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Abstract

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PHYSICAL CHEMISTRY

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THE INFLUENCE OF MOLECULAR WEIGHT ON THE LUMINESCENCE OF HIGH-MOLECULAR COMPOUNDS

(Presented by Academician V. N. Kondrat' ev, 14 IV 1960)

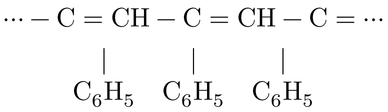
Many polymers, as well as biopolymers, possess bright fluorescence in the solid and dissolved states. In the present work, polymers of the most diverse chemical structure have been qualitatively investigated, both possessing a continuous chain of conjugated bonds and not containing such a chain: polyphenylacetylenes, poly-para-carbotoxyphenylmethacrylamides, polystyrenes, polymethacrylates, a number of proteins, amino acids, the nucleic acids DNA and RNA, etc. The fluorescence spectra were photographed on "Panchrome" spectral plates with a glass spectrograph of aperture ratio 1 : 5 and inverse dispersion in the region 660–670 mμ equal to 14 mμ per 1 mm. A PRK-2 lamp with a UFS-4 light filter served as the excitation source. Microphotometry of the spectra was carried out on an MF-4 microphotometer.

In Fig. 1 (see insert facing p. 1331) the fluorescence spectra of some of the compounds listed are given. We clearly see the common structure of all the spectra, irrespective of the diversity of the chemical composition and structure of the polymers.

The fluorescence spectra of all the indicated and many other polymers not presented here extend as a continuous continuum over the region from 300 to 700 mμ. This fluorescence is not the characteristic fluorescence of molecules. For all the compounds listed above it consists of maxima, constant in position, in the red part of the continuum and of an adjacent broad diffuse maximum in the blue-violet part. The latter maximum changes its position from compound to compound and with changes in the magnitude of the molecular weight within one and the same homologous series.

The study of the dependence of fluorescence spectra on changes in the magnitude of molecular weight is of great practical interest, since, if a connection is found between molecular weight and some spectral characteristic of a polymer, this may make it possible to develop a method for determining the molecular weights of polymers in the solid state. Such a method is not yet known to us, and, owing to the insolubility of many polymers, there is a great need for it.

The change in fluorescence spectra with change in the molecular weight of a polymer with a continuous chain of conjugated bonds in its molecule was investigated on samples of polyphenylacetylenes, which have the structure



$$\begin{array}{ccccccccccc} \cdots - & C & = CH - & C & = CH - & C & = \cdots \\ & | & & | & & | & \\ & C_6H_5 & & C_6H_5 & & C_6H_5 & \end{array}$$

In Fig. 2 are presented microphotograms of the fluorescence spectra of solutions of polyphenylacetylenes obtained by thermal polymerization in an inert gas at 150, 300, and 400°, with average molecular weights, respectively, of 1100, 1300, and 1500 (^1).

Examining the microphotograms, we see that the spectra of all three samples of polyphenylacetylenes represent, as already indicated,

one and the same system of fluorescence bands: with maxima at 670, 610, 560 mμ, several bands in the region of the green and blue mercury lines* and a broad blue-violet band. It is characteristic that the positions of the bands in the spectra of all the samples studied are one and the same and that fluorescence bands of different polyphenylacetylenes, identical in this sense, differ from one another only in intensity. An exception is the broad blue-violet maximum, which exhibits a red shift increasing in parallel with the increase in the molecular weight of the polymer. In addition, attention is drawn to the redistribution of band intensities over the entire range of the fluorescence spectrum: as the molecular weight increases, the intensity of the long-wavelength fluorescence bands increases relative to the intensity of the blue-violet band. Thus, in polyphenylacetylene with molecular weight 1100 the broad blue-violet band is the most intense, while the long-wavelength bands, unchanged in their position in the spectrum, are weak. In polyphenylacetylene with molecular weight 1300 the broad blue-violet band and the red bands are equivalent in intensity, whereas in polyphenylacetylene of molecular weight 1500 the maximum of the blue-violet band is already considerably shifted toward longer wavelengths and is greatly weakened in intensity relative to the long-wavelength bands, which are stable in position in the spectrum and have become intense.

Fig. 2. Microphotograms of the fluorescence spectra of solutions of polyphenylacetylenes in benzene:
1 –mol. weight 1100; 2 –mol. weight 1300; 3 –mol. weight 1500

Specially performed photometric measurements also showed that, with increasing molecular weight of the polyphenylacetylenes, the integral fluorescence yield over the whole spectral range decreases markedly. As an example of the change

Fig. 2. Microphotograms of the fluorescence spectra of solutions of polyphenylacetylenes in benzene: 1 —mol. weight 1100; 2 —mol. weight 1300; 3 —mol. weight 1500

Figure 1: Fig. 2. Microphotograms of the fluorescence spectra of solutions of polyphenylacetylenes in benzene: 1 —mol. weight 1100; 2 —mol. weight 1300; 3 —mol. weight 1500

Fig. 3. Microphotograms of fluorescence spectra of polystyrenes in the solid state: 1 —mol. weight 180,000; 2 —mol. weight 250,000; 3 —mol. weight 300,000

Figure 2: Fig. 3. Microphotograms of fluorescence spectra of polystyrenes in the solid state: 1 —mol. weight 180,000; 2 —mol. weight 250,000; 3 —mol. weight 300,000

in the fluorescence spectrum with change in the molecular weight of polymers that do not have continuous chains of conjugated bonds, let us consider the spectra of polystyrenes of various molecular weights. It is especially interesting to compare the fluorescence spectra of these polymers with the spectra of polyphenylacetylenes described above, as compounds which, by their structure, are hydrogenated polyphenylacetylenes.

* These bands are readily detected on plates that have no dip in the green region of the spectrum.

In Fig. 3 are shown microphotograms of the fluorescence spectra of three polystyrenes with viscosity-average molecular weights of 300,000, 250,000, and 180,000. The spectrum of one of them is also given in Fig. 1. We see that these are exactly the same fluorescence spectra as the spectra of polyphenylacetylenes and other polymers, but with the intensities of all bands redistributed in accordance with their individuality. Here the broad blue-violet band has the maximum intensity; its maximum, as well,

Fig. 3. Microphotograms of fluorescence spectra of polystyrenes in the solid state: 1 —mol. weight 180,000; 2 —mol. weight 250,000; 3 —mol. weight 300,000

as in the polyphenylacetylenes, shifts with increasing molecular weight toward longer waves and decreases in intensity significantly more than the intensity of all the other bands. In addition, the same redistribution of the intensities of all bands is observed as in all the other polymers, namely: the relative intensity of the longer-wavelength bands increases regularly. This is especially clearly seen for the bands at 670, 610, and 560 mμ.

Thus, an increase in the degree of polymerization, both in the case of polymers with a continuous chain of conjugated bonds and without such bonds, entails: an overall, total decrease in the intensity of the fluorescence spectrum; a shift of the broad blue-violet maximum toward longer waves; a directed relative redistribution of the intensities of all fluorescence bands—the long-wavelength bands increase in intensity relative to the diminishing short-wavelength bands.

All these effects are sharply pronounced for polymers containing in the molecule a continuous chain of conjugated bonds, and weakly pronounced for polymers whose molecules do not contain them.

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