Polymer Bulletin 2, 719-726 (1980)

Polymer Bulletin

Polymer Analysis by Higher-Order UV/VIS-Derivative Spectrophotometry

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Dedicated to Professor Kurt Dialer on his 60th birthday

Summary

High resolution higher-order UV/VIS derivative spectrophotometry (HODS) has been used for some selected analytical problems of polymers, such as copolymer composition, determination of unconverted monomer in polymer and analysis of polymer additives.

1. Introduction

Usually, UV spectra of dissolved substances or liquids aren't very characteristic. Except for pure substances or mixtures, which show isolated UV absorption maxima for the components, it can't be used for quantitative analysis.

Derivative spectra (HODS) make it possible to determine flat maxima, to isolate shoulders and weak signals from an unwanted background of superimposed spectra. How HODS can be used for analytical problems of polymers will be described in this paper.

2. Copolymer analysis

The composition of copolymers can be determined for example by ultimate analysis, refractive index, turbidimetric titration but also by spectroscopical methods like NMR, IR and UV.

The normal UV spectroscopy is a sensitive method for copolymers of the structure **1** (KERBER et al., 1976), but it didn't work in the case of azo-polycarbonates (**2**) (TALSKY et al., 1979; KERBER et al., 1979):

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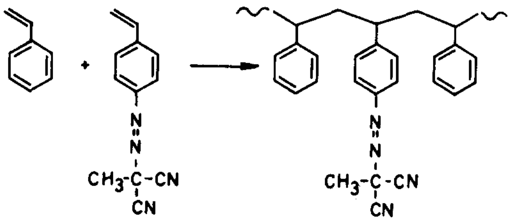

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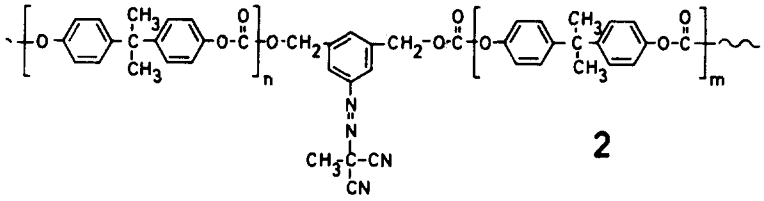

2

because in **2** the UV absorption of the azo group at 290 nm was superimposed by the UV absorption of the polycarbonate backbone. However, the 4th derivation of the normal UV spectrum of **2** yields a separated peak at 290 nm which depends linear upon the concentration of azo groups in the polymer and this could therefore be used, after calibration, for quantitative analysis. (TALSKY et al., 1979).

3, Decomposition kinetics of the azo groups of 2

HODS was also used for kinetical measurements. The decrease of the signal of azo groups (290 nm) was followed with time at different temperatures (4th derivation, Fig. 1). The rate constants, determined by HODS agree with those resoluted by other methods (NUYKEN et al., 1979).

4. Analysis of unconverted monomer

Normally unconverted monomer in polymers effects the polymer properties badly and decreases their applicability. On the other hand most of the monomers are injurious to health. Therefore it is of great interest to know the quantitative amount of residual monomer in polymers. As shown in Fig. 2b, 3b, 4b the normal

UV spectroscopy can't be used with sense for these analytical problems. The possibilities and advantage of HODS compared to normal UV are demonstrated in 3 examples.

a) Styrene/polystyrene:

To a solution of polystyrene in THF increasing amounts of styrene were added. These solutions were compared with pure solvent. Peak B in the 4th derivation (Fig. 2a) of the normal UV (Fig. 2b) grows with the logarithm of the monomer concentration (Fig. 7) and was therefore used for the quantitative analysis. Concentrations of ~ 0,02 weight % styrene in polystyrene were detectable by this method. Using polystyrene/THF instead of pure THF for comparison, this method becomes more sensitive by the factor of ~ 100, and ~ 0,002 weight % styrene could be determined.

b) Acrylamid/polyacrylamid:

Fig. 3a and 3b show the differences between normal UV and HODS for solutions of acrylamid/polyacrylamid in water, compared with pure water. Signal B in the 4th derivation (Fig. 3a) grows linearly with monomer concentration (Fig. 6). Using this signal, less than 1 weight % acrylamid in polymer were measurable.

c) Vinylacetate/polyvinylacetate.

The 4th derivation (Fig. 4a) of the normal UV (Fig.4b) of vinylacetate/polyvinylacetate in methanol compared with a methanolic polymer solution shows a sharp signal B,which grows linearly with the monomer concentration (Fig. 6). About 0.05 weight % monomer in polymer were still detectable.

5. Polymer additive

Polymer additives, especially antioxidants of the phenolic type are difficult to detect beside a polymer like polystyrene by normal UV (Fig. 5b).The 4th derivation (Fig. 5a) and the 5th derivation (Fig. 5c) of the normal UV of the antioxidant IRGANOX 1010 ^{R} in polystyrene, dissolved in THF, show sharp signals, which were used for the quantitative analysis.

Meanwhile the signals A (4th and 5th derivation) grow linearly with the additive concentration (Fig.6), the signal B of the 5th derivation is proportional to the logarithm of the additive concentration (Fig.7) which is profitable particularly for low additive concentrations. 0.05 weight % IRGANOX 1010 ^{R} in polystyrene were measurable. The sensitivity can be increased by elimination of polystyrene, using a polystyrene solution instead of the pure solvent for comparison.

6. Experimental part

Solvents: methanol and THF were used in commercial quality (Merck, Uvasol).

Monomers: The monomers were destabilized with 2n NaOH, dried and fractionated destilled.

azo-polycarbonate: The synthesis was already described (KERBER et al., 1979).

Polymers free of additives: We wish to thank the BASF, Ludwigshafen for polystyrene, and the Wacker, Burghausen, for polyvinylacetate.

IRGANOX 1010 ^{R}: Was kindly given by the Ciba-Geigy/ Basel.

UV-Spectrophotometry: To a polymer solution of 0,5-1 weight % a monomer-polymer-solution(0,05-1 weight % monomer, 0,5-1 weight % polymer) was added step by step and then the normal UV and the HODS were taken at times.

Instruments: UV-spectrophotometer: Philips Pye Unicam SP 8 - 100.
Analog-differentiator: self constructed, soon commercially available (Fa. Lucius u. Baer, D-8192 Geretsried).

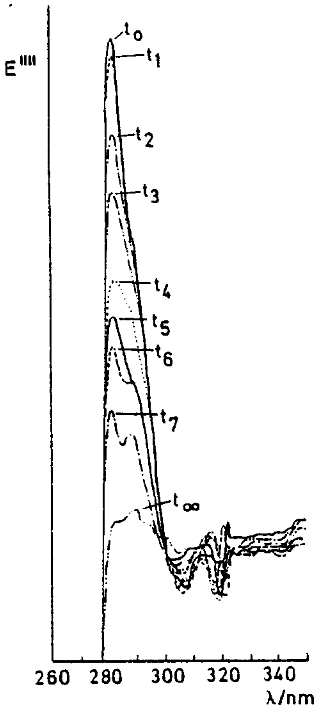

Fig.1:
[azo in **2**]= f(t) at constant temperature followed by derivative UV (E'''' = 4th derivation of the normal absorption E)

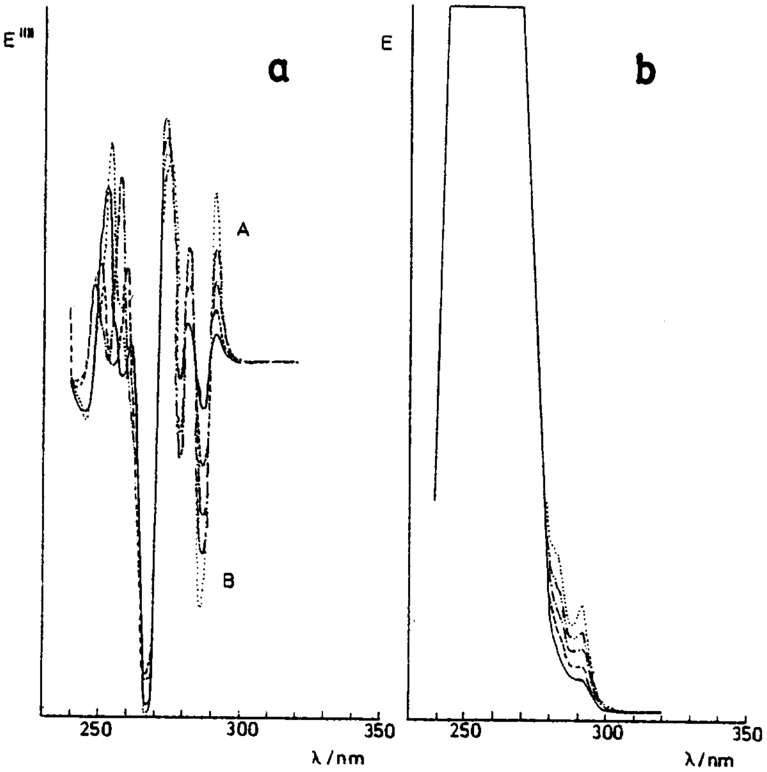

Fig.2:
4th derivative (2a) and normal UV(2b) of styrene/ polystyrene in THF - variation of [styrene] .

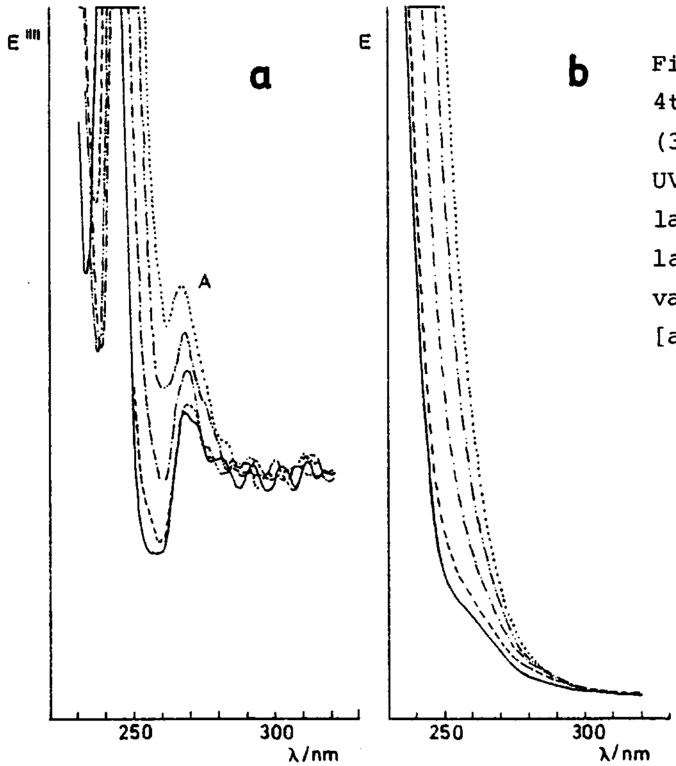

Fig.3:
4th derivative (3a) and normal UV(3b) of acrylamid/polyacrylamid in water variation of [acrylamid]

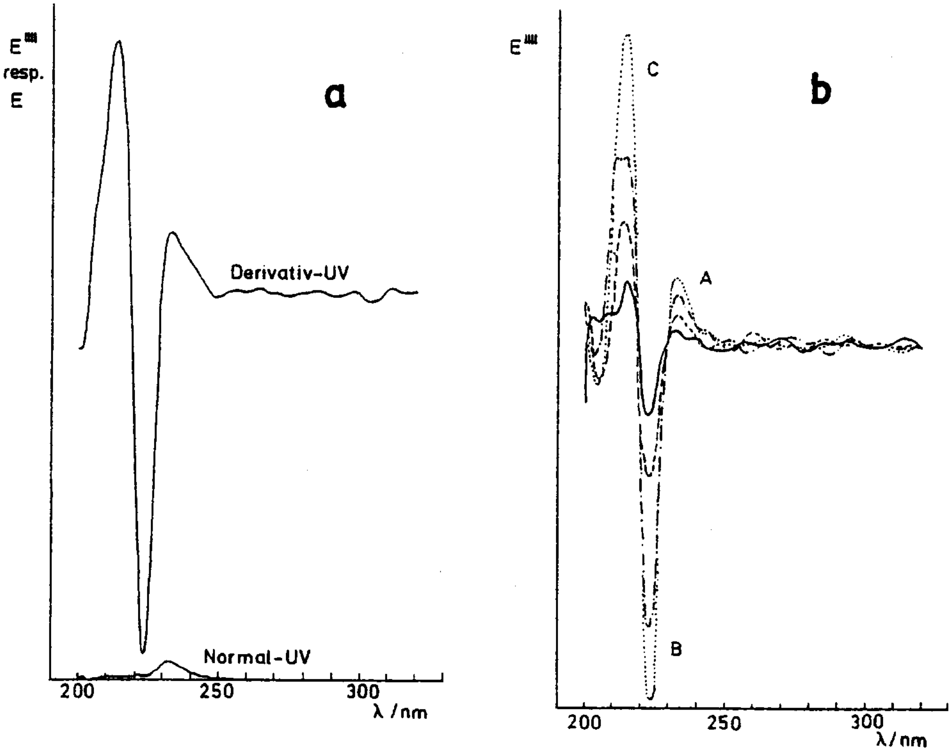

Fig.4:
4th derivative(4a) and normal UV(4b) of vinylacetate/polyvinylacetate in methanol-variation of [vinylacetate] .

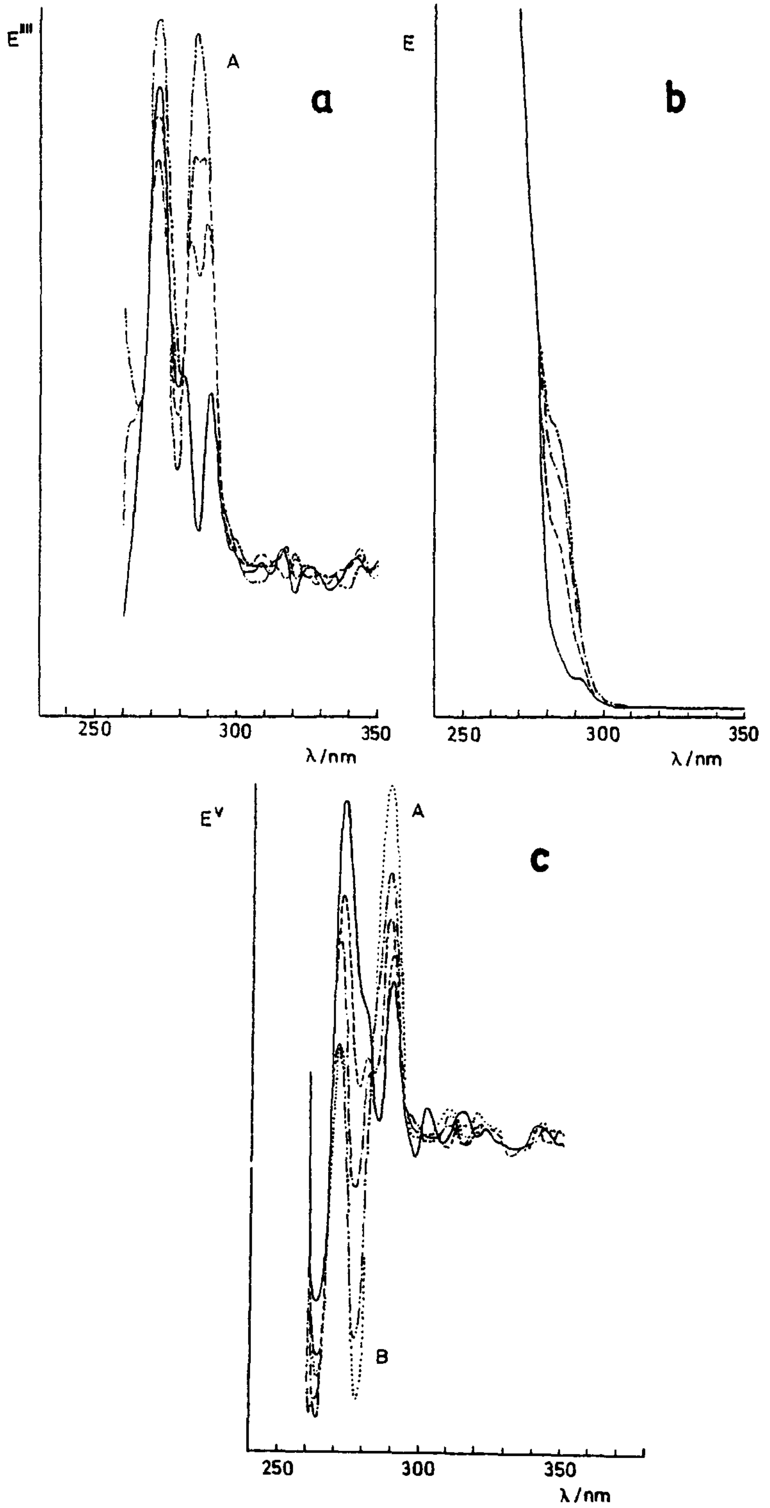

Fig.5:
4th(5a), 5th derivative(5c) and normal UV(5b) of IRGANOX 1010^{R}/polystyrene in THF-variation of [additive].

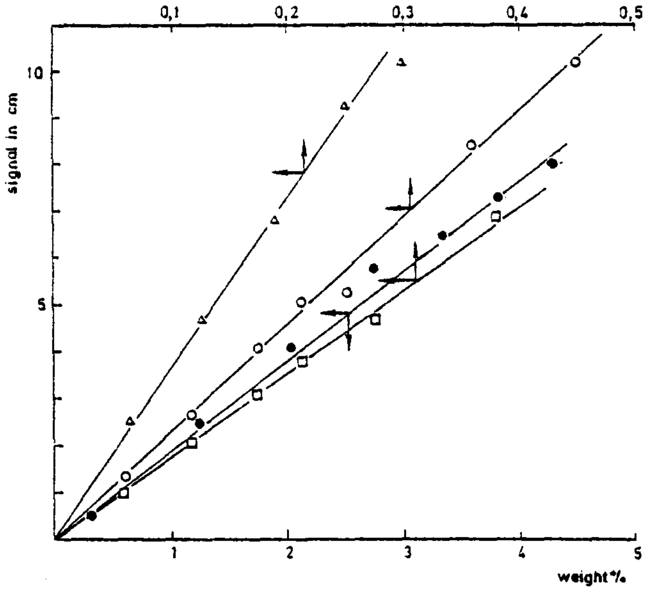

Fig.6:
calibration of the
derivative spectra
● Fig.3a Signal A
▲ Fig.4a Signal B
○ Fig.5a Signal A
□ Fig.5c Signal A

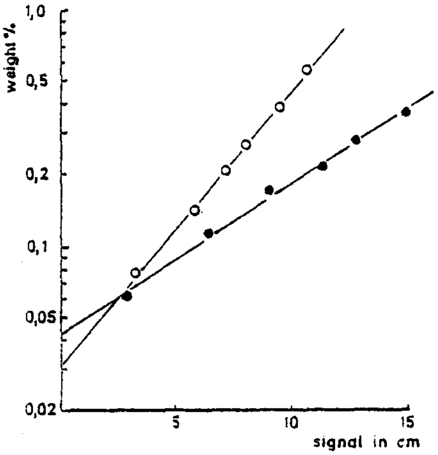

Fig.7:
calibration of the derivative spectra
○ Fig.2a Signal B
● Fig.5c Signal B

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Received May 5 / Accepted May 13, 198o