Refractive Index of Solutions Containing Poly(vinyl Acetate) and Poly(methyl Methacrylate)

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SYNOPSIS

Refractive index measurements can be used successfully for on-line evaluation of extent of reaction in solution polymerization reactors. For this reason, the refractive index of solutions containing *tert*-butanol (TBOH), methyl methacrylate (MMA), vinyl acetate (VA), poly(methyl methacrylate) (PMMA), and poly(vinyl acetate) (PVA) were measured and a mathematical correlation was developed to fit the experimental data. The correlation can be extended to fit published data obtained with different solvents.

INTRODUCTION

Refractive index measurements are very effective for the on-line evaluation of extent of reaction in solution polymerization reactors. This technique was used successfully by different researchers to study continuous solution homopolymerization reactions of MMA in ethyl acetate (see Schmidt[1]) and of VA in TBOH (see Teymour[2]). However, no attempt was made to extend the results obtained to conditions other than the normal operation conditions used in their experiments. Besides, no experimental data are available for solutions containing both monomers MMA and VA and both polymers PMMA and PVA. These data are fundamental for the study of copolymerization reactions.

In order to study the continuous solution copolymerization reaction of MMA and VA in TBOH, solutions containing different concentrations of MMA, VA, TBOH, PMMA, and PVA were prepared and their refractive indexes were measured. The experimental results were correlated, based on the equations developed by Lorimer[3,4] and Lorimer and Jones[5] for the refractive index of polymer solutions. The basic set of equations can be slightly changed to accommodate some results published previously and tabulated by Brandrup and Immergut[6] for solutions containing different solvents.

EXPERIMENTAL

The chemical species used throughout our work were *tert*-butanol (99.5% pure), vinyl acetate (99.9% pure), methyl methacrylate (99.9% pure), ethyl acetate (99.5% pure), acetone (99.5% pure), poly(vinyl acetate) (medium molecular weight) and poly(methyl methacrylate) (medium molecular weight). Vinyl acetate was bought from Pfaltz and Bauer, while the other chemicals were bought from Aldrich Chemical Co. The substances were not additionally purified because it was observed that the refractive index measurements were not sensitive to these small amounts of impurities and also because VA and MMA should contain small amounts of inhibitor (hydroquinone) in order for spontaneous thermal polymerization to be avoided during the preparation of the polymer solutions.

The polymer solutions were prepared under reflux conditions and with continuous agitation. The amount of heat had to be carefully controlled as it takes too much time for polymer to dissolve spontaneously in the solvent at low temperatures and

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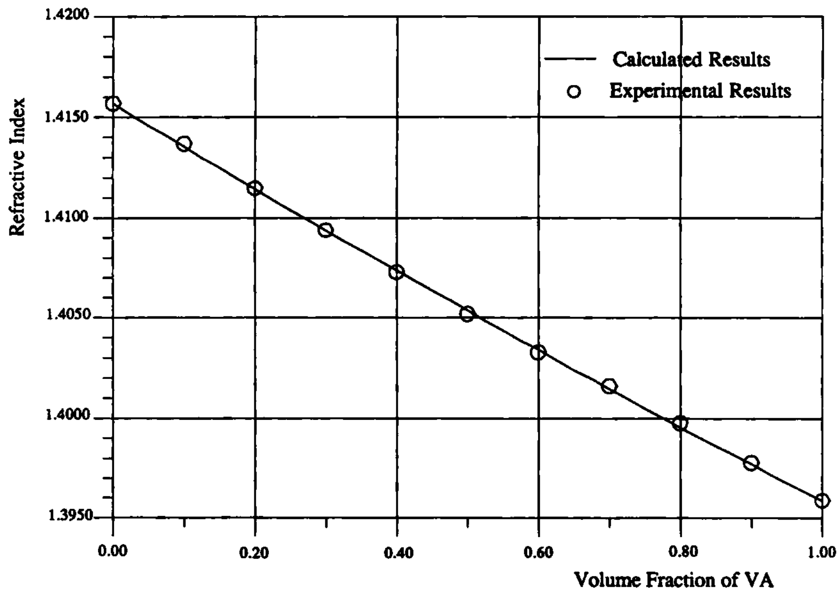

Figure 1 Refractive index of MMA/VA solutions.

homogeneous solutions cannot be prepared at large reflux rates. The refractive indexes were measured with a Bausch and Lomb, Model 33-45-56, desk top refractometer, at 1 atm and 20°C. The precision was equal to 0.0002.

Liquid solvents were prepared volumetrically with high precision pipettes. The final polymer solutions were prepared gravimetrically, with a Mettler PB30 scale (precision of 0.005 g) and a fixed amount of liquid solvent of 50 mL. Typically, one solution was prepared and four different refractive indexes were measured and saved for parameter evaluation. Additional solutions of equal composition were only prepared to check previous data when the difference between the largest and smallest measured refractive indexes was larger than 0.0015, which is the maximum oscillation expected at process conditions.

RESULTS

Three different sets of experimental results were obtained. The first set was used for parameter estimation and only contains results for binary non-

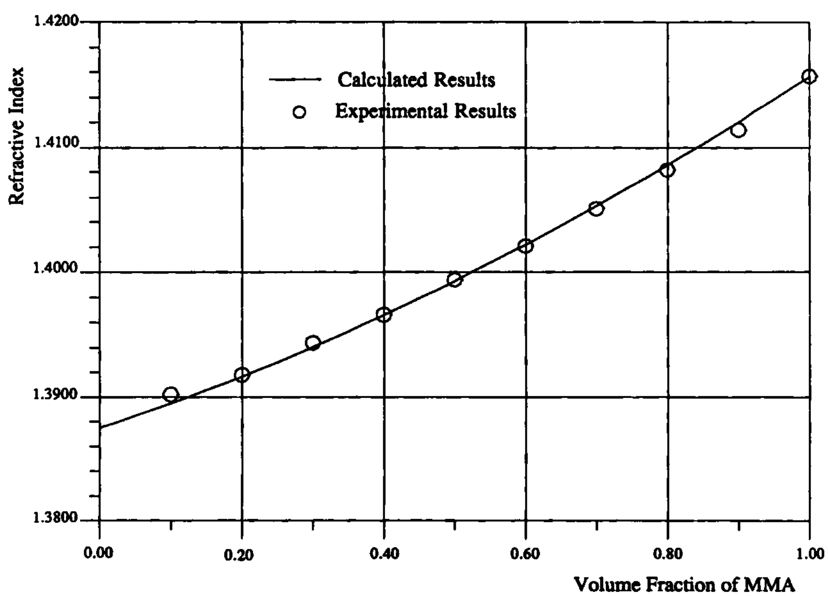

Figure 2 Refractive index of MMA/TBOH solutions.

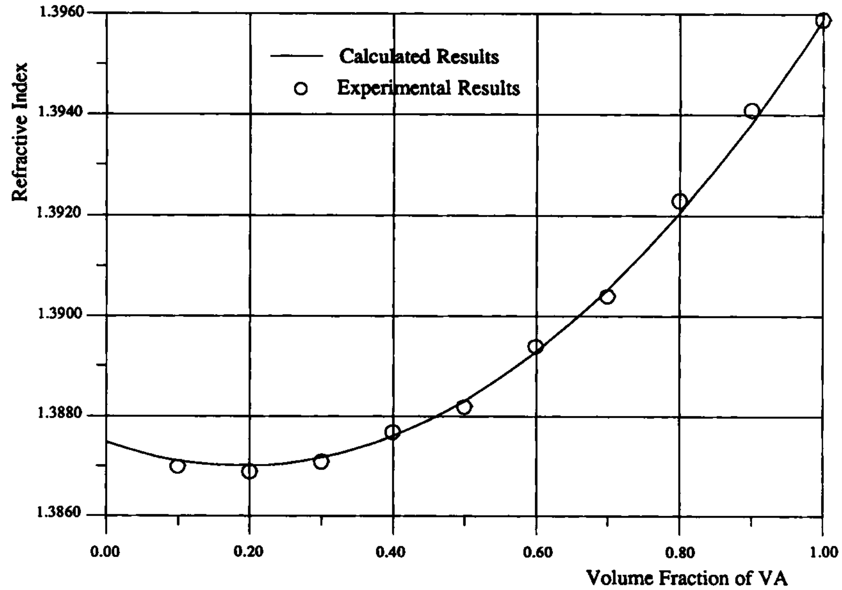

Figure 3 Refractive index of VA/TBOH solutions.

polymer solutions and binary and ternary polymer solutions. The basic set of solutions prepared for parameter estimation were:

—MMA + VA, at different concentrations
—MMA + TBOH, at different concentrations
—VA + TBOH, at different concentrations
—MMA + PMMA, at different concentrations
—MMA + PVA, at different concentrations
—VA + PMMA, at different concentrations
—VA + PVA, at different concentrations
—MMA + TBOH + PMMA, two different nonpolymer solutions at different polymer concentrations
—MMA + TBOH + PVA, two different nonpolymer solutions at different polymer concentrations
—VA + TBOH + PMMA, two different nonpolymer solutions at different polymer concentrations
—VA + TBOH + PVA, two different nonpolymer solutions at different polymer concentrations.

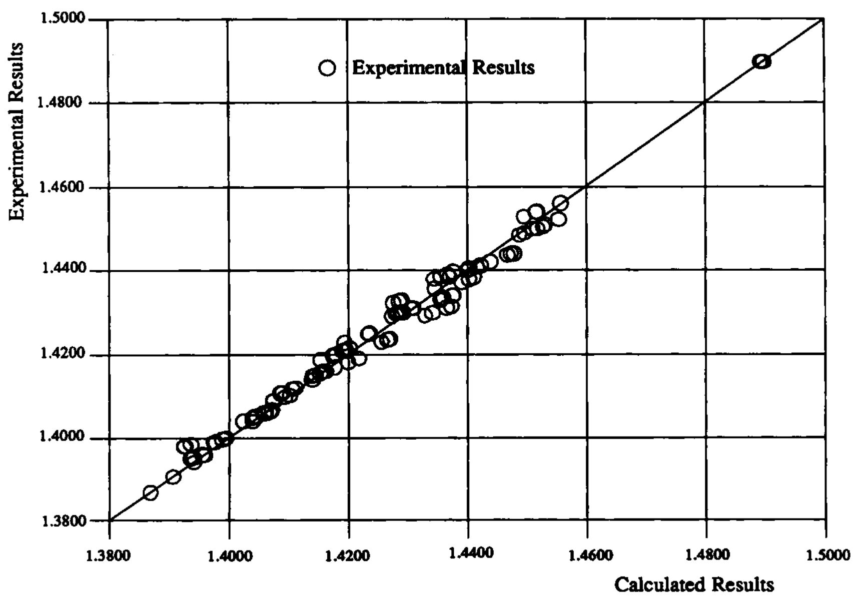

Figure 4 Refractive index of PMMA solutions.

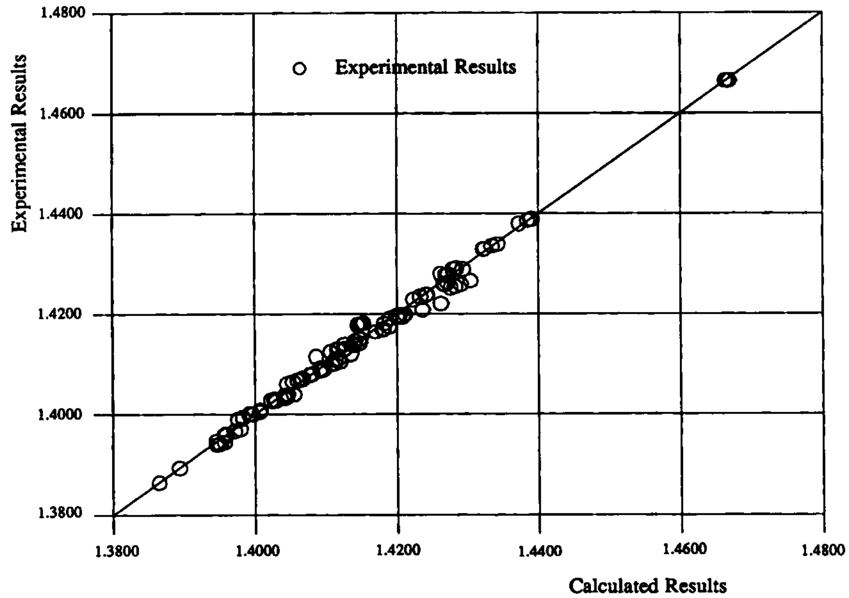

Figure 5 Refractive index of PVA solutions.

The results obtained are presented in Figures 1–5. All the data can be found in Tables I–IV of the supplementary material.

The second set of experimental data was used to check the results obtained and the performance of the mathematical correlation for more complex solutions. It contains refractive indexes of ternary nonpolymer solutions and four- and five-component polymer solutions. The solutions prepared were:

—MMA + equal-volume solution of TBOH and VA, at different concentrations
—VA + equal-volume solution of TBOH and MMA, at different concentrations
—MMA + VA + TBOH + PMMA + PVA, at different concentrations

The results obtained are presented in Figures 6–8. All the data can also be found in Tables A.V–A.VII of the supplementary material in Appendix A.

The third set of experimental data was used to evaluate how well the correlation obtained would fit the refractive index of PMMA and PVA solutions in other different solvents. The solutions prepared were:

—acetone + PMMA + PVA, at different concentrations

Table I Parameters Evaluated for the Empirical Correlation

Parameter	ν Evaluated from Measured Data	ν Evaluated from Brandrup and Immergut[6]
A_{12}	1.7193e-3	
A_{13}	−9.1899e-3	
A_{23}	−1.3516e-2	
a_1 PVA	−0.3081	0.1186
a_2 PVA	0.2144	−0.0893
ν_1 PVA	1.6098	1.1837
ν_2 PVA	−1.1032	−0.8000
a_1 PMMA	0.0910	−0.1898
a_2 PMMA	−0.0817	0.1276
ν_1 PMMA	1.1296	1.3603
ν_2 PMMA	−0.7328	−0.9058

Table II ν Tabulated in Brandrup and Immergut[6] for PMMA in Different Solvents

Solvent	Refractive Index	ν (Mean Value)
Acetone	1.3588	0.1310
Acetonitrile	1.3442	0.1385
Benzene	1.5011	0.0043
n-Butyl acetate	1.3941	0.0987
Carbon tetrachloride	1.4601	0.0230
Chlorobenzene	1.5241	−0.0233
Chloroform	1.4459	0.0602
Dioxane	1.4165	0.0712
DMF	1.4305	0.0624
Ethyl acetate	1.3723	0.1196
Methyl ethyl ketone	1.3788	0.1066
MMA	1.4140	0.0934
Toluene	1.4961	0.0072

Table III ν **Tabulated in Brandrup and Immergut[6] for PVA in Different Solvents**

Solvent	Refractive Index	ν (Mean Value)
Acetone	1.3588	0.1043
Acetonitrile	1.3442	0.1040
Benzene	1.5011	0.0038
n-Butyl acetate	1.3941	0.0716
Chlorobenzene	1.5241	−0.0458
Dioxane	1.4165	0.0280
Ethyl acetate	1.3723	0.0870
Ethyl formate	1.3598	0.0950
Methyl ethyl ketone	1.3788	0.0800
Methanol	1.3288	0.1262
Methyl isobuthyl ketone	1.3962	0.0680
Tetrahydrofuran	1.4050	0.0582

—ethyl acetate + PMMA + PVA, at different concentrations

The results obtained are shown in Figure 9. The data can also be found in Table A.VIII of the supplementary material in Appendix A.

THEORETICAL ANALYSIS

According to the Onsager–Böttcher theory (see Lorimer[3]), the refractive index of a mixture containing two or more different solvents can be calculated from

$$\frac{\eta^2 - 1}{\eta^2} = \sum_{i=1}^{NC} \phi_i \frac{(\eta_i^2 - 1)(2\eta_i^2 + \eta_i^{*2})}{\eta_i^2(2\eta^2 + \eta_i^{*2})} \tag{1}$$

where η_i^* is related to the molecular radius r_i and to the molecular polarizability α_i as

$$\eta_i^{*2} = \frac{[1 + 2(\alpha_i/r_i^3)]}{[1 - (\alpha_i/r_i^3)]} \tag{2}$$

According to Lorimer,[4] eqs. (1) and (2) can be changed for polymer solutions to

$$\eta = \eta_0 + \nu c_p + a c_p^2 \tag{3}$$

If the polymer is dissolved in a single solvent, ν and a are given by

$$\nu = \frac{\eta_1^3}{2}\left(\frac{2\eta_1^2 + \eta_1^{*2}}{2\eta_1^4 + \eta_1^{*2}}\right)\left[v_p\left(\frac{\eta_p^2 - 1}{\eta_p^2}\right)\left(\frac{2\eta_p^2 + \eta_p^{*2}}{2\eta_1^2 + \eta_p^{*2}}\right) - \bar{v}_p\left(\frac{\eta_1^2 - 1}{\eta_1^2}\right)\right] \tag{4}$$

$$a = \frac{(3\eta_1^2 - 2)\nu^2}{2\eta_1(\eta_1^2 + 2)} - \frac{(\eta_1^2 - 1)(\eta_1^2 + 2)}{12\eta_1}\frac{\partial \bar{v}_p}{\partial c_p} \tag{5}$$

If the actual solvent is a mixture of different chemical species, then ν and a are functions of ϕ_i and, although it is not difficult to derive the new equations, the new equations are very complex. Hert and Strazielle[7] observed, however, that ν was essentially a linear function of η_0. Sroda[8] found the same relationship between a and η_0 for some mixtures of TBOH, VA, and PVA. For these reasons, it is assumed from now on that the following equations hold:

$$\nu = \nu_1 + \nu_2\eta_0 \tag{6}$$

$$a = a_1 + a_2\eta_0 \tag{7}$$

Table IV Comparison Between Predicted and Measured Data

Correlation	Polymer	Maximum Deviation	Standard Deviation
Empirical	PMMA	0.0058	0.0023
ν from measured data	PVA	0.0041	0.0012
Empirical	PMMA	0.0080	0.0031
ν from Brandrup and Immergut[6]	PVA	0.0052	0.0014
Onsager–Böttcher and Lorimer[3] [a]	PMMA	0.0030	0.0014
	PVA	0.0025	0.0012
Experimental deviation	PMMA	0.0015[b]	0.0008
	PVA	0.0015[b]	0.0006

[a] Obtained with MMA and VA only.
[b] Condition imposed.

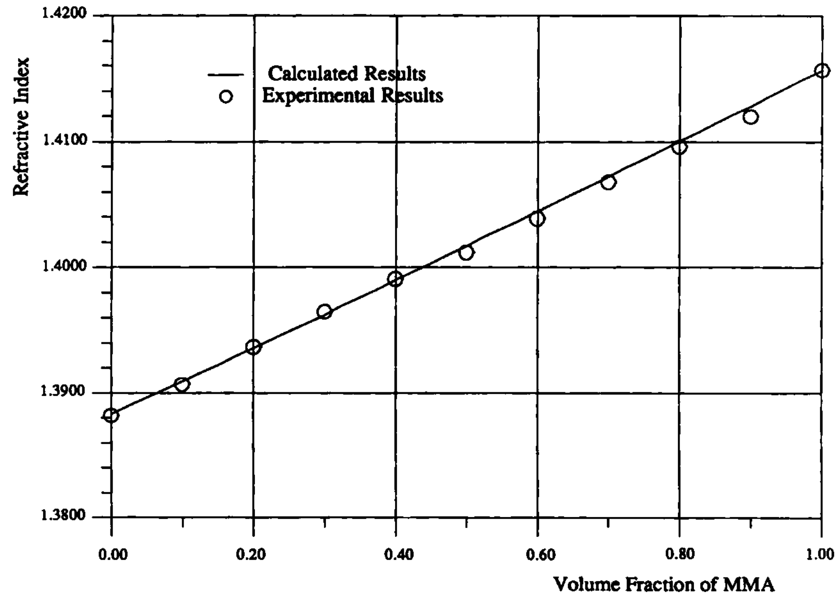

Figure 6 Refractive index of solutions containing MMA in equal volume solution of VA/TBOH.

Besides, in order to avoid using eq. (1) to solve eq. (3) in terms of ϕ_i and c_p, it is also assumed that η_0 can be calculated as

$$\eta_0 = \sum_{i=1}^{NC} \phi_i \eta_i + \sum_{i=1}^{NC-1} \sum_{j=i+1}^{NC} A_{ij} \phi_i \phi_j \qquad (8)$$

where the second term on the right-hand side compensates for deviations of the ideal law due to the interactions between two different chemical species. According to Brandrup and Immergut,[6] it can also be assumed that

$$\nu = \sum_{i=1}^{NP} \omega_i \nu_i \qquad (9)$$

$$a = \sum_{i=1}^{NP} \omega_i a_i \qquad (10)$$

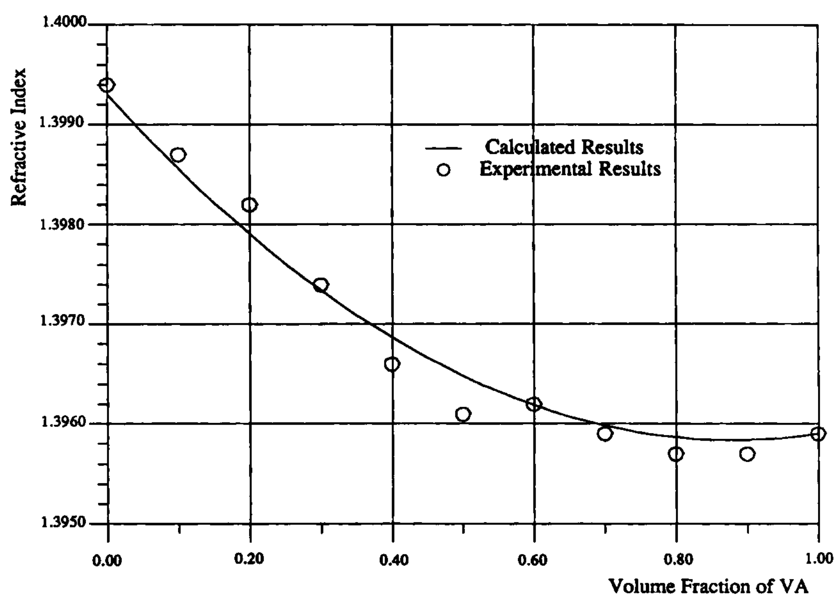

Figure 7 Refractive index of solutions containing VA in equal volume solution of MMA/TBOH.

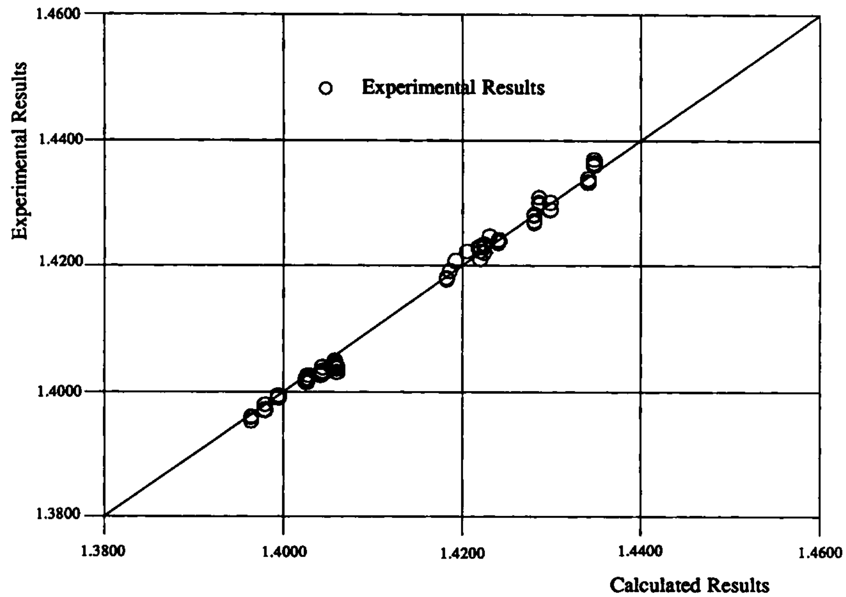

Figure 8 Refractive index of multicomponent solutions containing PVA and/or PMMA.

for mixtures containing more than one type of polymer or for copolymer solutions.

Equations (3) and (6)–(10) constitute the mathematical model analyzed, where the parameters A_{12} (MMA/VA), A_{13} (MMA/TBOH), A_{23} (VA/TBOH), ν_1, ν_2, a_1, and a_2 (for both PMMA and PVA) have to be evaluated. It is important to emphasize that ν and a were assumed to be independent of the average molecular weight, as always happens for medium and high molecular weight polymers.

PARAMETER EVALUATION AND DISCUSSION

All parameters described here were evaluated with the routines provided by the standard computational package MINPACK,[9] using standard least square technique. Parameters A_{12}, A_{13}, and A_{23} were evaluated only with the data presented in Figures 1, 2, and 3, respectively (Tables A.I–A.III of the supplementary material in Appendix A). The parameters

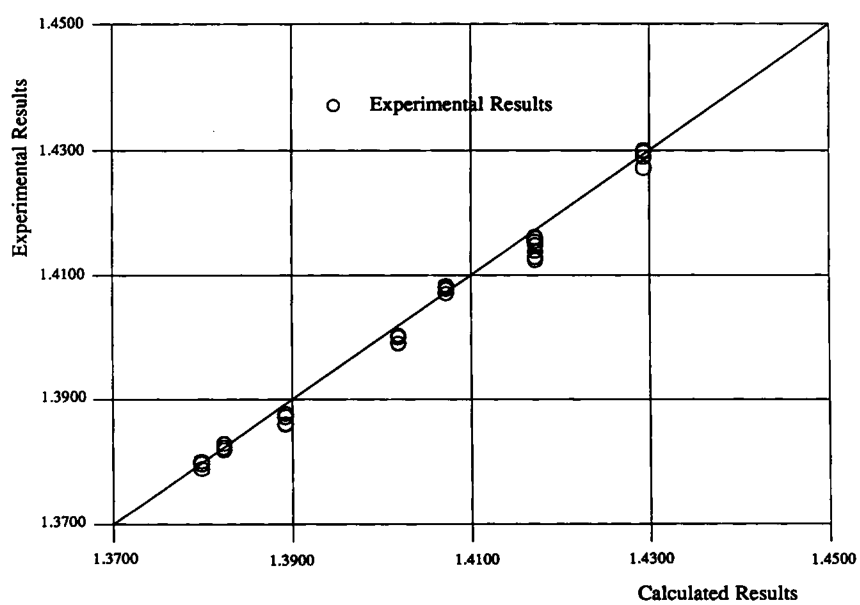

Figure 9 Refractive index of PMMA and PVA solutions in ethyl acetate and acetone.

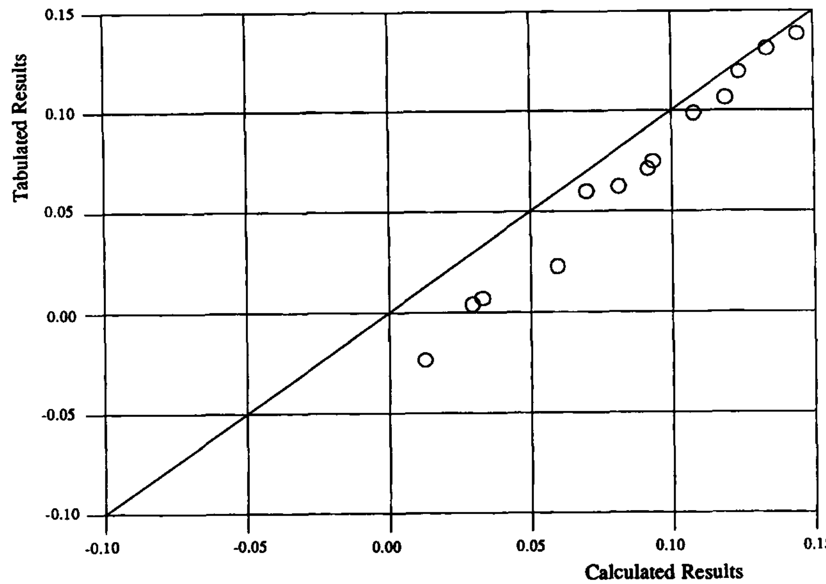

Figure 10 Comparison between calculated and tabulated ν for PMMA in different solvents.

ν_1, ν_2, a_1, and a_2 for both PMMA and PVA were evaluated with the other results obtained with the first set of experiments (Figs. 4 and 5 and Table A.IV of the supplementary material). The results are shown in Table I. It can be seen from Figures 1–5 that the parameters fit very well to the experimental data. Figures 6–9 show that the parameters estimated are also effective to describe the behavior of more complex solutions, containing multiple components and other different solvents.

If one compares the results tabulated by Brandrup and Immergut,[6] shown in Tables II and III, for the relationship between ν and η_0 for solutions of PMMA and PVA in different solvents against those obtained from eq. (6) and the parameters presented in Table I, then Figures 10 and 11 can be drawn. It can be seen that the calculated results are almost always larger than the results published previously for both PMMA and PVA. If the results presented in Tables II and III are used for the evaluation of ν_1 and ν_2 for

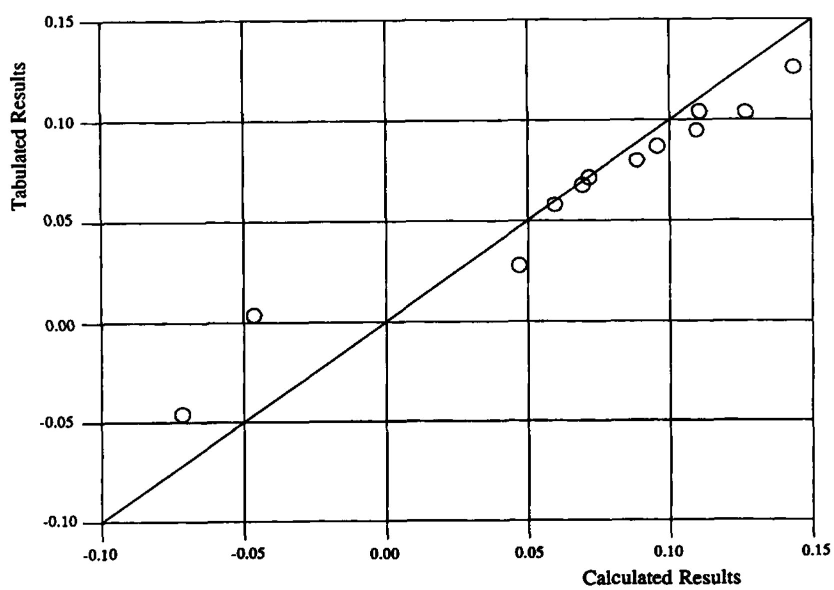

Figure 11 Comparison between calculated and tabulated ν for PVA in different solvents.

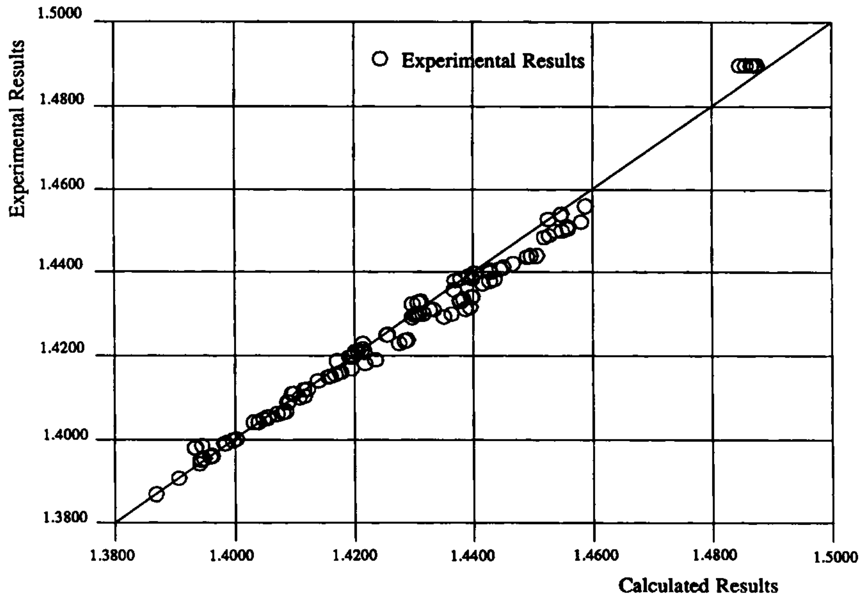

Figure 12 Refractive index of PMMA solutions (ν calculated from Table II).

both PMMA and PVA, and the results obtained with the first set of experiments are used to calculate a_1 and a_2 only, then the results shown in Table I can be obtained. Particularly, Figures 4, 5, 8, and 9 can be redrawn, as shown in Figures 12–15, showing that the new parameters still fit the experimental data very well.

Table IV shows some numbers for statistical analysis. It can be seen that model deviations are not very different from experimental deviations for PVA solutions, although they cannot be neglected for PMMA solutions.

The experimental data can also be used for the estimation of η_i^*, $\bar{v}_p$, and $\partial \bar{v}_p / \partial c_p$ in eqs. (1), (4), and (5). These parameters are shown in Table V, when only pure MMA and VA are used as solvents. The parameters estimated are very consistent, since the specific volume of PMMA and PVA are 0.8469

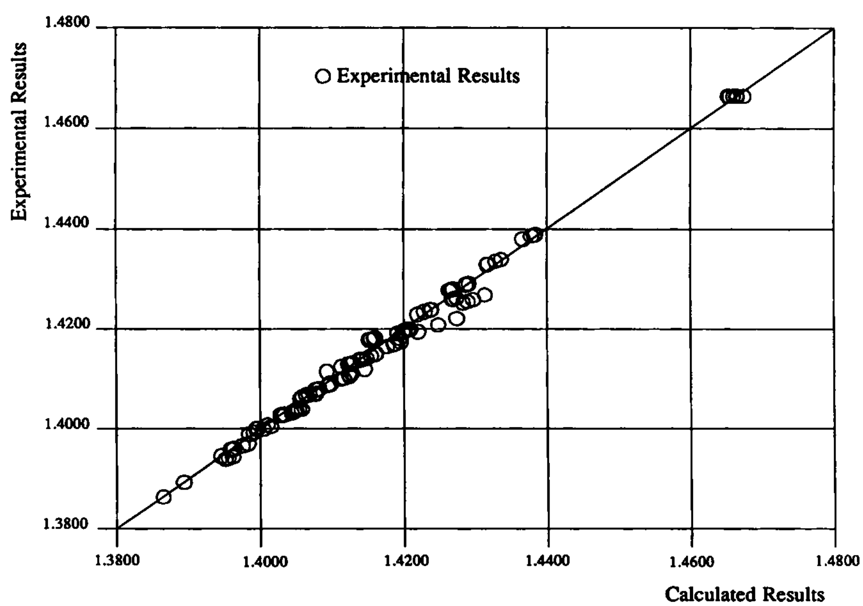

Figure 13 Refractive index of PVA solutions (ν calculated from Table III).

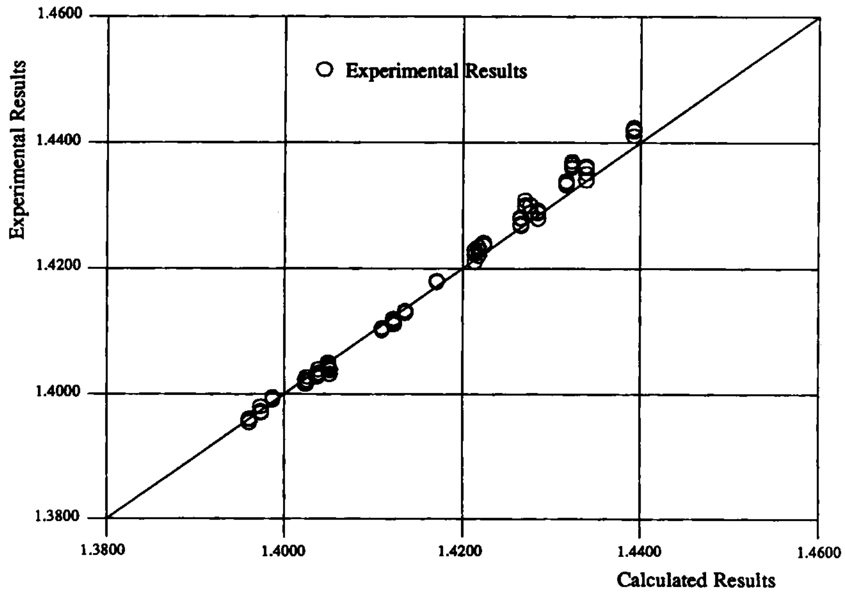

Figure 14 Refractive index of multicomponent solutions containing PVA and/or PMMA (ν calculated from Tables II and III).

and 0.8399 mL/g, respectively, and, as observed experimentally, MMA is a better solvent than VA and PVA dissolves faster than PMMA in both solvents. (It means that $\partial \bar{v}_p / \partial c_p$ should be larger for PMMA and VA solutions, as obtained and presented in Table V.)

Although Table IV suggests that the theoretical correlation is better than the empirical ones, one must realize that: (1) the theoretical correlation needs more parameters than the empirical ones; (2) the standard deviation for solutions containing PVA was the same, no matter which correlation was used; (3) the results obtained with the theoretical correlation considered only refractive indexes of simple solutions, without TBOH. If more complex solvents are to be used, eqs. (4) and (5) have to be changed

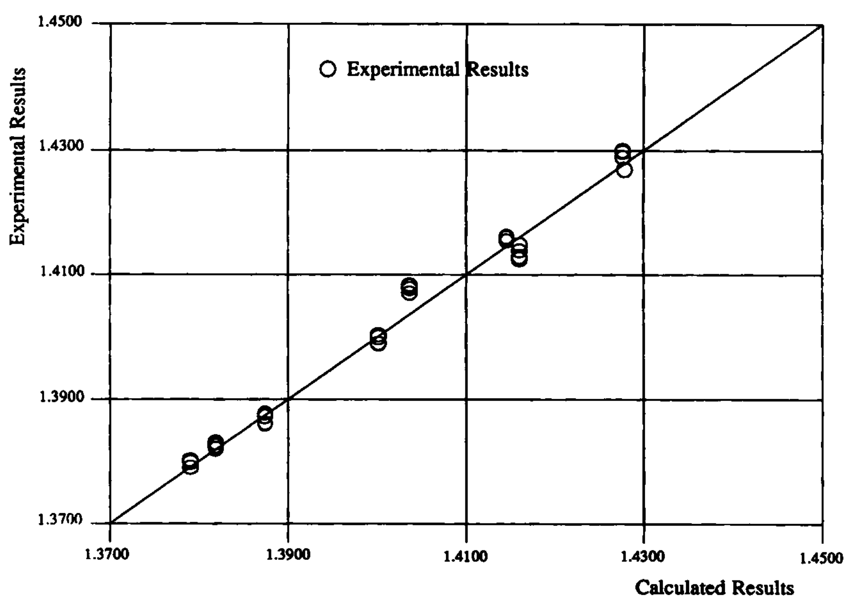

Figure 15 Refractive index of PMMA and PVA solutions in ethyl acetate and acetone (ν calculated from Tables II and III).

Table V Parameters Evaluated for the Onsager–Böttcher and Lorimer[3] Theoretical Correlation

Parameter	Solvent	Polymer	Result
η_p^*	MMA	PMMA	0.862
		PVA	0.508
	VA	PMMA	0.320
		PVA	1.070
$\bar{v}_p$	MMA	PMMA	0.862
		PVA	0.879
	VA	PMMA	0.887
		PVA	0.878
$\frac{\partial \bar{v}_p}{\partial c_p}$	MMA	PMMA	0.108
		PVA	0.022
	VA	PMMA	0.126
		PVA	0.066
η_{MMA}^*			3.88
η_{VA}^*			7.17
η_{TBOH}^*			0.00

and new sets of parameters have to be estimated, increasing the number of parameters even more. Besides, the standard deviation and maximum deviation will almost certainly increase if more complex solutions are taken into consideration.

CONCLUSION

Refractive indexes of solutions containing TBOH, MMA, VA, PMMA, and PVA were measured and parameters were evaluated to fit the experimental data using both an empirical correlation and a theoretical one. As the predictions obtained with the theoretical correlation were not better than those obtained with the much simpler empirical equations, the last ones can be safely used for on-line measurement of polymer concentration in solution polymerization reactors.

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NOMENCLATURE

a	second-order coefficient in eq. (3) [(g/mL)$^{-2}$]
a_1, a_2	coefficients in eq. (7)
A_{ij}	coefficients in eq. (8)
c_p	polymer concentration (g/mL)
NC	number of different chemical species
NP	number of different polymers in solution
r	molecular radius
v	specific volume (mL/g)
$\bar{v}$	partial volume (mL/g)

Greek

α	molecular polarizability
ϕ	volume fraction
η	refractive index
η^*	specific refractive index
ν	incremental coefficient in eq. (3) [(g/mL)$^{-1}$]
ν_1, ν_2	coefficients in eq. (6)
ω	mass fraction in the polymer or copolymer phase

Special Indexes

0	general solvent
1	1-component solvent
p	polymer

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APPENDIX A: SUPPLEMENTARY TABLES

Table A.I Refractive Index of MMA/VA Solutions

Composition Volume Fraction of VA	Refractive Index 1	2	3	4
0.00	1.3957	1.3959	1.3959	1.3961
0.10	1.3978	1.3978	1.3978	1.3977
0.20	1.3997	1.3998	1.3999	1.3999
0.30	1.4017	1.4015	1.4016	1.4016
0.40	1.4035	1.4033	1.4033	1.4032
0.50	1.4053	1.4052	1.4050	1.4052
0.60	1.4072	1.4072	1.4073	1.4076
0.70	1.4094	1.4095	1.4094	1.4094
0.80	1.4118	1.4113	1.4115	1.4114
0.90	1.4137	1.4136	1.4138	1.4137
1.00	1.4158	1.4155	1.4158	1.4157

Table A.II Refractive Index of MMA/TBOH Solutions

Composition Volume Fraction of MMA	Refractive Index 1	2	3	4
0.10	1.3902	1.3902	1.3903	1.3901
0.20	1.3917	1.3918	1.3919	1.3918
0.30	1.3944	1.3944	1.3942	1.3945
0.40	1.3964	1.3967	1.3966	1.3966
0.50	1.3994	1.3994	1.3995	1.3994
0.60	1.4019	1.4021	1.4022	1.4021
0.70	1.4052	1.4051	1.4051	1.4050
0.80	1.4082	1.4082	1.4082	1.4082
0.90	1.4113	1.4114	1.4113	1.4116
1.00	1.4158	1.4155	1.4158	1.4157

Table A.III Refractive Index of VA/TBOH Solutions

Composition Volume Fraction of VA	Refractive Index 1	2	3	4
0.10	1.3868	1.3871	1.3870	1.3870
0.20	1.3868	1.3869	1.3870	1.3869
0.30	1.3870	1.3871	1.3873	1.3870
0.40	1.3876	1.3879	1.3877	1.3877
0.50	1.3881	1.3883	1.3883	1.3882
0.60	1.3895	1.3894	1.3894	1.3894
0.70	1.3903	1.3906	1.3903	1.3904
0.80	1.3925	1.3922	1.3922	1.3923
0.90	1.3943	1.3941	1.3938	1.3941
1.00	1.3957	1.3959	1.3959	1.3961

Table A.IV Refractive Index of Polymer Solutions Set 01

Solvent Concentration Volume Fraction			Polymer Concentration Mass Fraction		Refractive Index			
MMA	VA	TBOH	PMMA	PVA	1	2	3	4
1.00	0.00	0.00	0.10	0.00	1.4209	1.4211	1.4211	1.4215
1.00	0.00	0.00	0.20	0.00	1.4297	1.4299	1.4301	1.4301
1.00	0.00	0.00	0.30	0.00	1.4385	1.4400	1.4400	1.4400
1.00	0.00	0.00	0.40	0.00	1.4485	1.4490	1.4500	1.4500
1.00	0.00	0.00	0.50	0.00	1.4529	1.4539	1.4540	1.4540
1.00	0.00	0.00	0.00	0.10	1.4195	1.4195	1.4195	1.4200
1.00	0.00	0.00	0.00	0.20	1.4230	1.4235	1.4240	1.4239
1.00	0.00	0.00	0.00	0.30	1.4278	1.4279	1.4280	1.4290
1.00	0.00	0.00	0.00	0.40	1.4330	1.4331	1.4336	1.4340
1.00	0.00	0.00	0.00	0.50	1.4381	1.4387	1.4389	1.4390
0.66	0.00	0.33	0.10	0.00	1.4108	1.4121	1.4110	1.4118
0.66	0.00	0.33[a]	0.20	0.00	1.4187	1.4197	1.4200	1.4197
0.33	0.00	0.66[a]	0.10	0.00	1.3950	1.3942	1.3950	1.3950
0.66	0.00	0.33	0.00	0.10	1.4079	1.4081	1.4089	1.4087
0.66	0.00	0.33	0.00	0.20	1.4131	1.4138	1.4142	1.4132
0.66	0.00	0.33	0.00	0.30	1.4197	1.4192	1.4199	1.4199
0.66	0.00	0.33	0.00	0.40	1.4263	1.4261	1.4260	1.4260
0.66	0.00	0.33	0.00	0.50	1.4311	1.4312	1.4320	1.4311
0.33	0.00	0.66	0.00	0.10	1.4002	1.4001	1.4009	1.4009
0.33	0.00	0.66	0.00	0.20	1.4065	1.4065	1.4070	1.4068
0.33	0.00	0.66	0.00	0.30	1.4115	1.4125	1.4130	1.4130
0.33	0.00	0.66	0.00	0.40	1.4180	1.4179	1.4183	1.4182
0.33	0.00	0.66	0.00	0.50	1.4230	1.4242	1.4238	1.4237
0.00	1.00	0.00	0.10	0.00	1.4043	1.4049	1.4052	1.4058
0.00	1.00	0.00	0.20	0.00	1.4149	1.4151	1.4160	1.4155
0.00	1.00	0.00	0.30	0.00	1.4311	1.4311	1.4297	1.4299
0.00	1.00	0.00	0.40	0.30	1.4383	1.4373	1.4373	1.4379
0.00	1.00	0.00	0.00	0.10	1.4027	1.4033	1.4035	1.4040
0.00	1.00	0.00	0.00	0.20	1.4092	1.4100	1.4106	1.4102
0.00	1.00	0.00	0.00	0.30	1.4165	1.4170	1.4171	1.4175
0.00	1.00	0.00	0.00	0.40	1.4253	1.4260	1.4256	1.4267
0.00	1.00	0.00	0.00	0.50	1.4281	1.4290	1.4292	1.4292
0.00	0.66	0.33	0.10	0.00	1.3990	1.3991	1.3997	1.4000
0.00	0.66	0.33	0.20	0.00	1.4089	1.4090	1.4099	1.4103
0.00	0.66	0.33	0.30	0.00	1.4230	1.4235	1.4230	1.4237
0.00	0.66	0.33	0.40	0.00	1.4331	1.4340	1.4341	1.4330
0.00	0.66	0.33	0.50	0.00	1.4427	1.4430	1.4415	1.4415
0.00	0.66	0.33	0.00	0.10	1.3960	1.3961	1.3967	1.3971
0.00	0.66	0.33	0.00	0.20	1.4028	1.4030	1.4038	1.4040
0.00	0.66	0.33	0.00	0.30	1.4110	1.4112	1.4112	1.4121
0.00	0.66	0.33[a]	0.00	0.40	1.4195	1.4195	1.4210	1.4209
0.00	0.33	0.66	0.10	0.00	1.3951	1.3950	1.3953	1.3960
0.00	0.33	0.66	0.20	0.00	1.4053	1.4060	1.4067	1.4065
0.00	0.33	0.66	0.30	0.00	1.4170	1.4181	1.4170	1.4185
0.00	0.33	0.66	0.40	0.00	1.4234	1.4245	1.4247	1.4234
0.00	0.33	0.66	0.50	0.00	1.4329	1.4327	1.4322	1.4329
0.00	0.33	0.66	0.00	0.10	1.3940	1.3940	1.3942	1.3945
0.00	0.33	0.66	0.00	0.20	1.3990	1.3993	1.4000	1.4005
0.00	0.33	0.66	0.00	0.30	1.4061	1.4071	1.4061	1.4072
0.00	0.33	0.66[a]	0.00	0.40	1.4151	1.4140	1.4147	1.4150

[a] We were not able to prepare solutions with higher polymer concentration.

Table A.V Refractive Index of MMA in Equal Volume Mixture of VA and TBOH

Composition Volume Fraction of MMA	Refractive Index			
	1	2	3	4
0.00	1.3881	1.3883	1.3882	1.3883
0.10	1.3907	1.3908	1.3907	1.3907
0.20	1.3937	1.3937	1.3937	1.3937
0.30	1.3965	1.3963	1.3965	1.3966
0.40	1.3992	1.3990	1.3990	1.3991
0.50	1.4010	1.4013	1.4012	1.4012
0.60	1.4039	1.4039	1.4039	1.4039
0.70	1.4064	1.4066	1.4068	1.4068
0.80	1.4097	1.4096	1.4095	1.4095
0.90	1.4119	1.4120	1.4121	1.4120
1.00	1.4158	1.4155	1.4157	1.4158

Table A.VI Refractive Index of VA in Equal Volume Mixture of MMA and TBOH

Composition Volume Fraction of VA	Refractive Index			
	1	2	3	4
0.00	1.3994	1.3994	1.3995	1.3994
0.10	1.3988	1.3986	1.3987	1.3987
0.20	1.3983	1.3981	1.3981	1.3982
0.30	1.3975	1.3974	1.3974	1.3974
0.40	1.3964	1.3967	1.3966	1.3966
0.50	1.3959	1.3961	1.3962	1.3961
0.60	1.3961	1.3963	1.3963	1.3962
0.70	1.3960	1.3959	1.3958	1.3959
0.80	1.3956	1.3957	1.3958	1.3957
0.90	1.3956	1.3958	1.3958	1.3957
1.00	1.3957	1.3959	1.3961	1.3959

Table A.VII Refractive Index of Polymer Solutions Set 02

Solvent Concentration Volume Fraction			Polymer Concentration Mass Fraction		Refractive Index			
MMA	VA	TBOH	PMMA	PVA	1	2	3	4
0.33	0.33	0.33	0.10	0.00	1.4031	1.4039	1.4032	1.4038
0.33	0.33	0.33	0.40	0.00	1.4361	1.4370	1.4365	1.4360
0.33	0.33	0.33	0.00	0.10	1.4019	1.4027	1.4021	1.4022
0.33	0.33	0.33	0.00	0.40	1.4235	1.4230	1.4230	1.4221
0.33	0.33	0.33	0.05	0.05	1.4029	1.4031	1.4033	1.4039
0.33	0.33	0.33	0.20	0.20	1.4300	1.4309	1.4301	1.4299
0.40	0.10	0.50	0.10	0.00	1.4047	1.4042	1.4050	1.4044
0.40	0.10	0.50	0.40	0.00	1.4339	1.4339	1.4335	1.4333
0.40	0.10	0.50	0.00	0.10	1.4015	1.4020	1.4021	1.4022
0.40	0.10	0.50	0.00	0.40	1.4215	1.4223	1.4229	1.4230
0.40	0.10	0.50	0.05	0.05	1.4031	1.4031	1.4027	1.4030
0.40	0.10	0.50	0.20	0.20	1.4269	1.4272	1.4280	1.4282
0.10	0.40	0.50	0.10	0.00	1.3991	1.3992	1.3995	1.3995
0.10	0.40	0.50	0.40	0.00	1.4290	1.4290	1.4289	1.4301
0.10	0.40	0.50	0.00	0.10	1.3955	1.3961	1.3960	1.3961
0.10	0.40	0.50	0.00	0.40	1.4180	1.4180	1.4179	1.4181
0.10	0.40	0.50	0.05	0.05	1.3970	1.3972	1.3980	1.3980
0.10	0.40	0.50	0.20	0.20	1.4241	1.4239	1.4237	1.4241
0.50	0.50	0.00	0.10	0.00	1.4129	1.4133	1.4131	1.4133
0.50	0.50	0.00	0.40	0.00	1.4411	1.4421	1.4423	1.4419
0.50	0.50	0.00	0.00	0.10	1.4101	1.4104	1.4103	1.4105
0.50	0.50	0.00	0.00	0.40	1.4280	1.4290	1.4292	1.4289
0.50	0.50	0.00	0.05	0.05	1.4111	1.4114	1.4118	1.4120
0.50	0.50	0.00	0.20	0.20	1.4345	1.4360	1.4351	1.4360

Table A.VIII Refractive Index of Polymer Solution Set 03

	Polymer Concentration Mass Fraction		Refractive Index			
Solvent	PMMA	PVA	1	2	3	4
Acetone	0.10	0.00	1.3700	1.3700	1.3701	1.3708
	0.50	0.00	1.4139	1.4130	1.4139	1.4125
	0.00	0.10	1.3670	1.3678	1.3671	1.3680
	0.00	0.50	1.4084	1.4071	1.4078	1.4082
	0.15	0.15	1.3860	1.3861	1.3875	1.3872
Ethyl acetate	0.10	0.00	1.3830	1.3829	1.3824	1.3820
	0.50	0.00	1.4289	1.4298	1.4285	1.4300
	0.00	0.10	1.3790	1.3798	1.3802	1.3802
	0.00	0.50	1.4149	1.4155	1.4160	1.4162
	0.15	0.15	1.3990	1.3991	1.4000	1.4004