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Correction of the number average molecular weight of hydroxylated liquid polybutadiene as determined by vapor pressure osmometry

L. Akcelrud[1],* and A. G. Tinoco[2]

[1]Instituto de Química, Universidade Federal do Rio de Janeiro, I. Fundão,
21910 Rio de Janeiro, Brazil
[2]Polymer Division Petrobras Research Center, Rio de Janeiro, Brazil

SUMMARY

Number average molecular weight ($\bar{M}n$) determinations of oligomers by vapor pressure osmometry (VPO) requires highly purified samples. As ultraviolet spectroscopy is a convenient technique for accurate evaluation of small concentrations, it was used to determine the concentration of 2,6-di-t-butyl-4-methylphenol antioxidant in commercial hydroxylated liquid polybutadiene in the $\bar{M}n$ = 2800-3000 range. The data were used to correct $\bar{M}n$ values measured by VPO, allowing the determination of correct molecular weights without previous polymer purification.

INTRODUCTION

The $\bar{M}n$ of hydroxylated liquid polybutadiene (HLPB) allows the evaluation of its functionality, which in turn determines the properties of the final products obtained. The $\bar{M}n$ of commercial HLPB is ∿ 3000. In this range, VPO is a common method for $\bar{M}n$ (1) determinations. HLPB is frequently stabilized with 2,6-di-t-butyl-4-methylphenol (Ionol BHT). For reliable $\bar{M}n$ evaluations the readings must be corrected, which requires a quantitative determination of the antioxidant present.

Ultraviolet spectroscopy is a convenient technique for analyzing small amounts of additives (2,7). Antioxidants are usually present in the 0.1 - 2% range. Thus it is advisable employ an analytical technique which does not require additive extraction.

HLPB is soluble in chloroform, and 2,6-di-t-butyl-4-methylphenol could be directly measured in the sample if the interference of the double bonds could be eliminated.

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*To whom offprint requests should be sent

According to Beer's law, the contributions to the absorption of a certain wavelength from different chromophores is additive:

$$A = A_1 + A_2 = \varepsilon_1 b\ c_1 + \varepsilon_2 b\ c_2 \qquad (1)$$

where A represents the absorption of the integral sample, b the optical path, ε_1 and ε_2 the specific absorptivity, c_1 and c_2 the concentrations (g/l), A_1 and A_2 the absorptions of components 1 and 2 respectively.

This work concerns the quantitative determination of 2,6-di-t-butyl-4-methylphenol in HLPB, as well as the calculations for $\bar{M}n$ determined by VPO.

EXPERIMENTAL

Solvent: Chloroform U.V. grade. The solvent spectrum in the 190-340nm range did not present any absorption, and was used without further purification.

Solutions: These were prepared in volumetric flasks, in the concentration range of 5 to 26 g/l for HLPB and 0.03 to 0.015 g/l for antioxidant. The measurements were made in triplicate. The observance of Beer's Law was checked in the measured range.

Instruments: UV - Vis Spectrophotometer Hewlett Packard 8451A. Vapor pressure osmometer - Wescan 232A. Standards for calibration - benzil 210 g/mol and monodisperse polystyrene 2000 g/mol.

Samples: HLPB Petroflex code CQ 110/103, 08, 11, 12 and 13.

RESULTS AND DISCUSSION

The determination of the correct wavelegth to be used was accomplished by measuring the absorbance of several solutions of HLPB and pure antioxidant. The corresponding spectra are shown in Figures 1 and 2. The chosen wavelength was 248nm, due to the high aromatic ring absorption and low double bond interference, as can be observed in the spectra.

The antioxidant concentration was calculated by means of Equation (1). ε_1 and ε_2 were determined from the calibration curves for each pure component, as shown in Figures 3 and 4.

The measured absorptivity for the antioxidant ε_1, was 9,120 while for HLPB double bonds, ε_2 was 0.016 showing the small contribution of this absorption, which, even in a low level, could be quantified. If A is the absorbance of an unknown sample and c the concentration of the prepared solution, which in turn is the sum of c_1 (antioxidant) and c_2 (oligomer), the amount of antioxidant is:

$$c_1 = \frac{A - \varepsilon_2 c}{\varepsilon_1 - \varepsilon_2} \qquad (2)$$

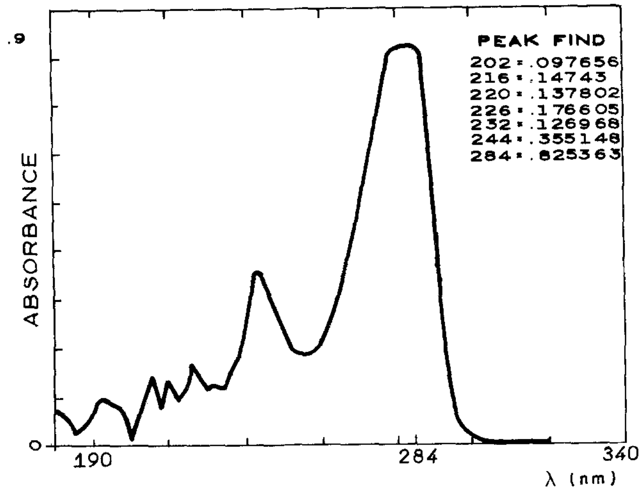

Figure 1 - Spectrum of 2,6 di-t-butyl-4-methylphenol. Solution concentration 0.064%.

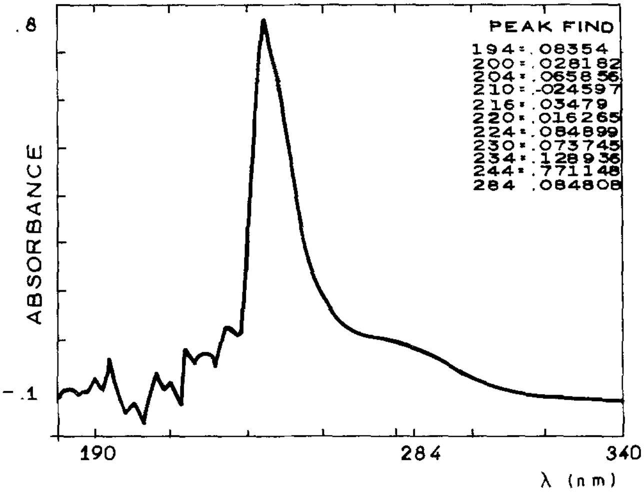

Figure 2 - Spectrum of HLPB. Solution concentration 0.492%.

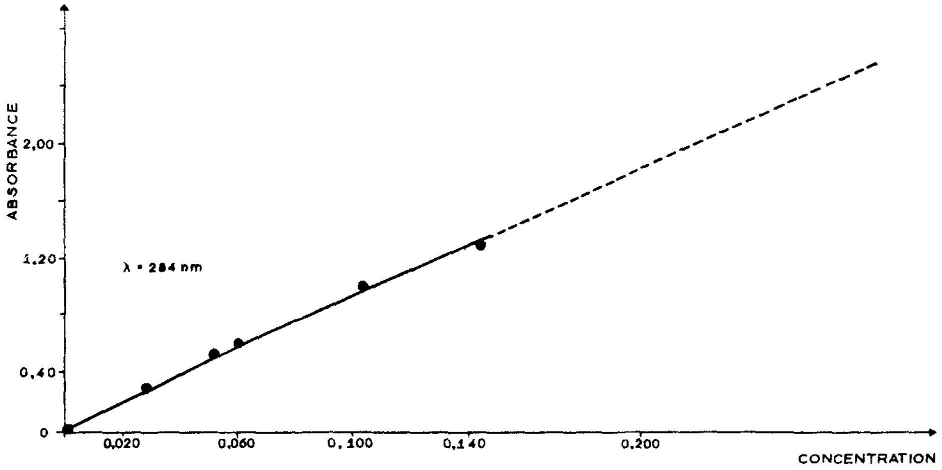

Figure 3 - Calibration curve for the di-t-butyl-4-methyl phenol.

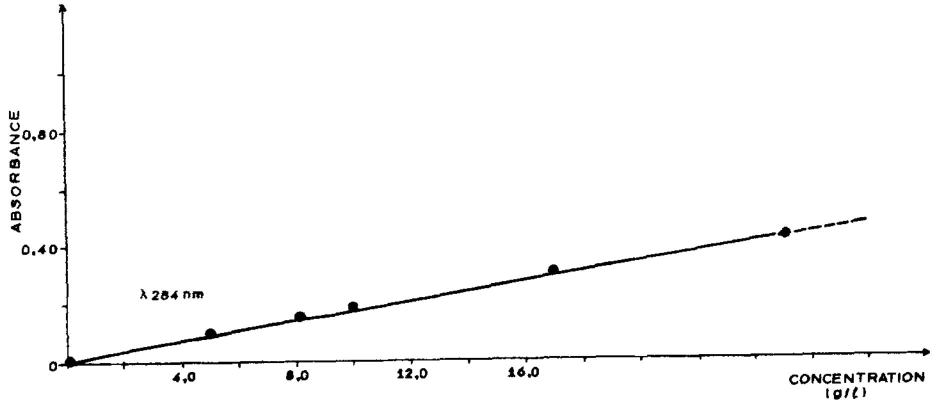

Figure 4 - Calibration curve for pure HLPB. Solvent: Chloroform

In Figure 5 a typical spectrum of an antioxidant containing HLPB is presented. Generally the concentrations of the additive were found to be around 0.5%.

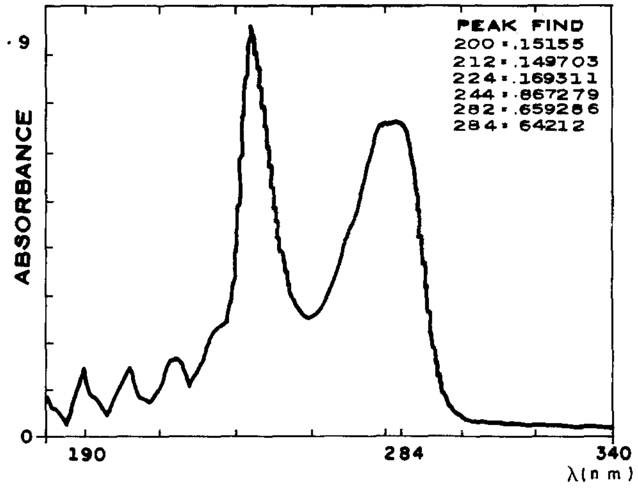

Figure 5 - Spectrum of a commercial sample of HLPB containing 0,52% antioxidant. Solution concentration 1,015%.

The reproducibility of the method was tested by measuring the absorbances of six samples of Petroflex HLPB containing the antioxidant. For each one eight readings were made, on the average. The standard deviation (0.0102) and the reproducibility (0.028) for concentration in the 0.5% range, indicated good reproducibility.

Once the analytical method was established, the $\bar{M}n$

obtained from VPO data could be corrected.

THEORY AND CALCULATIONS

For a narrow interval, the temperature variation ΔT corresponding to a pressure variation ΔP of a solution relative to the pure solvent can be expressed by equation (4) deduced from the Clausius-Clayperon Equation.

$$\Delta T = \frac{(\Delta P)\, RT^2}{\Delta Hv\; P_1{}^o} \tag{3}$$

Where ΔHv and $P_1{}^o$ represent the latent heat of vaporization and the vapor pressure of the solvent, respectively.

The theory of colligative properties tells us that:

$$\lim_{c_2 \to 0} \frac{\Delta P}{c_2} = - \frac{P_1{}^o\, V_1{}^o}{M} \tag{4}$$

where $c_2 V_1{}^o$ represents the solute concentration, partial molar volume and molecular weight, respectively.

The expanded form of equation (4) is

$$\frac{P}{P_1{}^o} = - V_1{}^o\, c_2 \left[\frac{1}{M} + Bc_2 + Cc_2^2 + \dots \right] \tag{5}$$

where B and C are the virial coefficients.

From (3) and (5) we can arrive to (7):

$$\frac{\Delta T}{c_2} = - \frac{RT^2 V_1{}^o}{\Delta Hv} \left[\frac{1}{M} + Bc_2 + Cc_2^2 + \dots \right] \tag{6}$$

Since for dilute solutions Bc_2 and Cc_2^2 can be neglected,

$$\frac{\Delta T}{c_2} = - \frac{RT^2 V_1^o}{\Delta\ Hv} \left[\frac{1}{M} \right] \tag{7}$$

or

$$\frac{\Delta T}{c_2} = - K_s \frac{1}{M} \tag{8}$$

where K_s is the "instrument constant". Various attempts to determine "a priori" K_s values were unsuccessful, and the instrument is calibrated for well determined working conditions: solvent, temperature, thermistor pair, and molecular weight standards. With polymeric samples it is advisable to calibrate the instrument with molecular weight standards of same order of magnitude as the samples.

As ΔT is directly proportional to the resistance variation $\Delta\Omega$ of the Whetstone bridge of the instrument, we can write eq(9):

$$\Delta T = K\Delta\Omega \qquad (9)$$

or

$$\frac{\Delta\Omega}{c_2} = K' \frac{1}{M} \qquad (10)$$

The desired molecular weight, which in case of a polymeric solute is given by an average, can be expressed by

$$\bar{M}n = \frac{K'}{\frac{\Delta\Omega}{c_2}} \qquad (11)$$

then, $\bar{M}n$ is a function of only c_2, which in turn is the sum of polymer concentration (c_p) and antioxidant (c_a).

$$c_2 = c_p + c_a \qquad (12)$$

By the use of the following symbolisms: $\bar{M}n_c$ = corrected molecular weight of HLPB, $\bar{M}n_m$ = measured molecular weight of HLPB, m_p = polymer mass, m_a = antioxidant mass, m_t = total mass, Ma = molecular weight of antioxidant, we will have:

$$\bar{M}n_m = \frac{m_t}{\frac{m_p}{\bar{M}n_c} + \frac{m_a}{Ma}} \qquad (13)$$

or,

$$\bar{M}n_c = \frac{\bar{M}n_m \cdot Ma \cdot m_p}{M_a \cdot m_t - Mn_m \cdot ma} \qquad (14)$$

but $m_t = m_p + m_a$

and if we make $m_t = 1$ and $m_p = x\%$ and $m_a = y\%$ we will obtain

$$\bar{M}n_c = \frac{Mn_m \cdot x \cdot M_a}{M_a - y \cdot \bar{M}n_m} \qquad (15)$$

CONCLUSIONS

1. A simple method for the quantitative determination of 2,6-di-t-butylphenol in HLPB was established. The method is based on absorbance measurements at 284nm at concentrations where Beer's law is obeyed. 2. The correction of $\bar{M}n$ obtained by VPO can be made by a simple equation (Eq. 15) if the amount of antioxidant is known.

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