JOURNAL OF APPLIED POLYMER SCIENCE VOL. 12, PP. 2359–2370 (1968)

Solubility Parameters of Polymers from Turbidimetric Titrations

K. W. SUH and J. M. CORBETT, *Plastics Production Research Service, The Dow Chemical Company, Midland, Michigan 48640*

Synopsis

The solubility parameters of sixteen polymers have been determined by the turbidimetric titration method. The results agree well with the reported values obtained from swelling and viscosity measurements. The method is sensitive to the choice of nonsolvents and to small changes in the copolymer composition.

INTRODUCTION

Determination of cohesive energy densities of polymers has been the subject of many investigations. Gee[1] studied the swelling of crosslinked polymers in a spectrum of solvents of known solubility parameter in which the solubility parameter of a polymer was taken to be equal to that of solvents exhibiting the greatest swelling. Bristow and Watson[2] employed swelling measurements and the Flory-Huggins interaction parameter χ to deduce the solubility parameters for polymers. This method is therefore limited to crosslinked polymers and may be applied to slightly crosslinked polymers such as styrene–divinylbenzene (99:1) copolymer. Bristow and Watson[3] also described a procedure for obtaining the solubility parameters of polymers based on viscosity measurements and the Fox-Flory theory.

Each of the above methods requires considerable experimental data to evaluate the constants and parameters, and accurate determination of the polymer solubility parameter is difficult. This emphasizes the need for developing a rapid and dependable method for determining the solubility parameters of amorphous polymers and random copolymers.

Determination of solubility parameters of polymers from turbidimetric titrations has been described in the preceding paper.[4] The solubility parameters of polymers were deduced from the Flory-Huggins interaction parameter χ. It is the purpose of this paper to test the expressions derived in the preceding paper[4] by making titration measurements on sixteen polymers and to present an improved procedure for the determination of polymer solubility parameters by turbidimetric titrations.

EXPERIMENTAL AND RESULTS

To choose suitable good solvents for each polymer, a gross solubility test was performed in 25 solvents whose solubility parameters varied from 6.4

TABLE I
Qualitative Solubility Tests[a]

Solvents	δ_1[b]	V_1	Poly-buta-diene	Poly-styrene	Poly-*o*-chloro-styrene	Poly-(methyl meth-acrylate)	PVC-1	Styrene–maleic anhy-dride-2	Styrene–methyl meth-acrylate-2	Styrene–acrylo-nitrile-2
Freon-215 ($C_2F_5Cl_3$)	6.40	143.9	i[c]	i	i	i	i	i	i	i
Isopentane	6.63	117.4	i	i	i	i	i	i	i	i
Isooctane	6.87	163.2	i	i	i	i	i	i	i	i
n-Pentane	7.05	116.0	ps	i	i	i	i	i	i	i
n-Hexane	7.29	131.6	s	i	i	i	i	i	i	i
n-Octane	7.57	164.0	s	i	i	i	i	i	i	i
Methylcyclo-hexane	7.84	128.3	s[c]	i[c]	i	i	i	i[c]	i[c]	i
Cyclohexane	8.20	108.0	s	ps	i	i[c]	i	i	i	i
Carbon tetra-chloride	8.64	97.1	s	s	s	i	i	ps	s	i[c]
Toluene	8.93	106.8	s	s[c]	s[c]	s[c]	i	s[c]	s[c]	ps
o-Xylene	9.01	121.2	s	s	s	s	i	s	s	i

Benzene	9.16	89.4	s	s	s	s	i[c]	s	s	s[c]
Methyl ethyl ketone	9.30	90.2	i	s	s	s	ps	s	s	s
Chlorobenzene	9.50	102.3	s[c]	s[c]	s[c]	s	i	s	s	s
Methylene chloride	9.70	65.0	s	s	s	s	ps	s	s	s
Acetone	9.81	74.0	i[c]	i	i	s	i	ps	s	s
Methyl isopropyl ketone	9.92	105.7	i	s	s	s	ps	s	s	s
o-Dichlorobenzene	10.10	112.95	s	s[c]	s[c]	s[c]	s[c]	s[c]	s[c]	s[c]
Cyclopentanone	10.40	88.45	s	s	s	s	s[c]	s	s	s
Pyridine	10.70	81.0	s	s	s	s	s	s	s	s
n-Amyl alcohol	10.90	108.7	i	i[c]	i[c]	i[c]	i[c]	i[c]	i[c]	i[c]
o-Toluidine	11.40	107.8	i	s	s	s	i	s	s	s
n-Propyl alcohol	11.90	75.1	i	i	i	i	i	i	i	i
Ethanol	12.83	58.8	i	i	i	i	i	i	i	i
Methanol	14.54	40.7	i	i	i	i	i	i	i	i

[a] s = soluble; ps = partially soluble; i = insoluble.

[b] δ_l for F-215 was taken from Bulletin D-73, Freon Products Division, E. I. du Pont de Nemours & Co., Inc., and other δ values were calculated from the heat of vaporization at 25°C.

[c] Solvents and nonsolvents used in titrations.

TABLE II
Turbidimetric Titration of Polymer Solutions at 25°C[a]

Polymer	Solvent	Nonsolvent, ml: Low δ value	Nonsolvent, ml: High δ value	δ_3	δ_3*	δ_p from intersection	Reported δ_p values	Ref.
Butadiene–styrene	Methylcyclohexane	13.0 Freon-215	11.58 Acetone	7.87	7.89	7.9	8.1	2,10
	Cyclohexane	15.1 "	11.76 "	8.00	7.84		8.33	5
	Isopropylbenzene	16.7 "	12.83 "	8.12	7.78		8.56	6
	Mesitylene	17.0 "	13.71 "	8.22	7.76		8.6	7
	m-Xylene	17.7 "	13.50 "	8.21	7.74			
	o-Xylene	18.5 "	14.02 "	8.27	7.70			
	Ethylbenzene	17.9 "	13.48 "	8.21	7.73			
	Toluene	18.4 "	13.60 "	8.24	7.71			
	Benzene	18.8 "	12.48 "	8.33	7.66			
	Chlorobenzene	20.5 "	15.9 "	8.43	7.57			
	Bromobenzene	20.7 "	18.2 "	8.60	7.47			
Polybutadiene	Methylcyclohexane	17.0 "	8.95 "	7.77	7.70	7.73	7.16	8
	Ethylbenzene	20.8 "	9.45 "	8.13	7.58		8.12	9
	Chlorobenzene	23.5 "	11.46 "	8.38	7.47		8.44	5
							8.45	7
							8.6	10
Butyl rubber	Methylcyclohexane	34.9 "	5.05 "	7.54	7.29	7.35	7.7	6
	Isopropylbenzene	27.2 "	2.40 "	7.83	7.20		7.8	2
	Chlorobenzene	38.7 "	2.25 "	8.19	7.08		7.84	5
Butadiene–acrylonitrile	*m*-Xylene	0.5 *n*-Hexane	6.7 *n*-Amyl alcohol	9.18	9.55	9.48	9.25	6
	Styrene	4.0 "	10.1 " "	9.40	9.50		9.38	5
	Bromobenzene	6.3 "	12.7 " "	9.72	9.44		9.4	10
							9.5	7

Polystyrene	Toluene	79	Methylcyclohexane	6.7	"	"	8.81	8.69	8.75	8.56	3
	o-Dichlorobenzene	120	"	8.8	"	"	9.20	8.36		8.73	11
										9.1	6,7,10
										8.6	9
Poly-*o*-chlorosty-rene	Toluene	14.3	Methylcyclohexane	4.72	*n*-Amyl alcohol		8.91	8.89	8.90		
	o-Dichlorobenzene	25.0	"	5.6	"	"	8.76	9.41			
Poly(methyl methacrylate)	Toluene	4.92	Cyclohexane	16.9	"	"	9.43	9.93	9.71	9.08	3
	o-Dichlorobenzene	13.3	"	27.5	"	"	9.85	9.59		9.5	10
										9.7	12
Poly(vinyl chloride)-1	Cyclopentanone	200	Benzene	15.0	"	"	9.98	9.54	9.51	9.53	3
	o-Dichlorobenzene	40.5	"	2.5	"	"	9.82	9.53		9.54	9
										9.7	10
										9.42	8
										9.48	13
Poly(vinyl chloride)-2	Cyclopentanone	207	"	14.0	"	"	9.97	9.52	9.53		
	o-Dichlorobenzene	42	"	2.6	"	"	9.83	9.52			
Styrene–maleic anhydride-1	Toluene	9.5	Methylcyclohexane	6.3	"	"	9.03	9.13	9.08		
	o-Dichlorobenzene	21.5	"	8.1	"	"	9.49	8.90			
Styrene–maleic anhydride-2	Toluene	3.06	"	3.6	"	"	9.06	9.18	9.18		
	o-Dichlorobenzene	9.40	"	5.9	"	"	9.68	9.28			
Styrene–methyl methacrylate-1	Toluene	7.0	"	16.1	"	"	9.30	9.66	9.46		
	o-Dichlorobenzene	18.0	"	26.4	"	"	9.64	9.20			
Styrene–methyl methacrylate-2	Toluene	6.8	"	16.3	"	"	9.31	9.67	9.46		
	o-Dichlorobenzene	17.5	"	26.1	"	"	9.64	9.22			
Styrene–acry-lonitrile-1	Benzene	2.5	Carbon tetrachloride	4.5	"	"	9.38	9.61	9.58		
	o-Dichlorobenzene	17.9	" "	8.8	"	"	9.83	9.56			
Styrene–acry-lonitrile-2	Benzene	1.11	" "	3.9	"	"	9.38	9.60	9.60		
	o-Dichlorobenzene	14.1	" "	8.5	"	"	9.86	9.61			
Styrene–acry-lonitrile-3	Chlorobenzene	5.55	Toluene	4.75	"	"	9.62	9.75	9.76		
	o-Dichlorobenzene	10.6	"	5.35	"	"	9.94	9.78			

[a] 0.03 g polymer/10 ml solvent.

for Freon-215 to 14.54 for methanol. A small sample of polymer was added to a few milliliters of each reagent-grade solvent in separate test tubes. Upon standing for 24 hr, each was classified as soluble, partially soluble, or insoluble. Table I shows the results for typical homopolymers and copolymers.

Based on the above qualitative screening tests, two solvents were chosen for each polymer, one near the lower solubility parameter limit and one near the higher solubility parameter limit. Two nonsolvents were also chosen, which were just in the insoluble classification (the borderline nonsolvent on the solvent spectrum). Solvents and nonsolvents which were used for titrations of each polymer are so denoted by superscript c in Table I. To be consistent with the previous work,[4] polymer solutions were prepared by dissolving 0.3 g of polymer in 100 ml of solvent; 10-ml aliquots were used in the titration. Table II gives the results of these titrations.

In the earlier paper,[4] the expression for the solubility parameter of a polymer was derived for ideal systems in which the interaction of solvents with the polymer is very small as compared with the interaction between solvent and nonsolvent:

$$\delta_3 = \frac{\sqrt{V_{ml}}\,\delta_{ml} + \sqrt{V_{mh}}\,\delta_{mh}}{\sqrt{V_{ml}} + \sqrt{V_{mh}}} \tag{1}$$

For nonideal systems in which the polymer interacts preferentially with the solvent and behaves as if its chemical composition were that of the good solvent with respect to the solvent–nonsolvent mixture, the solubility parameter of a polymer may be expressed by

$$\delta_3^* = \delta_{ml} + \sqrt{V_{mh}/V_{ml}}\,(\delta_{mh} - \delta_1) \tag{2}$$

where subscripts *ml* and *mh* represent the mixture of solvent and nonsolvent of lower solubility parameter and mixture of solvent and nonsolvent of higher solubility parameter at the cloud points, respectively, and

$$V_m = V_1V_2/(\phi_1V_2 + \phi_2V_1) \tag{3}$$

$$\delta_m = \phi_1\delta_1 + \phi_2\delta_2 \tag{4}$$

where subscripts 1, 2, 3 represent solvent, nonsolvent, and polymer, respectively; ϕ is the volume fraction, and V the molar volume. If the solubility parameter of a solvent is exactly equal to that of a polymer, then either eq. (1) or (2) yields the correct value for the solubility parameter of the polymer.

The values of δ_3 and δ_3^* were calculated for each polymer based on the data given in Table II. Figures 1 and 2 show plots of δ_1 versus δ_3 and δ_3^* for several typical polymers. As shown in Figure 1, the experimental data are consistent so only two or three solvents may be used to determine the solubility parameters of polymers. The intersection of either δ_1 versus δ_3 or δ_1 versus δ_3^* with the $\delta_3 = \delta_1$ line is sufficient to give the solubility parameter of a polymer. In this work, both calculations have been made as a

check. Table II shows the results obtained by this method for sixteen polymers and copolymers. The description of polymers used is given in Table III.

The solubility parameter of polybutadiene is slightly lower than expected, but is about midway between reported values. The δ values for butadiene–styrene copolymer and butyl rubber are also lower than expected but appear in line with that of polybutadiene. The solubility parameters for butadiene–acrylonitrile copolymer, polystyrene, poly(methyl methacrylate),

TABLE III
Description of Polymers

Polymer	Description
Butadiene–styrene	Random copolymer (75B/25S), $\bar{M}_w$ = 100,000, $\bar{M}_w/\bar{M}_n$ = 7.8, ρ = 0.92 g/cc
Polybutadiene	Commercial diene 55A-NF (Firestone, 38% *cis*, 8% vinyl 1,2, and 54% *trans*), $\bar{M}_w$ = 310,000, $\bar{M}_w/\bar{M}_n$ = 2.2, ρ = 0.90 g/cc
Butyl rubber	Commercial Polysar Butyl 100 (Polymer Corp. Ltd., Sarnia, Canada)
Butadiene–acrylonitrile	Random copolymer (75B/25 VCN), ρ = 0.96 g/cc, commercial Goodyear Chemigun
Polystyrene	Thermally polymerized, $\bar{M}_w$ = 295,000 (Dow), $\bar{M}_w/\bar{M}_n$ = 2.0, ρ = 1.05, g/cc
Poly-*o*-chlorostyrene	$\bar{M}_w$ = 200,000 (Dow), $\bar{M}_w/\bar{M}_n \simeq$ 2,3, ρ = 1.25 g/cc
Poly(methyl methacrylate)	Commercial Lucite 130 (DuPont)
Poly(vinyl chloride)-1	$\bar{M}_w$ = 62,500 (Dow), $\bar{M}_w/\bar{M}_n$ = 2.5, ρ = 1.40 g/cc
Poly(vinyl chloride)-2	$\bar{M}_w$ = 150,000 (Dow), $\bar{M}_w/\bar{M}_n$ = 2.0, ρ = 1.40 g/cc
Styrene–acrylonitrile-1	Random copolymer (75.5 S/24.5 VCN), $\bar{M}_w$ = 171,000, $\bar{M}_w/\bar{M}_n$ = 2.2, ρ = 1.08 g/cc
Styrene–acrylonitrile-2	Random copolymer (75.5 S/24.5 VCN), $\bar{M}_w$ = 209,000, $\bar{M}_w/\bar{M}_n$ = 2.2, ρ = 1.08 g/cc
Styrene–acrylonitrile-3	Random copolymer (71S/29 VCN), $\bar{M}_w$ = 207,000, $\bar{M}_w/\bar{M}_n$ = 2.2, ρ = 1.08, g/cc
Styrene–methyl methacrylate-1	Random copolymer (40 S/60 MMA), $\bar{M}_w$ = 132,800, $\bar{M}_w/\bar{M}_n$ = 2.0, ρ = 1.14 g/cc
Styrene–methyl methacrylate-2	Random copolymer (40 S/60 MMA), $\bar{M}_w$ = 182,500, $\bar{M}_w/\bar{M}_n$ = 1.9, ρ = 1.14 g/cc
Styrene–maleic anhydride-1	Random copolymer (95.29 S/4.71 MA), $\bar{M}_w$ = 240,000, $\bar{M}_w/\bar{M}_n \simeq$ 2.0, ρ = 1.067 g/cc
Styrene–maleic anhydride-2	Random copolymer (84.8 S/15.2 MA), $\bar{M}_w$ = 200,000, $\bar{M}_w/\bar{M}_n \simeq$ 2.0, ρ = 1.107 g/cc

and poly(vinyl chloride) agree well with reported values obtained from either swelling measurements or viscosity measurements. The δ values for styrene–acrylonitrile, styrene–methyl methacrylate, and styrene–maleic anhydride copolymers are in line with δ values for the constituent homopolymers. The experimental data for styrene–acrylonitrile and styrene–methyl methacrylate copolymers seem to indicate that the solubility parameter shows no dependence on molecular weight. The solubility pa-

rameter of a copolymer depends on the composition of the copolymer as shown in Table II.

EFFECT OF CHOICE OF SOLVENTS AND NONSOLVENTS

Butadiene–styrene copolymer and polystyrene were titrated in several different solvents. The results gave good correlation as shown in Figure 1 and Table IV. Considering the limited number of solvents used, it appears that the choice of solvent is not critical. Nitrogen-containing solvents such as pyridine, *o*-toluidine, and dimethylformamide were omitted because of their irregular solvent behavior.

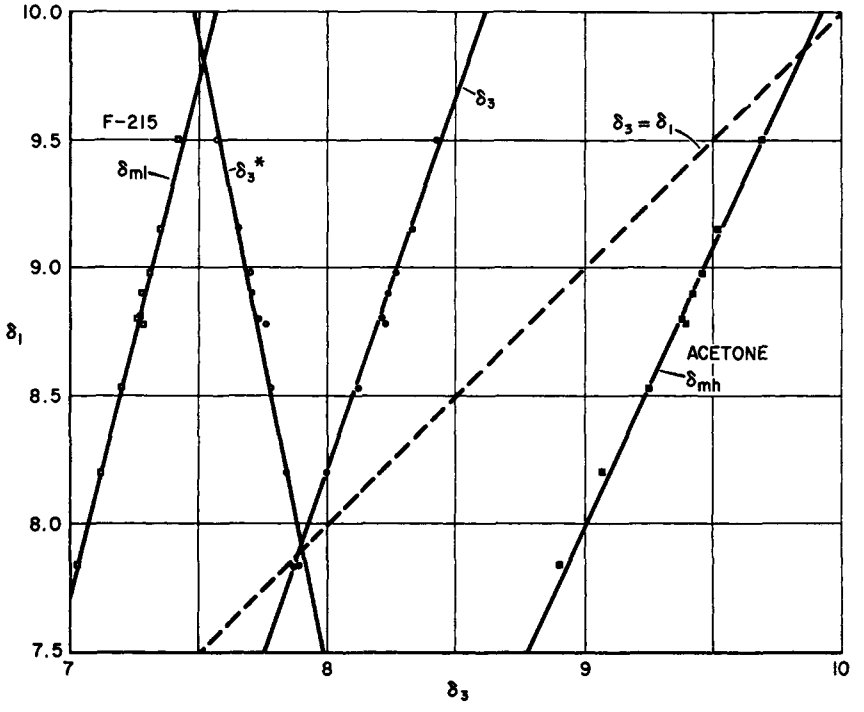

Fig. 1. Determination of the solubility parameter for butadiene–styrene copolymer (75B/25S) from the turbidimetric titration with Freon-215 and acetone.

Effect of Choice of Nonsolvents of Lower Solubility Parameter

To determine the effect of different nonsolvents of low solubility parameter, solutions of polystyrene and styrene–acrylonitrile-1 copolymer were titrated with the following nonsolvents: Freon-215 (δ = 6.4), isooctane (δ = 6.87), *n*-pentane (δ = 7.05), *n*-hexane (δ = 7.29), and methylcyclohexane (δ = 7.84). A common nonsolvent of high solubility parameter, *n*-amyl alcohol (δ = 10.9), was used to determine the δ_p values. Table V shows the δ_p values obtained for each set of nonsolvents. These results

TABLE IV
Effect of Nonsolvent of High Solubility Parameter

Polymer	Solvent	Nonsolvent, ml: Low δ value	Nonsolvent, ml: High δ value	δ_3	δ_3*	δ_p from intersection
Polystyrene	Toluene	79 Methylcyclohexane	65 Acetone	8.71	8.56	
	o-Dichloro-benzene	120 "	92.3 "	8.82	7.82	8.70
	20 solvents	*n*-Hexane	Acetone			8.72[a]
	Toluene	79 Methylcyclohexane	6.7 *n*-Amyl alcohol	8.81	8.69	
	o-Dichloro-benzene	120 "	8.8 "	9.20	8.36	8.75
	Benzene	14.45 *n*-Hexane	7.08 *n*-Butyl alcohol	9.02	8.90	
	o-Dichloro-benzene	120 Methylcyclohexane	8.11 "	9.38	8.72	8.93
	Benzene	14.45 *n*-Hexane	3.40 Methanol	9.14	9.13	
	o-Dichloro-benzene	120 Methylcyclohexane	3.90 "	9.58	9.17	9.13
	20 solvents	*n*-Hexane	"			9.07[b]
	Toluene	79 Methylcyclohexane	18.7 Cyclohexanol	9.26	9.55	
	o-Dichloro-benzene	120 "	21.6 "	9.50	8.96	9.34
Styrene–methyl methacry-late-1	Toluene	7.0 "	16.1 *n*-Amyl alcohol	9.30	9.66	
	o-Dichloro-benzene	18.0 "	26.4 "	9.64	9.20	9.46
	Benzene	6.8 *n*-Hexane	14.05 Methanol	10.03	10.65	
	o-Dichloro-benzene	11.59 "	14.40 "	10.25	10.35	10.28

* Data of Suh and Clarke.[4]

TABLE V
Effect of Nonsolvent of Low-Solubility Parameter

Polymer	Solvent	Nonsolvent, ml: Low δ value	Nonsolvent, ml: High δ value	δ_3	δ_3*	δ_p from intersection
Polystyrene	Toluene	10.7 Isooctane	6.7 *n*-Amyl alcohol	8.74	8.58	
	o-Dichloro-benzene	16.35 "	8.8 " "	9.21	8.43	8.62
	Toluene	13.0 *n*-Pentane	6.7 " "	8.78	8.64	
	o-Dichloro-benzene	20.5 "	8.8 " "	9.28	8.41	8.68
	Toluene	13.0 *n*-Hexane	6.7 " "	8.83	8.75	
	o-Dichloro-benzene	21.32 "	8.8 " "	9.32	8.53	8.78
	Toluene	79 Methylcyclohexane	6.7 " "	8.81	8.69	
	o-Dichloro-benzene	120 "	8.8 " "	9.20	8.36	8.75
	Toluene	9.9 Freon-215	6.7 " "	8.66	8.41	
	o-Dichloro-benzene	13.3 Freon-215	8.8 " "	9.18	8.34	8.44
Styrene–acrylonitrile-1	Benzene	2.5 Carbon tetrachloride	4.5 " "	9.38	9.61	
	o-Dichloro-benzene	17.9 "	8.8 " "	9.83	9.56	9.59
	Benzene	0.79 *n*-Hexane	4.5 " "	9.36	9.57	
	o-Dichloro-benzene	41.9 "	8.8 " "	9.86	9.63	9.59
	Benzene	0.95 Freon-215	4.5 " "	9.31	9.47	
	o-Dichloro-benzene	4.45 "	8.8 " "	9.70	9.32	9.42

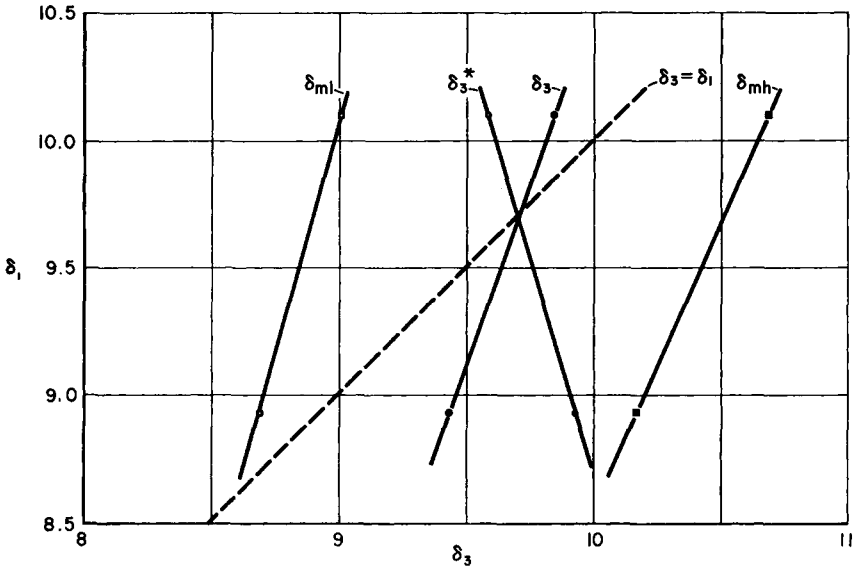

Fig. 2. Determination of the solubility parameter for poly(methyl methacrylate) from the turbidimetric titration with cyclohexane and *n*-amyl alcohol.

would indicate that the choice of nonsolvent of low solubility parameter is not as critical as the choice of nonsolvent of high solubility parameter. However, some variations were observed in the calculated δ values for the polymer when the difference between solubility parameters of nonsolvent and polymer was held above about 2.1 units.

Effect of Choice of Nonsolvents of Higher Solubility Parameter

Choice of nonsolvents whose solubility parameters are greater than that of the polymer is much more restrictive. The following examples with polystyrene illustrate this point. In these titrations, acetone (δ = 9.81), *n*-amyl alcohol (δ = 10.9), *n*-butyl alcohol (δ = 11.4), cyclohexanol (δ = 11.83) and methanol (δ = 14.54) were used as nonsolvents of higher solubility parameter, and methylcyclohexane (δ = 7.84) or *n*-hexane (δ = 7.29) were used as nonsolvents of lower solubility parameter. Table IV shows the δ_p values obtained for polystyrene in each set of nonsolvents.

These data indicate that when the difference between solubility parameters of nonsolvent and polymer was held below about 2.1 units, fairly consistent results were obtained. When the difference was greater than about 2.1 units, larger variations were observed in the calculated δ values for the polymer. The same effect was observed in other polymers, for instance styrene–methyl methacrylate-1 copolymer as shown in Table IV.

The authors are grateful to Mr. A. F. Roche for his comments and suggestions and to D. Kaufman, R. Johnston, and J. Kuipers of the Analytical Laboratory for titration measurements.

References

1. G. Gee, *Trans. Faraday Soc.*, **38**, 418 (1942).
2. G. M. Bristow and W. F. Watson, *Trans. Faraday Soc.*, **54**, 1731 (1958).
3. G. M. Bristow and W. F. Watson, *Trans. Faraday Soc.*, **54**, 1742 (1958).
4. K. W. Suh and D. H. Clarke, *J. Polym. Sci. A-1*, **5**, 1671 (1967).
5. C. J. Sheehan and A. L. Bisio, *Rubber Chem. Technol.*, **39**, 149 (1966).
6. P. A. Small, *J. Appl. Chem.*, **3**, 71 (1953).
7. R. L. Scott and M. Magat, *J. Polym. Sci.*, **4**, 555 (1949).
8. A. Di Benedetto, *J. Polym. Sci. A*, **1**, 3459 (1963).
9. A. Tobolsky, *Properties and Structure of Polymers*, Wiley, New York, 1960.
10. H. Burrell, *Interchem. Rev.*, **14**, 3 (1955).
11. J. Green, *Nature*, **183**, 818 (1959).
12. Rohm and Haas Co., *Quart. Rev., Or-Chem. Topics*, No. 12 (1962).
13. H. Mark and A. Tobolsky, *Physical Chemistry of High Polymers*, Interscience, New York, 1950, p. 263.

Received March 14, 1968