# NOTES

## Refractive Index Increments of Polyolefins

### INTRODUCTION

Polyethylene (PE) is the most important industrial polyolefin. Its solution properties have been investigated in a large number of studies. Lately, however, industrial polymers are increasingly widely met which, in addition to ethylene, contain other olefinic comonomer components. To characterize such samples, one has to know, besides the content, also the basic properties of the given component.

In the determination of molecular weights by the light scattering method, such a basic parameter is the refractive index increment of the polymer, $dn/dc$. The $dn/dc$ values of PE (linear and branched) have been summarized and supplemented earlier for a number of solvents and wavelengths.[1]

We have applied the developed differential refractometry method[1] also to other polyolefins, in order to answer the question to what extent the comonomers present in PE may affect the refractive index increments. Data on $dn/dc$ of polyolefins are reported only sporadically,[2,3] and values by various authors often differ considerably.[4-7] The range of wavelengths was chosen similarly as in the PE measurement. The use of red light ($\lambda_0 = 633$ nm) was desirable because of He–Ne lasers being employed in modern light scattering devices.

The usual temperature in the characterization of PE and its copolymers is 135°C. For this reason, all measurements were carried out at this temperature, even though some polyolefins dissolve already at room temperature.

### EXPERIMENTAL

The procedure for determination of refractive index increments has been described elsewhere.[1] Industrial samples of Czechoslovak and foreign origin were used in the measurements.

Two basic solvents were employed, viz., 1-chloronaphthalene and 1,2,4-trichlorobenzene, which are also those most frequently applied in the characterization of PE. Purity of these solvents (FLUKA, Switzerland) as checked by gas chromatography was >99.5%.

### RESULTS AND DISCUSSION

Results of the measurements are summarized in Table I. For the polyolefins under investigation, the $dn/dc$ dependences on the reciprocal square wavelength are linear. The optical dispersion parameter which is proportional to the slope of these dependences is similar for all polymers investigated in this study.

If our results (Table I) are compared with the reported data, an acceptable fit can be stated in many cases at 546 nm (e.g., for polypropylene in 1-chloronaphthalene, $dn/dc$ values from −0.184 to −0.195 cm$^3$/g have been published[5-7]). On the other hand, the absolute increment values given for blue light ($\lambda_0 = 436$ nm) are much higher than those measured by us (e.g., for polypropylene in 1-chloronaphthalene, $dn/dc$ values from −0.227 to −0.231 cm$^3$/g have been reported[4,8,9]).

The refractive index increments for PE, the two polypropylenes, and poly-1-butene are very similar (Table I). The differences lie at the limit of experimental error. Hence, with respect to differential refractometry and molecular weight determination by light scattering, the presence of usual comonomer components in polyethylene virtually need not be taken into account, even if their content is of the order of tens of percent. On the contrary, the refractive index increments of polyisobutylene differ considerably from those of PE. Since the isobutylene content in industrial PE samples is usually low (several percent), in this case too there is no hazard of a major error in the molecular weight determination, if correction for the presence of isobutylene structural units is neglected. Butyl rubber, on the other hand, is quite a different case, as it contains more than 90% of isobutylene units.

TABLE I
Refractive Index Increments, $dn/dc$ (cm³/g), of Some Polyolefins at 135°C for Various
Wavelengths *in Vacuo* $\lambda_0$ (nm)

| Solvent | Polymer[a] | $dn/dc$ at $\lambda_0^b$ | | | | |
|---|---|---|---|---|---|---|
| | | 403 | 436 | 546 | 578 | 633 |
| 1-Chloronaphthalene | PE1 | | −0.215 | −0.192 | −0.188 | −0.183 |
| | PEb | | −0.212 | −0.189 | −0.184 | −0.178 |
| | PPa | c | −0.211 | −0.188 | −0.183 | −0.177 |
| | PPi | | −0.205 | −0.184 | −0.180 | −0.173 |
| | PB | | −0.206 | −0.187 | −0.183 | −0.177 |
| | PIB | | −0.146 | −0.131 | −0.128 | −0.122 |
| 1,2,4-Trichlorobenzene | PE1 | −0.130 | −0.125 | −0.110 | −0.108 | −0.107 |
| | PEb | −0.122 | −0.117 | −0.105 | −0.103 | −0.102 |
| | PPa | −0.130 | −0.123 | −0.111 | −0.109 | −0.105 |
| | PPi | −0.128 | −0.121 | −0.107 | −0.105 | −0.102 |
| | PB | −0.127 | −0.120 | −0.108 | −0.105 | −0.103 |
| | PIB | −0.070 | −0.066 | −0.054 | −0.053 | −0.051 |

[a] PE1 = linear polyethylene[1]; PEb = branched polyethylene[1]; PPa = atactic polypropylene (Chemopetrol, Czechoslovakia); PPi = isotactic polypropylene (TATREN FE-153, Slovchémia, Czechoslovakia); PB = isotactic poly-1-butene (Polysciences Inc., U.S.A.); PIB = polyisobutylene (Opanol, BASF, West Germany).

[b] Error in determination of $dn/dc$ is ±0.002 cm³/g.

[c] Beyond the range of measurement of differential refractometer.

**SUMMARY**

The refractive index increments of polyethylene (linear and branched), polypropylene (atactic and isotactic), polyisobutylene, and poly-1-butene in two solvents were determined. The measurements were performed at 135°C for wavelengths of light 403, 436, 546, 578, and 633 nm. The results suggest that the presence of usual comonomer components in polyethylene virtually leaves the refractive index increment unaffected.

**References**

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