This result confirms the usefulness of IGC as a technique to evaluate the solubility parameters of polymers. In IGC, usually the measurements are carried out at a temperature 50°C above the T_g of a polymer which will be far above the room temperature. In order to evaluate the solubility parameter at room temperature, it has been the practice to use the linearly extrapolated value of χ_{12} from higher temperature. Since this has been proved wrong [16], we have calculated the solubility parameter at 25°C by linear extrapolation of solubility parameter data at higher temperatures, a process which gave an excellent linear fit (Table 5).

Acknowledgement—One of the authors (AMF) acknowledges CSIR (India) for a Fellowship.

REFERENCES

1. J. E. G. Lipson and J. E. Guillet. *Development in Polymer Characterization—3.* (Edited by J. V. Dawkins), p. 33. Applied Science, London (1982).
2. J. S. Aspler. *Pyrolysis and GC in Polymer Analysis, Chromatographic Science Series,* Vol. 29, Chap. IX (Edited by S. A. Liebman and E. J. Levy). Dekker, New York (1985).
3. R. Vilcu and M. Leca. *Polymer Thermodynamics by Gas Chromatography.* Elsevier, New York (1990).
4. *Inverse Gas Chromatography—Characterization of Polymers and Other Materials. ACS Symposium Series—391* (Edited by D. R. Lloyd, T. C. Ward and H. P. Schreiber). American Chemical Society, Washington, DC (1989).
5. O. Smidsrod and J. E. Guillet. *Macromolecules* **2,** 272 (1969).
6. G. DiPaola-Baranyi and J. E. Guillet. *Macromolecules* **11,** 228 (1978).
7. Z. Y. Al-Saigh and P. Munk. *Macromolecules* **17,** 803 (1984).
8. A. B. Littlewood, C. S. G. Phillips and D. T. Price, *J. Chem. Soc.* 1480 (1955).
9. J. E. Guillet and J. M. Braun. *Adv. Polym. Sci.* **21,** 107 (1976).
10. B. D. Smith and Srivastava. *Thermodynamic Data for Pure Components' Physical Science Data 25 Part A & B.* Elsevier, Amsterdam (1986).
11. R. C. Reid, T. K. Sherwood, J. M. Prausunitz and B. E. Poling. *Properties of Gases and Liquids.* McGraw-Hill, New York (1987).
12. D. Patterson. *Pure Appl. Chem.* **31,** 133 (1972).
13. G. M. Bristow and W. F. Watson. *Trans. Faraday Soc.* **54,** 1731 (1958).
14. C. Uriarte, M. J. Fdes-Berridi, J. M. Elorsa, J. J. Iruin and L. Kleintjens. *Polymer* **30,** 1493 (1989).
15. R. D. Newman and J. M. Prausnitz. *J. Paint Tech.* **45,** 33 (1973).
16. A. M. Farooque and D. D. Deshpande. *Polym. Sci., [Symp. Proc. Polym. '91],* Vol. 2 (Edited by S. Sivaram), p. 598. Tata McGraw-Hill, New Delhi (India) (1991).