

Refractive Indices of Monomer-Polymer Mixtures of Vinyl Formate, Vinyl Acetate, Vinyl Propionate, and Vinyl Butyrate

RICHARD A. MEYER and ARTHUR A. VERNON, *Department of Chemistry, Northeastern University, Boston, Massachusetts*

INTRODUCTION

The variations in index of refraction of monomer-polymer mixtures with per cent of polymer offers a convenient method of analyzing such mixtures. To establish data for such a method, the indices of refraction of monomer-polymer mixtures of vinyl formate, vinyl acetate, vinyl propionate, and vinyl butyrate were determined over a wide range of concentration.

EXPERIMENTAL

Materials

Monomers of the vinyl esters were distilled in an unpacked Vigreux column and then in a 56-plate glass helix-packed Todd column. The refractive indices were measured with an Abbé refractometer and sodium lamp for illumination. The boiling points and refractive indices of the purified monomers are given in Table I.

TABLE I

Vinyl ester	B.p., °C.	n_D^{25}
Vinyl formate	46.6	1.3859
Vinyl acetate	72.7	1.3949
Vinyl propionate	94.9	1.4038
Vinyl butyrate	116.7	1.4097

Method of Measurement

The purified samples were exposed to the radiation of a quartz mercury lamp, to produce several per cent polymer. The index of refraction of a weighed sample was measured and the sample reweighed to determine the loss of material. The mixture was then placed in an ice-water bath which in turn was in a container that could be evacuated. The pressure was reduced, to remove some of the monomer, and then the sample was re-

moved. The ice-water bath lowered the monomer vapor pressure and thus gave good control over the amount of monomer removed.

The new mixture was weighed, the index of refraction determined, and the mixture again weighed. This process was continued until the mixture was too viscous for further measurement. Then the remainder was kept

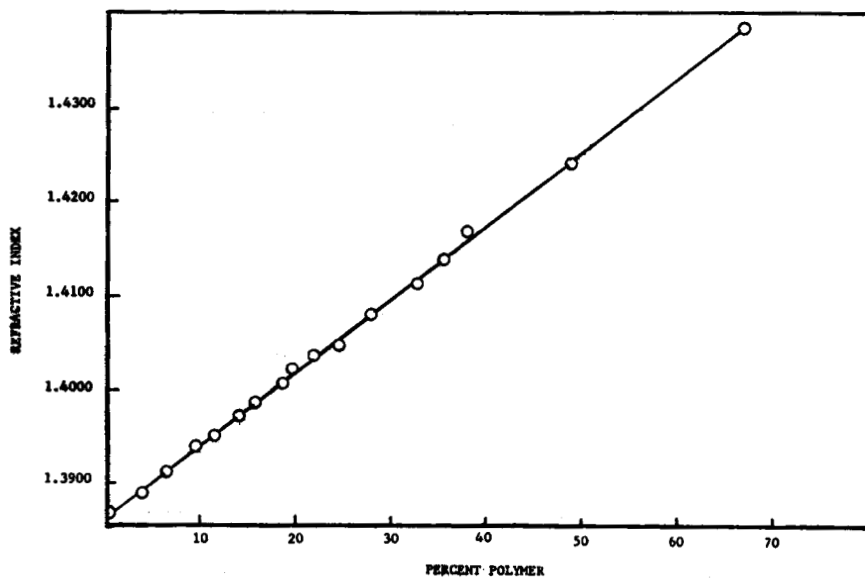


Fig. 1. Refractive index of monomer-polymer mixtures of vinyl formate.

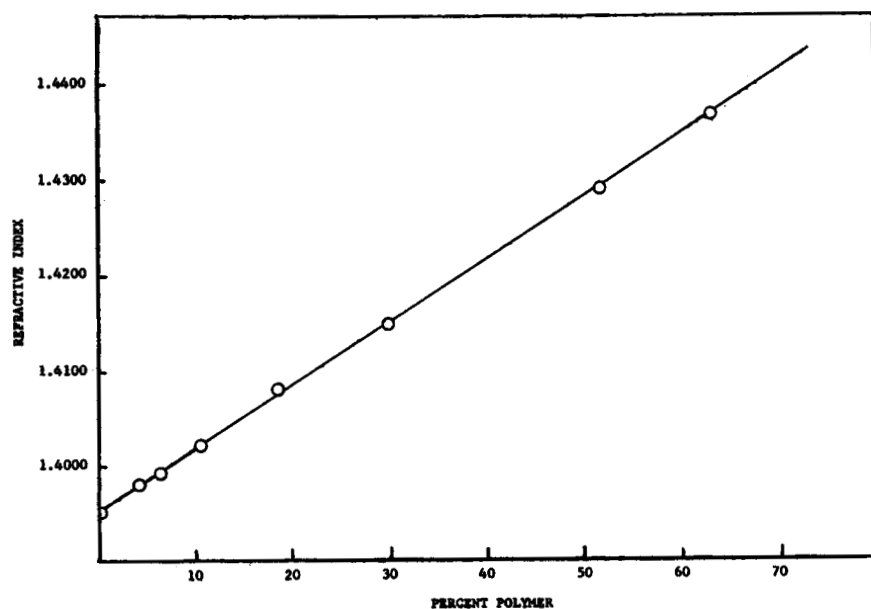


Fig. 2. Refractive index of monomer-polymer mixtures of vinyl acetate.

under a vacuum exhaust system until constant weight was obtained. The per cent of polymer in each sample was then calculated from the mixture and corrected for the loss due to the measurement.

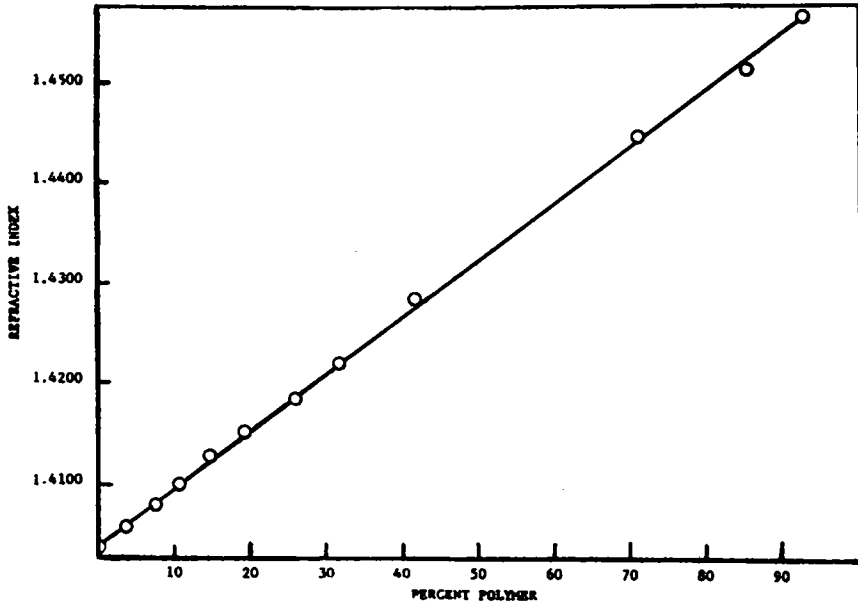


Fig. 3. Refractive index of monomer-polymer mixtures of vinyl propionate.

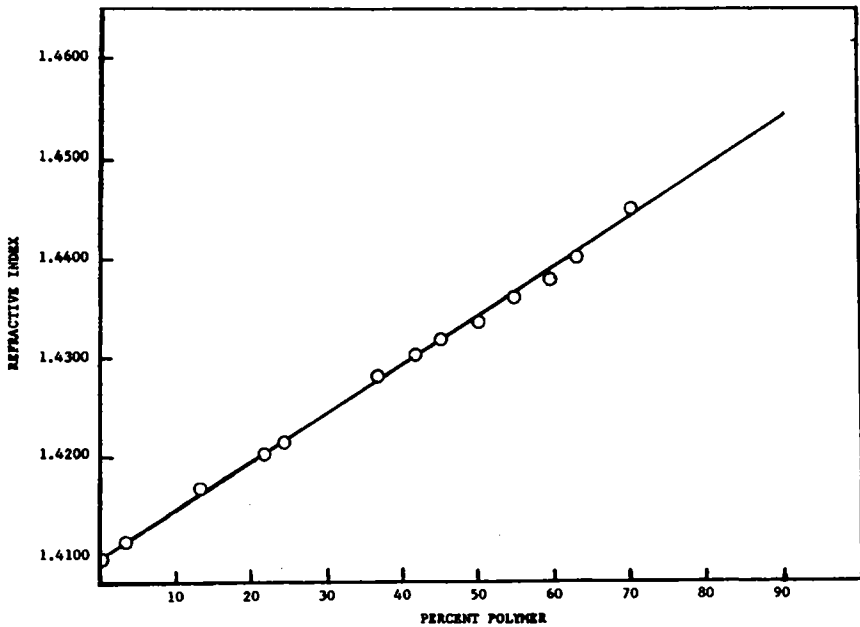


Fig. 4. Refractive index of monomer-polymer mixtures of vinyl butyrate.

TABLE II
Refractive Indices of Monomer-Polymer Mixtures of Vinyl Formate

Polymer, %	n_D^{25}	Polymer, %	n_D^{25}
0.0	1.3859	19.9	1.4016
2.5	1.3880	24.9	1.4048
5.5	1.3980	28.3	1.4077
9.0	1.3927	33.2	1.4112
12.0	1.3950	35.5	1.4135
16.7	1.3989	49.2	1.4242
19.1	1.4003	67.5	1.4391
		83.5	1.4510

TABLE III
Refractive Indices of Monomer-Polymer Mixtures of Vinyl Acetate

Polymer, %	n_D^{25}	Polymer, %	n_D^{25}
0.0	1.3934	30.5	1.4148
4.5	1.3980	43.0	1.4232
6.5	1.3990	51.5	1.4291
10.5	1.4020	63.0	1.4368
13.5	1.4039	69.5	1.4404
18.5	1.4081	90.3	1.4532
21.0	1.4091		

TABLE IV
Refractive Indices of Monomer-Polymer Mixtures of Vinyl Propionate

Polymer, %	n_D^{25}	Polymer, %	n_D^{25}
0.0	1.4038	14.9	1.4129
2.0	1.4049	19.5	1.4148
3.9	1.4059	26.0	1.4182
4.5	1.4065	31.6	1.4219
5.2	1.4068	41.5	1.4282
7.5	1.4080	71.0	1.4442
9.0	1.4088	85.1	1.4510
10.9	1.4100	92.8	1.4565
11.5	1.4103		

TABLE V
Refractive Indices of Monomer-Polymer Mixtures of Vinyl Butyrate

Polymer, %	n_D^{25}	Polymer, %	n_D^{25}
0.0	1.4097	45.0	1.4318
3.5	1.4161	49.8	1.4332
13.7	1.4111	54.5	1.4360
14.4	1.4169	59.5	1.4380
21.6	1.4205	63.0	1.4400
24.3	1.4212	64.0	1.4410
36.9	1.4281	69.9	1.4450
41.9	1.4303		

RESULTS

The results of the measurements are given in Tables II, III, IV, and V. These data are plotted in Figures 1, 2, 3, 4.

Synopsis

Monomers of vinyl formate, vinyl acetate, vinyl propionate, and vinyl butyrate were carefully purified by distillation in a Vigreux column and in a 56-plate glass helix-packed Todd column. The refractive indices and boiling points of the purified monomers agreed with those given in the literature. The purified samples were exposed to the radiation of a quartz mercury lamp in order to produce several per cent polymer. The refractive indices are tabulated and plotted in graphs.

Résumé

Les monomères, acétate de vinyle, formiate de vinyle, propionate de vinyle et butyrate de vinyle ont été soigneusement purifiés par distillation dans une colonne Vigreux et dans une colonne Todd à 56 plateaux contenant des éléments de verre de forme hélico-élicidale. Les indices de réfraction et les points d'ébullition des monomères purifiés s'accordent avec ceux donnés dans la littérature. Les échantillons purifiés sont exposés aux radiations d'une lampe de quartz à mercure pour produire plusieurs pourcents de polymère. Les résultats des mesures d'indices de réfraction ont été rassemblés dans des tableaux et mis en graphiques.

Zusammenfassung

Die Vinylester von Ameisensäure, Essigsäure, Propionsäure und Buttersäure wurden in einer Vigreux-Kolonnen und in einer 56-bödigen, mit spiralenförmigen Glaskörperchen angefüllten Todd'schen Bodenkolonne mittels Distillation sorgfältig gereinigt. Die Brechungszahlen und Siedepunkte der gereinigten Monomere stimmen mit den in der Literatur angeführten Werten überein. Die gereinigten Proben wurden unter Anwendung einer Quarzquecksilberlampe bestrahlt, um einige Prozente Polymeres herzustellen. Die sich ergebenden Brechungszahlen sind sowohl in einer Tabelle wie auch graphisch dargestellt.

Received February 8, 1962