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Spectra of the Universal Fluorescence of Polymers

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Abstract

Full Text

Spectra of the Universal Fluorescence of Polymers

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In work (1) the universality of the fluorescence spectra of a large group of different high-molecular compounds was demonstrated, and certain regularities were found in the homologous series of polyphenylacetylenes, polystyrenes, and other polymers, relating the structure of the spectra to the magnitude of the molecular weight.

In the present work, using an ISP-73 spectrosensitometer, a quantitative study was carried out of the fluorescence spectra of polymers already considered earlier (1), and of a number of others. The results obtained showed that their universal luminescence depends not only on the chemical structure and degree of polymerization, but also on the crosslinking of linear chains into spatial two-dimensional or three-dimensional networks, on the state in which the polymer is found (solid or dissolved), on temperature, on deformation, and on other factors. The presence in the chains of a continuous system of conjugated bonds, as a rule, in all the cases studied causes a sharp shift of the luminescence intensity toward the long-wavelength side of the spectrum.

In Fig. 1, as examples, spectra of the universal fluorescence of polyphenylacetylenes, polystyrenes, and poly-para-carbethoxyphenyl methacrylamides in the solid state and of polyhexynes in the liquid state are given in relative equienergetic units. Taking into account the nonuniform sensitization of spectral photographic plates, one might have expected that on microphotograms of fluorescence spectra some maxima would be false ones, not reflecting the picture of the actually existing spectra, and that in reality the fluorescence spectrum contains a smaller number of bands. However, comparing the results obtained in the present work with the conclusions drawn on the basis of the qualitative data of work (1), we see that quantitative treatment made it possible to detect far more details in the structure of the spectra. Indeed, from the data obtained it is evident that in polyphenylacetylenes, as in polystyrenes and other polymers, there exists an identical system of numerous fluorescence bands constant in position in the spectrum. A whole series of these bands is distinctly resolved in the visible region of the spectrum. In addition, in the far red region new maxima at 675 and 690 mμ were found. All the bands merge into a continuous continuum extending from the excitation lines at 366 mμ over the entire visible region. This circumstance is the cause of strong masking of many bands of the universal luminescence of polymers. According to preliminary data, the fluores-

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Fig. 1

Figure 1: Fig. 1

cence spectrum is not limited to the visible region, but extends farther into the near infrared region of the spectrum. The structure of the spectra of universal luminescence in this region is currently being studied.

Before quantitative treatment, an exception to the general picture of the fluorescence spectrum of polymers was a broad blue-violet band which, unlike the other bands, showed, with increasing degree of polymerization, a shift toward the red side of the spectrum (see work (1)). However, after quantitative treatment of the spectra this band proved to be complex in all polymers. Within this band six clearly expressed maxima were found: ~390, ~420, ~430, ~450, ~470, and

~490 mμ. Apparently, the maximum at 450 mμ, the most intense of these, is a maximum of complex structure*. This is indicated by small inflections observed in the spectra of a number of polymers on its short-wavelength side and, in some cases, on its long-wavelength side. Such a phenomenon may be due to the complexity of the spectral maximum or to the influence on it of closely located bands in the spectrum. The results obtained suggest that the "shift" of this maximum, like the "shift" of the blue-violet band (1), with increasing molecular weights of polymers toward longer wavelengths is an effect of an apparent shift, which in reality does not exist. This effect may be due to a redistribution of intensities in two adjacent unresolved fluorescence bands, of which the 450 mμ maximum may consist. Indeed, if the intensity of the shorter-wavelength band decreases with polymerization more than the intensity of the longer-wavelength band, then this causes a shift of the maximum of their envelope (i.e., of the 450 mμ maximum) into the long-wavelength region of the spectrum. If in the region of the spectrum at 450 mμ there are not two unresolved bands, but one band stable in position in the spectrum, then the effect of a "shift" may be caused by the influence on it, as was stated above, of a redistribution of the intensities of adjacent bands located close to it.

Fig. 1. Spectra of universal fluorescence (in relative equienergetic units). **a** —polyphenylacetylenes with average molecular weights: 1 —1200; 2 —1300 and 3 —1500 (slit 0.3 mm; exposure 15 min.); **b** —polystyrenes with average molecular weights: 1 —180,000; 2 —250,000 and 3 —300,000 (slit 0.3 mm; exposure 3 min.); **c** —poly-*p*-carbethoxyphenylmethacrylamides with fractionated molecular weights: 1 —220,000; 2 —355,000 and 3 —870,000 (slit 0.3 mm; exposure 12 min.); **d** —polyhexenes with average molecular weights: 1 —8000 (slit 0.3 mm; exposure 24 min.), 2 —80,000 (slit 0.3 mm; exposure 60 min.).

* This maximum, like the blue-violet maximum in work (1), also shifts with increasing degree of polymerization toward the long-wavelength side of the spectrum, but less significantly.

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To bring complete clarity to this question, additional measurements on an instrument with higher resolving power are, of course, necessary.

The total intensity of all bands of the continuous continuum of the universal luminescence of polymers, as is seen from Fig. 1, decreases with increasing degree of polymerization. The accompanying redistribution of intensities among the individual bands in the spectrum may be regarded, with some exceptions, as quenching of each short-wavelength band to a greater extent than the neighboring long-wavelength one. It is still difficult to say what causes this redistribution of intensities. It may be connected with a change in the electronic state of the whole macromolecule as a whole. If, however, the redistribution of intensities is based on the different nature of bands or of systems of bands associated with individual electronic transitions, then this redistribution and the decrease in the total fluorescence intensity may be connected with a change in the electronic states of different groups of the macromolecule.

All changes in the fluorescence spectra of polymers that are associated with changes in their molecular weight, as already mentioned, are much more sharply expressed for polymers whose chains possess a continuous system of conjugated bonds. This is clearly seen in the example of polyphenylacetylenes and polyhexynes (Fig. 1). The role of the system of conjugated bonds is illustrated especially clearly by the spectra of polyphenylacetylenes and polystyrenes—polymers differing only in their chains. The chains of polyphenylacetylenes contain a continuous system of conjugated bonds, whereas the chains of polystyrenes, which may be regarded as hydrogenated chains of polyphenylacetylenes, do not have such a system. Considering the change in the spectra of these two compounds as a function of their molecular weight (Fig. 1), we see in both cases one and the same regularity, characteristic of all polymers, but in polyphenylacetylenes expressed to a considerably greater degree. Thus, the system of conjugated bonds introduces nothing new into the spectrum of the universal fluorescence of a polymer, but only enhances the effects, determined by the degree of polymerization, that are already produced by a polymer chain not possessing a continuous system of conjugated bonds.

In conclusion, it is important to emphasize that, when the polymer chain is lengthened, the intensity maximum in its fluorescence spectrum gradually shifts toward the long-wavelength bands; the bands themselves, however, do not shift toward the red region of the spectrum, as might have been expected on the basis of existing notions. Thus, the energy of electronic transitions does not change with lengthening of the polymer chain: only their intensity changes.

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Note: Figure translations are in progress. See original paper for figures.

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