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Specific Refractive Index Increments of Polybutadiene, Styrene-Butadiene Rubber, Crepe Rubber, Polystyrene, Polymethyl Methacrylate, and Styrene-Methyl Methacrylate in Various Solvents and Variation of Refractive Index Increment with Molecular Weight

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ABSTRACT

The specific refractive index increments (ν) of polybutadiene (PB) at 5460 and 4360 Å wavelengths and of styrene-butadiene rubber at 4360 Å wavelength were determined in various solvents, whereas the values of ν for crepe rubber at 5460 and 4360 Å and for polystyrene, polymethyl methacrylate, and styrene-methyl methacrylate at 5460 Å wavelength were taken from the literature. From these values mathematical equations are proposed whereby the refractive index of these polymers can be determined from the refractive index of solvents only. The variation of ν with molecular weight was also studied by fractionating PB and determining the ν of these different molecular weight samples. No significant difference in the ν values could be observed in the molecular weight range of 33,000 to 350,000.

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INTRODUCTION

The determination of refractive index increment $(d\bar{n}/dc)_{c\to 0} = \nu_m$ or ν_c or ν is an important parameter for molecular weight determination by light-scattering gel permeation chromatography for the determination of the composition of copolymers. The usual procedure for determining ν is by measuring the refractive index increments ν of solutions at various concentrations by differential refractometer and extrapolating to infinite dilution:

$$\left(\frac{d\bar{n}}{d\bar{c}}\right)_{\lambda,T} = \lim_{c\to 0}\left(\frac{\Delta n}{c}\right)_{\lambda,T} = \nu$$

This procedure for determining ν is time consuming. A simplified method would be helpful.

Several studies have been reported for the determination of ν for a specific polymer from correlations with the refractive index of the solvent. Among these, those of Lorenz-Lorenz [2] and Gladstone and Dale [2] were discarded on the grounds that they frequently gave inaccurate results due to the extrapolations and use of reciprocal densities. The specific refractive index increment for a polymer solvent pair depends on the intrinsic refractive index of each component and their densities.

$$\nu = \frac{\tilde{n}_2}{d_2} - \left(\frac{1}{d_1}\right)\tilde{n}_1 \qquad (1)$$

where $\tilde{n}_2$, the refractive index of the polymer, can be calculated by plotting ν against $\tilde{n}_0$ and extrapolating to $\nu = 0$.

Angulo et al. [3] determined the specific refractive index increments for Guayule rubber in four different solvents and gave mathematical expressions of the straight-line relationship between ν and n_0. Lange and Baumann [4] observed a similar relationship for different composition of SAN copolymers in various solvents using n_D^{25}. In this communication we report the linear relationship applicable for polybutadiene (PB), styrene-butadiene rubber (SBR), crepe rubber, polystyrene (PS), polymethyl methacrylate (PMMA), and styrene-methyl methacrylate (SMMA) in several solvents for calculating the value of ν.

Variation of ν with molecular weight has also been reported in the literature [5]. Several workers [6, 7] report that ν is independent of

molecular weight above 10,000. Others [8] have observed that ν varies with molecular weight with asymptotic behavior above 50,000. Our investigation showed that ν is independent of molecular weight in the range of 33,000 to 350,000 in the case of cis-PB in two solvents–toluene and chloroform.

EXPERIMENTAL

For the Determination of ν of PB and SBR in Various Solvents

Materials

PB (from M/s Indian Petrochemicals Ltd., Baroda, India) and SBR (from M/s Synthetics & Chemicals, Bareilly, India) were purified by the method of Kolthoff and Lee [9] and then dissolved in the solvents (concentration approximately 0.3%). The solutions were then centrifuged (15,000 rpm) to remove any gel. The concentrations were determined by evaporation. Solutions of desired concentrations were then made by dilution with fresh solvent.

Solvents

The solvents used in this work are given in Table 1 and along with their refractive indices at the specified wavelengths. Except for butanone, carbon tetrachloride, and acetone, all solvents were purified by distillation followed by deacetylation by nitrogen.

Differential Refractometry

A Brice-Phoenix differential refractometer, model BP-2000-V, was used to measure the refractive index difference between the solution and the solvent. The instrument constant was determined by using an NaCl solution for which the displacement was measured. ϕ was calculated from

$$\Delta n = \phi \Delta d$$

where Δd is the displacement observed. The Δn values used in the calibration were taken from the literature [10].

Concentrations of PB in the different solvents used were below 1.0×10^{-3} g/mL. Ten determinations of Δn were made for each concentration of PB at 25 ± 0.02°C at 4360 and 5460 Å wavelength. Taking the average by least squares, ν was calculated from the extrapolated value of $c \to 0$.

TABLE 1. Refractive Indices of the Solvents at 5460 and 4360 Å Wavelengths

No.	Solvents	$n^{25}_{5460\ Å}$	$n^{25}_{4360\ Å}$	Refs.
1	n-Hexane	1.3802	1.3737	3
2	Cyclohexane	1.4010[a]	1.4330[a]	-
3	Benzene	1.5020	1.5200	12
4	Cumene	-	1.4701[a]	-
5	n-Heptane	1.3870	1.3936	13
6	Toluene	1.4980	1.5151	3
7	Carbon tetrachloride	1.4610	1.4700	12
8	Butanone	1.3790	1.3860	12
9	Acetone	1.3570[a]	-	-
10	Chlorobenzene	1.5240[a]	1.5068[a]	-
11	Chloroform	1.4446	1.4536	3
12	THF	1.4066	1.4134	3
13	Cyclohexene	1.4400	1.4550	13
14	Decaline	1.4680[a]	1.4781[a]	-
15	m-Xylene	-	1.4943[a]	-

[a]These values were experimentally determined.

For the Study of the Effect of Molecular Weight on ν

For studying the influence of molecular weight on ν, purified PB was fractionated at 30°C with benzene-methanol as the solvent-nonsolvent system. Four fractions were obtained whose molecular weights were determined by viscosity measurements in benzene using reported k and α values [11]. The ν values of these fractions were experimentally determined in toluene and cyclohexane as solvents.

RESULTS AND DISCUSSION

The ν values for PB/SBR (experimentally determined) and for crepe rubber, PS, PMMA, and SMMA (taken from the published literature [1])

TABLE 2. Refractive Index Increments ν of PB, SBR, Crepe Rubber, PS, PMMA, and SMMA in Different Solvents

No.	Solvents	PB		SBR,	Crepe rubber		PS,	PMMA,	SMMA,
		λ, 4360 Å	λ, 5460 Å	λ, 4360 Å	λ, 4360 Å	λ, 5460 Å	λ, 5460 Å	λ, 5460 Å	λ, 5460 Å
1	n-Hexane	0.2181	0.1523 0.1520[a]	-	0.1886	0.1802	-	-	-
2	Cyclohexane	0.1345	0.1174 0.1174[a]	0.1336 0.1240[a]	0.1305	0.1238	-	-	-
3	Benzene	0.0160	0.0099	0.0336	-	-	0.1064	-0.010	0.0680
4	Cumene	0.0820	-	-	-	-	-	-	-
5	n-Heptane	0.1843 0.1510[a]	0.1421 0.1410[a]	-	-	-	-	-	-
6	Toluene	-	-	0.0380	-	-	0.1040	-	-
7	CCl_4	-	-	-	-	-	0.1460	00.0230	0.1030
8	Butanone	-	-	-	-	-	0.2200	0.1140	0.1850
9	Acetone	-	-	-	-	-	-	0.1340	-
10	Chlorobenzene	-	-	-	-	-	-	-	0.0450
11	Chloroform	-	-	-	0.1000	0.0950	-	-	-
12	Cyclohexene	-	-	-	0.0988	0.0943	-	-	-
13	Decaline	-	-	-	0.0669	0.0605	-	-	-

[a]Values from literature.

in different solvents at 4360 and 5460 Å wavelengths are given in Table 2. Plots of ν versus the solvent refractive index at 4360 Å for PB, SBR, and crepe rubber and at 5460 Å for PB, crepe rubber, PS, PMMA, and SMMA-solvent systems, corrected by least squares, are shown in Figs. 1 and 2, respectively. As expected, the plots show the classical linear relationship whose coordinates are given by the following.

(a) For PB-solvent system:

$$n^{25}_{4360\ \text{Å}} = 2.0836 - 1.3604\tilde{n}_0 \tag{2a}$$

and:

$$n^{25}_{5460\ \text{Å}} = 1.6841 - 1.1132\tilde{n}_0 \tag{2b}$$

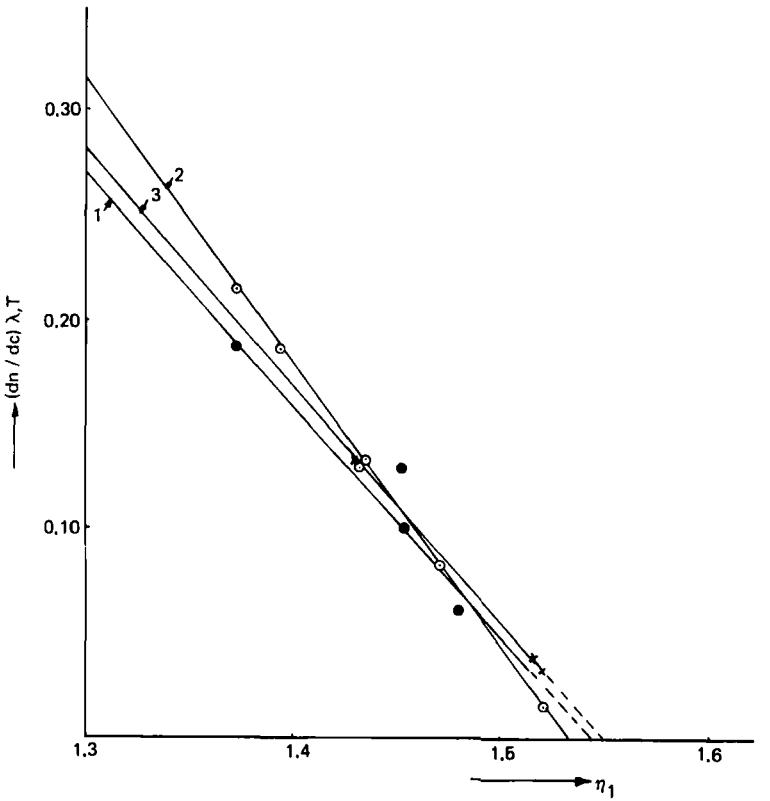

FIG. 1. Specific refractive index increment ν for PB (⊙), crepe rubber (●), and SBR (×) at λ = 4360 Å and 25°C. Curves 1-3 are least square lines.

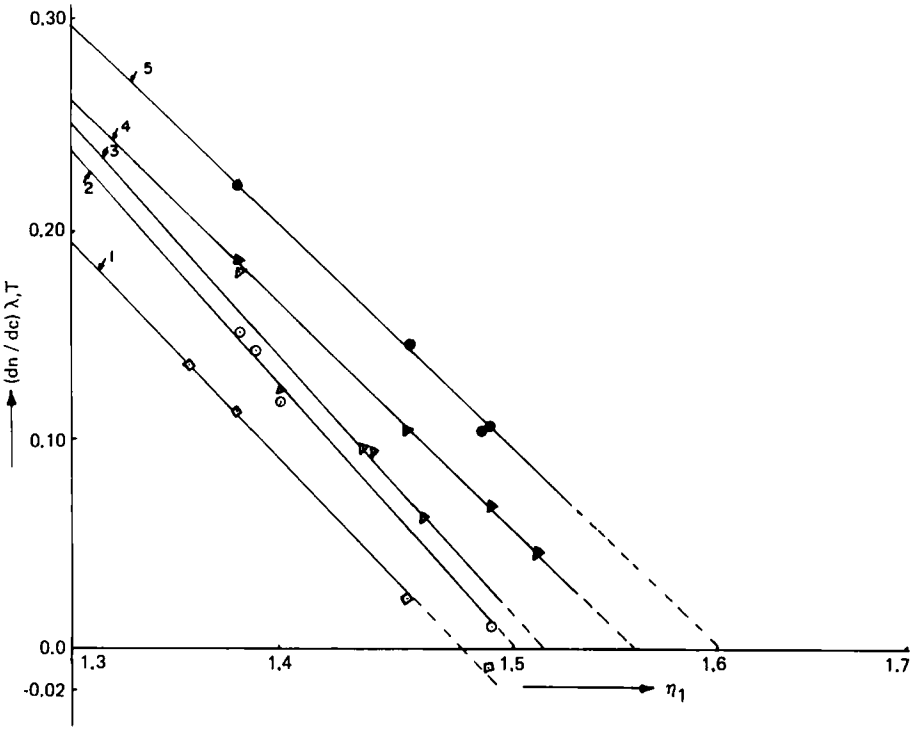

FIG. 2. Specific refractive index increment ν for PB (⊙), crepe rubber (▲), PS (●), PMMA (⊡), and SMMA (▲) at λ = 5460 Å and 25°C. Curves 1-5 are least square lines.

(b) For SBR (30:70)-solvent system:

$$n^{25}_{4360\ \text{Å}} = 2.3795 - 1.5514\tilde{n}_0 \tag{3}$$

(c) For crepe rubber-solvent system:

$$n^{25}_{4360\ \text{Å}} = 1.7220 - 1.1156\tilde{n}_0 \tag{4a}$$

and:

$$n^{25}_{5460\ \text{Å}} = 1.6963 - 1.1111\tilde{n}_0 \tag{4b}$$

(d) For PS-solvent system:

$$n^{25}_{5460\ \text{Å}} = 1.5363 - 0.9536\tilde{n}_0 \tag{5}$$

(e) For PMMA-solvent system:

$$n^{25}_{5460\ \text{Å}} = 1.5312 - 1.0289\tilde{n}_0 \tag{6}$$

(f) For SMMA (70:30)-solvent system:

$$n^{25}_{5460\ \text{Å}} = 1.5243 - 0.9710\tilde{n}_0 \tag{7}$$

Substituting n = 0 in these equations, the refractive indices of these polymers at 4360 and 5460 Å wavelengths were calculated and are given in Table 3. The refractive index values for PB and SBR at their respective wavelengths are in good agreement (±2%) with those mentioned by the manufacturers. In the case of the other polymers, viz., crepe rubber, PS, PMMA, and SMMA, agreement could not be confirmed due to the nonavailability of the refractive index values of these polymers at the desired wavelengths.

Equations (2a) to (7) can also be used for other solvents. Equations (3) and (7) are applicable to SBR (styrene:butadiene = 30:70) and SMMA (styrene:MMA = 70:30), respectively. For other compositions of these copolymers, the coordinates of Eqs. (3) and (7) will be different, since the ν values of the copolymers depend upon the composition. For verification, the ν values of PB in three solvents and SBR in two solvents were experimentally determined and compared with those derived from

TABLE 3. Specific Refractive Index of PB, SBR, Crepe Rubber, PS, PMMA, and SMMA Derived from Eqs. 2(a) to 7

No.	Polymer	$n^{25}_{5460\ \text{Å}}$	$n^{25}_{4360\ \text{Å}}$
1	PB	1.5128	1.5316
2	SBR (30:70)	-	1.5338
3	Crepe rubber	1.5267	1.5436
4	PS	1.6111	-
5	PMMA	1.4882	-
6	SMMA	1.5698	-

TABLE 4. Comparison of Refractive Index Increment Values of PB and SBR in Different Solvents

			Values at 25°C					
			Determined experimentally		Obtained from derived equations		Difference (%)	
No.	Polymer	Solvent	λ, 4360 Å	λ, 5460 Å	λ, 4360 Å	λ, 5460 Å	λ, 4360 Å	λ, 5460 Å
1	PB	Toluene	0.0229	0.0162	0.0225	0.0165	-1.7467	+1.8518
2	PB	Chloroform	0.1070	0.0773	0.1061	0.0760	-0.8411	-1.6817
3	PB	THF	0.1600	0.1184	0.1601	0.1183	+0.5	-0.0845
4	SBR (30:70)	m-Xylene	0.0622	-	0.0612	-	-1.6077	-
5	SBR (30:70)	Chlorobenzene	0.0411	-	0.0419	-	+1.9465	-

TABLE 5. Molecular Weight and Refractive Index Increment of PB Fractions

No.	Molecular weight of the fractions	Solvent	$\left(\frac{dn}{dc}\right)_{c-0}$ λ=4360 Å t=25°C	$\left(\frac{dn}{dc}\right)_{c-0}$ λ=5460 Å t=25°C
PB/1	33,000	Toluene	0.0227	0.0164
		Chloroform	0.1067	0.0767
PB/2	69,700	Toluene	0.0228	0.0163
		Chloroform	0.1064	0.0770
PB/3	200,000	Toluene	0.0226	0.0167
		Chloroform	0.1069	0.0763
PB/4	350,000	Toluene	0.0227	0.0162
		Chloroform	0.1068	0.0769
PB/5 (unfractionated)	150,000	Toluene	0.0229	0.0162
		Chloroform	0.1070	0.0773

Eqs. (2a), (2b), and (3). The results are given in Table 4. The calculated and experimental values show good agreement (±2%).

The ν values of the fractionated PB samples as well as the unfractionated PB samples at 4360 and 5460 Å wavelengths were measured in toluene and chloroform and are given in Table 5. The variation of the ν values in the respective solvents and at the respective wavelengths was less than 1%, although the molecular weights of the samples varied over a wide range. In other words, the ν values may be taken to be constant in the molecular weight range of 33,000 to 350,000.

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REFERENCES

[1] J. Brandrup and E. H. Immergut, Polymer Handbook, Wiley-Interscience, New York, 1966, pp. IV-284 to IV-294.
[2] S. Glasstone, Textbook of Physical Chemistry, Macmillan, London.
[3] J. L. Angulo-Sanchez, A. Gallagos, M. A. Ponce Velez, and E. Campos-Lopez, Polymer, 18, 922-924 (1977).
[4] H. Lange and H. Baumann, Angew. Makromol. Chem., 14, 25-42 (1970).
[5] E. M. Barral, M. J. R. Cantow, and J. E. Johnson, J. Appl. Polym. Sci., 12, 1373 (1968).
[6] I. Ziegler, I. Freund, H. Benoit, and W. Kern, Makromol. Chem., 37, 217 (1960).
[7] P. Rempp, J. Chem. Phys., 54, 421 (1957).
[8] D. Margerison, D. R. Bain, and B. Kiely, Polymer, 14, 133 (1973).
[9] I. M. Kolthoff and T. S. Lee, J. Polym. Sci., 2, 206 (1947).
[10] Technical Manual, Brice Phoenix Differential Refractometer, Model BP-2000 V.
[11] F. Danusso, G. Moraglis, and G. Gianott, J. Polym. Sci., 51, 475 (1961).
[12] Operating Manual, Brice Phoenix Light Scattering Photometer, O M-2000, 1963.
[13] F. D. Rossini, B. J. Mair, and A. J. Streiff, Hydrocarbons from Petroleum, Reinhold, New York, 1953, pp. 226-236.

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