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Functional Polymers. XXV. Fluorescence Spectra of Derivatives of Methyl Salicylate and Copolymers of Methyl Vinylsalicylates

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Functional Polymers. XXV. Fluorescence Spectra of Derivatives of Methyl Salicylate and Copolymers of Methyl Vinylsalicylates

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ABSTRACT

Ultraviolet absorption and fluorescence spectra of methyl salicylate, isomers of methyl salicylate derivatives, and polymers with units of isomers of methyl salicylate have been investigated. The λ_{\max} of methyl salicylate and its derivatives is centered around 310 nm. When the phenolic hydroxyl group is acetylated, the maximum is at 285 nm. Fluorescent emission maxima depend on the excitation wavelength. Two groups of maxima centered at 350 and 460 nm indicate that two molecular species (already present in the ground state) of the methyl salicylate moiety, probably tautomers, play essential parts as photoexcited states in the photophysics of methyl salicylate derivatives.

INTRODUCTION

Chemical sunscreens, compounds capable of absorbing the photon energies associated with incident ultraviolet light and to dissipate these energies in a harmless way, are of great interest and importance for both material and skin protection. Numerous review articles have appeared over the last few years discussing, e.g., light-induced degradation reactions in plastics [1], the interaction of ultraviolet radiation with pigments in the human skin [2], and the use of chemical sunscreens [1, 3].

A wide range of compounds is useful as ultraviolet protective absorbers, most of which belong to only a few classes of compounds: 2-hydroxybenzophenones, 2-hydroxyphenylbenzotriazoles, 4-aminobenzoate esters, α -cyano- β , β -diphenylacrylate esters, and salicylate esters. In order to prolong the ultraviolet-stabilizing efficiency in, e.g., a polymer film or fiber, the concept of polymerizable ultraviolet absorbers arose. When incorporating a stabilizer by attaching it chemically into the matrix of a polymeric material, its stabilizers' mobility is greatly reduced and the possibility for it to evaporate or to be leached out is eliminated.

In our laboratory, a wide range of polymerizable ultraviolet stabilizers has been synthesized, including derivatives of methyl salicylate [4-7]. The fluorescence spectra of these compounds reveal some aspects by which the absorbed ultraviolet light energy is dissipated.

In this communication we report fluorescence spectra of methyl salicylate (MS), methyl 4-ethylsalicylate (M4ES), methyl 3-ethylsalicylate (M3ES), methyl 5-vinylsalicylate (M5VS), methyl 3-ethylacetyl-salicylate (M3EAS), and of the copolymers of methyl methacrylate (MMA) with M3VS or M5VS.

EXPERIMENTAL PART

Materials

Cyclohexane, 1,2-dichloroethane, methanol, and methyl salicylate (MS) were analytical grade supplied by the Beijing Chemical Works. MS was purified by distillation before use.

The derivatives of methyl salicylate, isomers of the methyl vinylsalicylates, and their copolymers with MMA were prepared in our laboratory; their syntheses have been reported previously [4, 6, 7].

Measurements

The UV-absorption spectra were recorded on a Zeiss Specord UV-Vis Spectrophotometer, the fluorescence spectra on a Hitachi MPF-4 Fluorescence Spectrophotometer. Slit width of the first monochro-

mater was 10 nm, and the second one was 6 nm. Measurements were done at room temperature; all the fluorescence spectra reported are corrected.

RESULTS AND DISCUSSION

The ultraviolet absorption, fluorescence emission, and fluorescence excitation spectra of MS, derivatives of MS, and polymers containing MS units have been studied; their numeric values are shown in Table 1.

The ultraviolet absorption spectra of MS showed a λ_{\max} at 310 nm, that of M4ES a λ_{\max} also at 310 nm, M3ES a λ_{\max} at 312 nm, and M5ES a λ_{\max} at 336 nm; M3EAS, where the phenolic -OH is acetylated, a λ_{\max} of only 285 nm (Fig. 1).

For the fluorescence excitation spectra, some years ago Sandros [8] showed that the ultraviolet emission at 340 nm and the blue emission at about 450 nm of MS resulted in different fluorescence excitation spectra. These results pointed to the evidence of two different molecular species which are in equilibrium with each other already in the ground state. He attributed this behavior to the emission of two tautomers, the ultraviolet emission to Tautomer A, which is responsible for the normal fluorescence of MS, and the blue emission to Tautomer B, which exhibits a strong hydrogen bonding between the proton of the phenolic OH group and the carbonyl oxygen of the carbonyl group. Upon excitation, the phenolic proton is quickly and apparently completely transferred to the oxygen of the carbonyl group, possibly creating charged intermediates, generating blue emission:

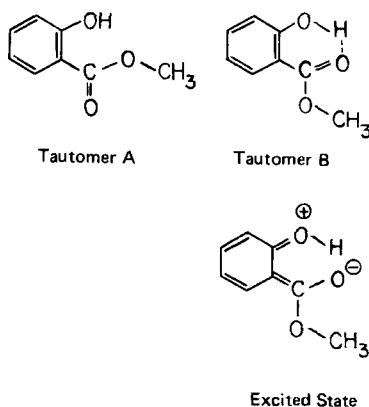


TABLE 1. UV-Absorption and Fluorescence Spectra^a of Methyl Salicylate, Derivatives of Methyl Salicylate, and Some Polymers with Methyl Salicylate Units

Compound	Absorption, ^b		Fluorescence ^b emission			Fluorescence ^b excitation		Fluorescence ^c emission	
	λ_{\max}		λ_{Ex}	λ_{max}		λ_{Em}	$\lambda_{\text{Ex, max}}$	λ_{Ex}	λ_{max}
MS	310		315	440, 460		460	310	356	410
			280	335, 350, 370, 440-460		355	275		
M4ES	310		310	440, 457, 475		450	310	350	410
			280	335, 352, 370, 440-460		354	275		
M3ES	312		320	445, 470, 485		470	320	360	420
			285	335, 350, 370, 460-490		355	375-280		
M5VS	336		333	390, 465, 490		480	330	380	440-460
			270	390, 465, 480		410	330	300	440-460
M3EAS	285		285	330		330	285	290	345
Poly(M3VS-co-MMA) ^d			325	460-490		460	300-330		
			280	360		360	280		
Poly(M5VS-co-MMA) ^d			325	470-490		460	300-340		
			280	360, 460-500		360	280		

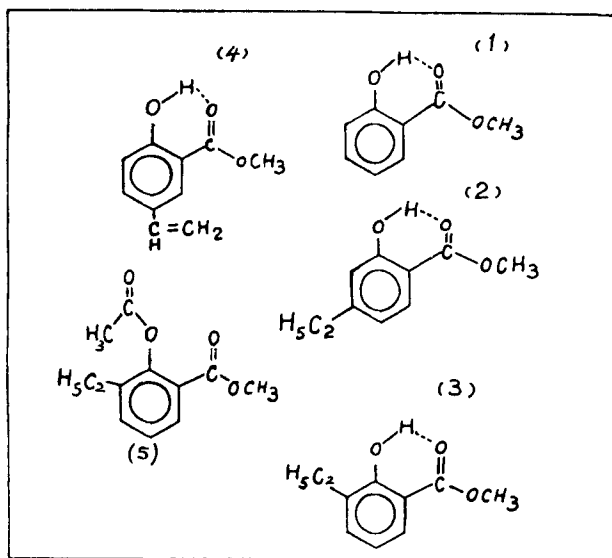
^a λ expressed in nanometers.

^bCyclohexane, 2×10^{-4} mol/L.

^cMethanol, 2×10^{-3} mol/L.

^dCyclohexane/1,2-dichloroethane (1/1); concentration 0.5 g/L.

The hydrogen-bonded formulas of MS (1), M4ES (2), M3ES (3), M5VS (4), and M3AS (5) are shown in



Kloepffer [9, 10] came to similar conclusions, based on excitation studies in the vapor phase.

In this investigation we studied the fluorescence emission of MS, derivatives of MS, and polymers with MS units in the polymer chain in basically two solvent systems: MS and derivatives of MS were measured in cyclohexane, a nonpolar hydrocarbon solvent, and in methanol, a polar hydrogen bond-breaking solvent of strong solvating power. The effect of methanol cannot be interpreted unequivocally as the effect of pure and anhydrous methanol as even highly dried methanol, not uncommonly, has a small amount of water in the system, and it is possible that this trace amount could be completely or in part responsible for the effect seen in Table 1, Column 4.

The two polymers studied, poly(M3VS-co-MMA) and poly(M5VS-co-MMA), for solubility reasons were measured in a 1:1 (v/v) mixture of cyclohexane and 1,2-dichloroethane.

The fluorescence emission spectrum of MS is shown in Fig. 2. When excited with light of a wavelength of 315 nm, Spectrum A was obtained with a double λ_{\max} of 440 and 460 nm, whereas with an excitation wavelength λ_{Ex} of 280 nm, two groups of λ_{\max} for the emission spectrum were found, the group at 440 and 460 nm of reduced intensity, but also a group of maxima at 335, 350, and 370 nm with the λ_{\max} of 350 nm

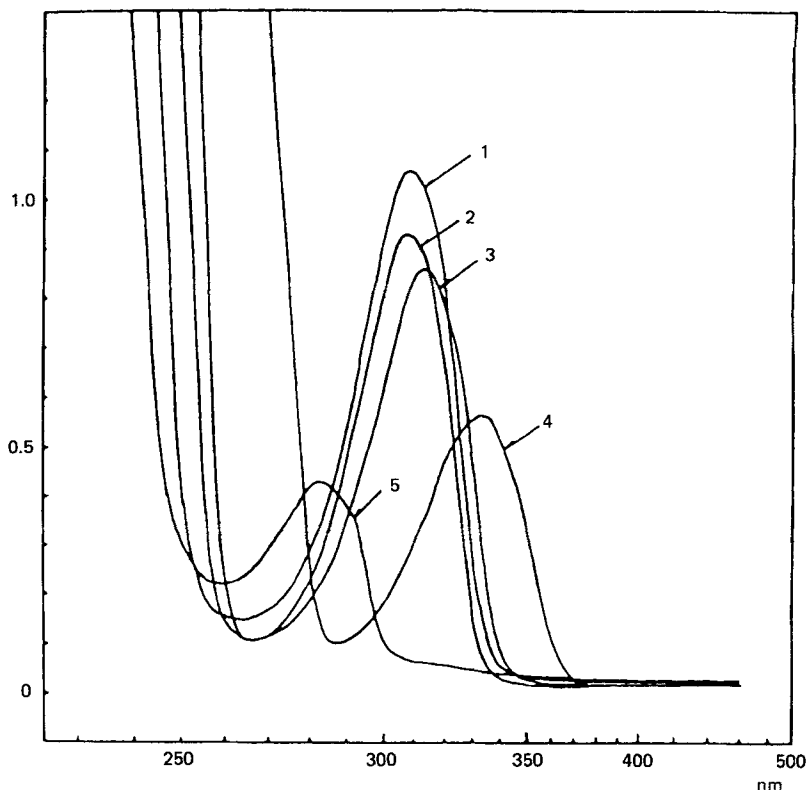


FIG. 1. Absorption spectra of different derivatives of methyl salicylate (MS) in cyclohexane. Concentration: 2×10^{-4} mol/L. (1) Methyl salicylate (MS). (2) Methyl 4-ethylsalicylate (M4ES). (3) Methyl 3-ethylsalicylate (M3ES). (4) Methyl 5-vinylsalicylate (M5VS). (5) Methyl 3-ethylacetylsalicylate (M3EAS).

the dominating wavelength of emission. The insert in Fig. 2 shows a $\lambda_{\text{Ex,max}}$ of 275 nm from a λ_{Em} of 355 nm and a $\lambda_{\text{Ex,max}}$ of 310 nm from a λ_{Em} of 460 nm.

Figure 3 shows the fluorescence emission spectrum of M4ES. When excited with light of a wavelength of 310 nm, Spectrum A was obtained with a broad peak of 457 nm with shoulders at 440 and 475 nm, and when excited at 280 nm with a double peak, similar to Fig. 2, a residual emission at 460 to 490 nm, but a new set of peaks at 335, 352, and 370 nm with the 352 nm peak the most prominent. The insert in Fig. 3 shows the fluorescence excitation spectrum. A λ_{Em} of 354

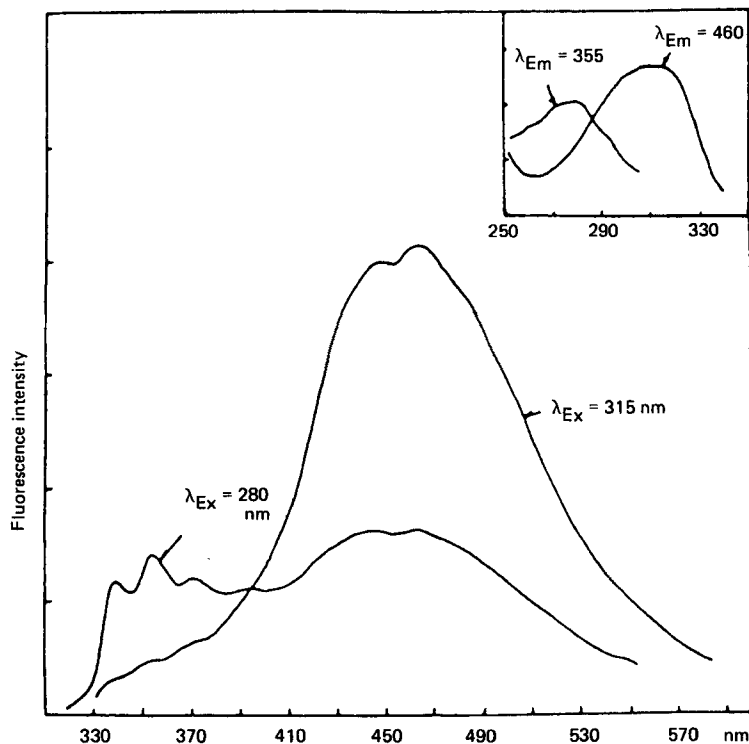


FIG. 2. Fluorescence emission spectra of methyl salicylate (MS) in cyclohexane (insert: excitation spectra). Concentration: 2×10^{-4} mol/L.

nm gives a $\lambda_{\text{Ex,max}}$ of 275 nm, and a λ_{Em} of 450 nm gives a $\lambda_{\text{Ex,max}}$ of 310 nm.

The fluorescence emission spectra and excitation spectra of M3ES are shown in Fig. 4, and the actual values of the wavelengths in Table 1. Although in general similar to the spectra of M4ES (Fig. 3), there are subtle differences, with slight differences in the λ_{max} of the major emission peak, and also slight differences in the intensity of the higher and lower wavelength intensity of the shoulder associated with the major peak at around 460 nm when the λ_{Ex} was 320 nm, but the lower wavelength peaks of the λ_{max} of 270 nm is less prominent (Fig. 5) and the plateaus appeared in both emission spectra with different wavelengths.

The fluorescence emission and excitation spectra of M3EAS, as an example of an MS derivative that has the phenolic hydroxyl group

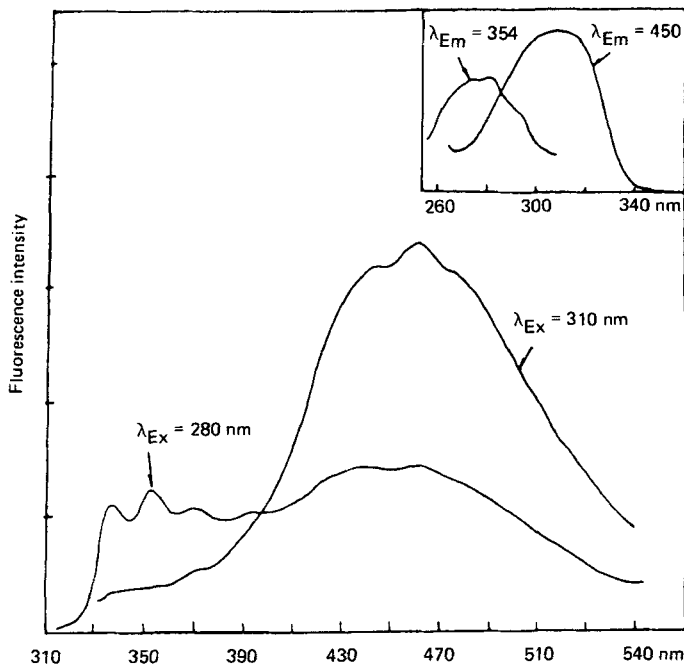


FIG. 3. Fluorescence emission spectra of methyl 4-ethylsalicylate (M4ES) in cyclohexane (insert: excitation spectra). Concentration: 2×10^{-4} mol/L.

acetylated, are much simpler. (From other work it was also known that MS derivatives, as are 2-hydroxybenzophenones or 2-hydroxybenzotriazoles, powerful ultraviolet absorbers and stabilizers, when acetylated are completely ineffective as ultraviolet stabilizers [11-13].)

The fluorescence spectrum (Fig. 6) is simple. At a λ_{Ex} of 285 nm, a λ_{max} of 330 nm was observed; the structure of this spectrum is simple and without detail. The blue emission bands are absent. Also simple is the fluorescence excitation spectrum, where at a λ_{Em} of 330 nm, a $\lambda_{Ex,max}$ of 285 nm was found.

Figure 7 shows the fluorescence spectra of MS, M4ES, M3ES, M5VS, and M3EAS in methanol. The fluorescence emission is simple and the λ_{max} without much detail. This effect would be expected when hydrogen bond breaking (assisted by the solvent) is an important factor in the photophysical process of the excited states of these compounds.

With λ_{Ex} of 350 to 360 nm, λ_{max} of emission of 410 nm were ob-

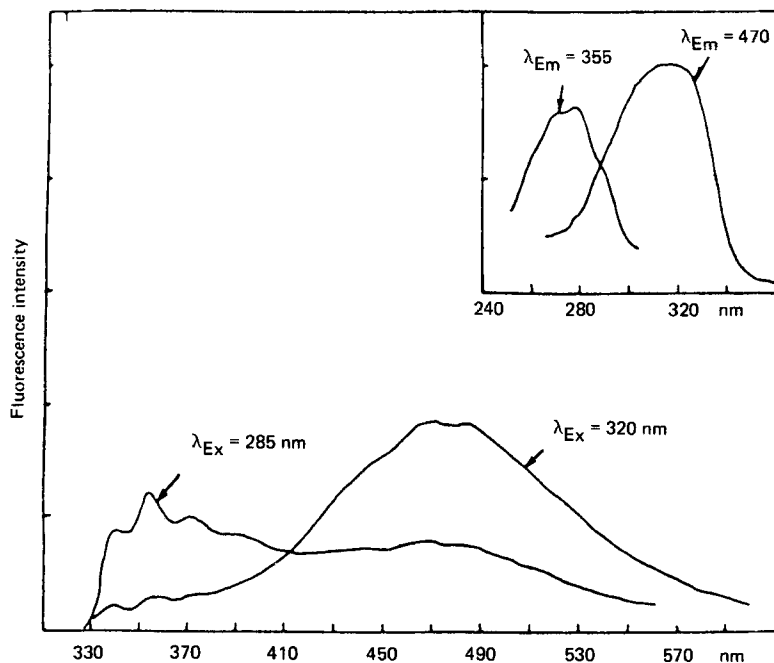


FIG. 4. Fluorescence emission spectra of methyl 3-ethylsali-cylate (M3ES) in cyclohexane (insert: excitation spectra). Concentration: 2×10^{-4} mol/L.

served. Exceptions were M5VS where a λ_{Ex} of 330 or 380 nm produced a λ_{max} of 440 to 460 nm, or M3EAS where a λ_{Ex} of 290 nm produced a λ_{max} of 345 nm. From these results it can be seen that the dual fluorescence, whose relative intensity depends upon the excitation wavelength λ_{Ex} , had disappeared and the uncommonly large Stokes shift of about 150 is also not present.

One of the practical conclusions of these investigations is that these derivatives of MS are used as effective ultraviolet stabilizers; they should be used in a hydrocarbon (oil) matrix rather than in a matrix with hydroxyl groups, aqueous phase, or with polar groups in the system. If such MS compounds are attempted to be used as ultraviolet stabilizers, they should not be expected to be effective in polymeric systems or matrices with these characteristics.

The fluorescence (both emission or excitation) spectra of polymers (copolymers) containing MS (M3VS or M5VS) units in the polymers,

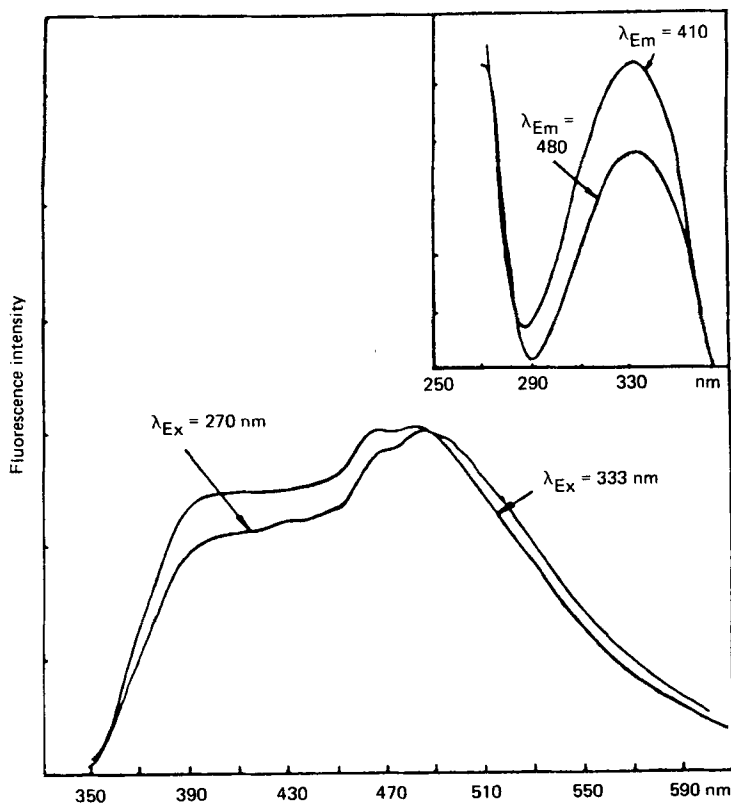


FIG. 5. Fluorescence emission spectra of methyl 5-vinylsalicylate (M5VS) in cyclohexane (insert: excitation spectra). Concentration: 2×10^{-4} mol/L.

MS, units attached at the 3 or 5 position of the MS units on the polymer chain are shown in Figs. 8 and 9. The spectra were taken only in one solvent, the 1:1 (v/v) mixture of cyclohexane and 1,2-dichloroethane, the solvent of the copolymer. The spectra show the general characteristics of the typical low molecular compounds M3ES and M5VS, but, as might be expected, with less detail in the structure and broadened peaks of the fluorescence intensity (Figs. 8 and 9).

The fluorescence emission spectra of poly(M3VS-co-MMA) have a broad λ_{max} of 360 to 490 nm at an excitation wavelength of 325 nm and a λ_{max} of 360 nm for a λ_{Ex} of 280. The fluorescence excitation gave a $\lambda_{\text{Ex,max}}$ of 280 nm at a λ_{Em} of 360 nm and a $\lambda_{\text{Ex,max}}$ of 300 to 330 nm at a λ_{Em} of 460 nm.

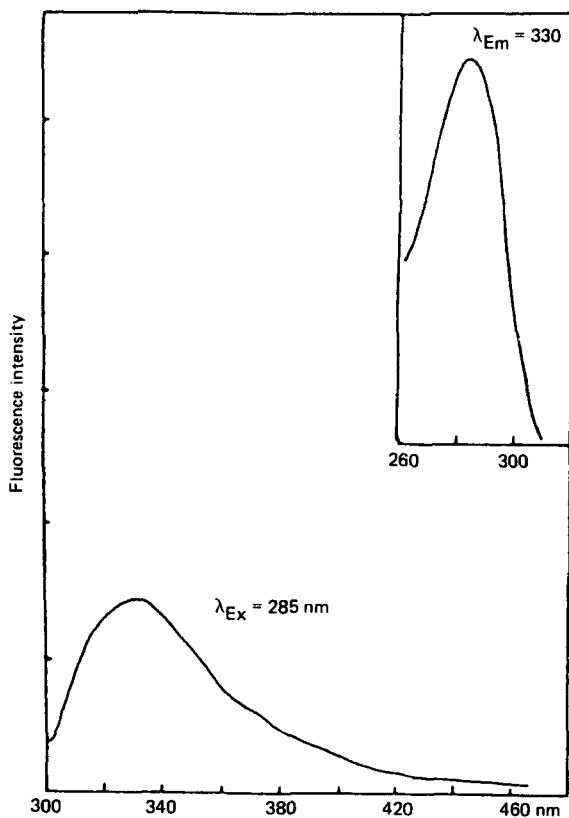


FIG. 6. Fluorescence emission spectra of methyl 3-ethylacetyl-salicylate (M3EAS) in cyclohexane (insert: excitation spectra). Concentration: 2×10^{-4} mol/L.

Essentially the same data were found for poly(M5VS-co-MMA).

The absorption maxima of all MS derivatives are in the range of 310 nm; M3EAS is at 285 nm and its intensity is much less than the intensities shown by the maxima of the salicylates which have a free hydroxyl group. Excitation of these compounds with monochromatic light at wavelengths corresponding to the absorption maxima produced fluorescence emission spectra which show Stokes shifts of approximately 150 nm, except M3EAS where the Stokes shift is only 45 nm, from 285-330 nm. The fluorescence emission spectra of all compounds depended upon the wavelength of the excitation radiation wavelength except in the case of M5VS, the only compound in the series having a vinyl group attached to the aromatic system and consequently

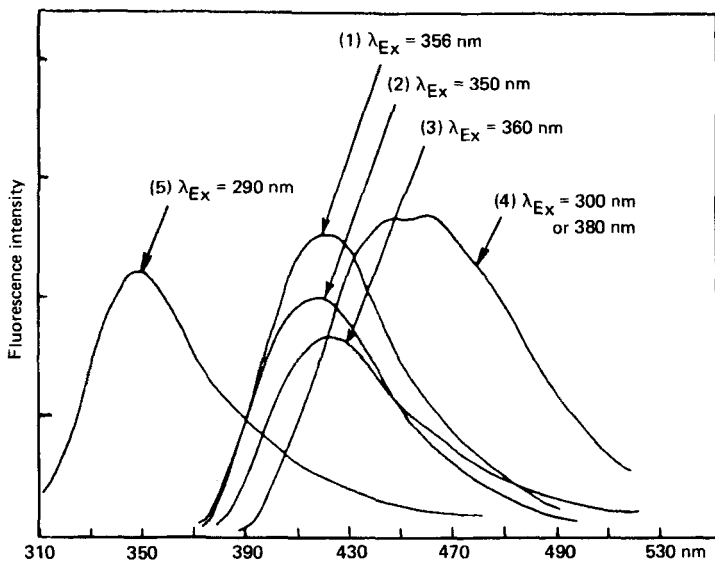


FIG. 7. Fluorescence emission spectra of various derivatives of salicylic acid in methyl alcohol. Concentration: 2×10^{-3} mol/L. (1) Methyl salicylate (MS). (2) Methyl 4-ethylsalicylate (M4ES). (3) Methyl 3-ethylsalicylate (M3ES). (4) Methyl 5-vinylsalicylate (M5VS). (5) Methyl 3-ethylacetylsalicylate (M3EAS).

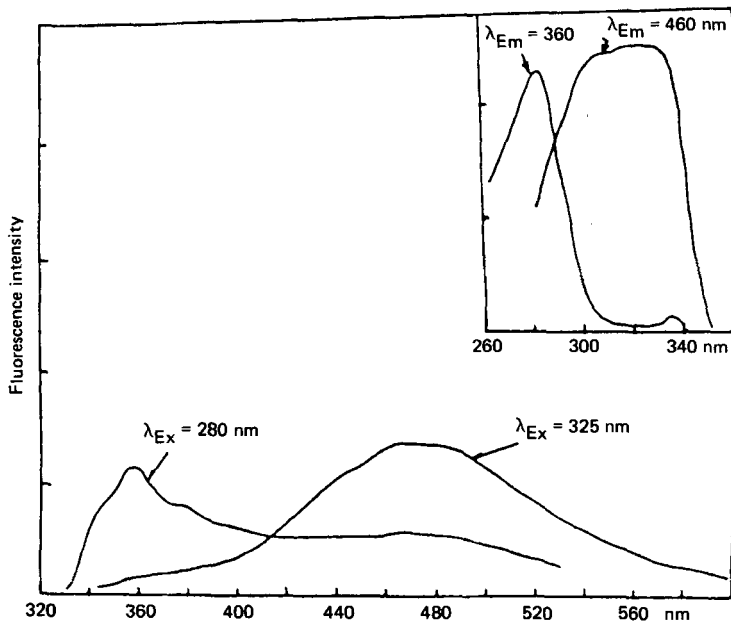


FIG. 8. Fluorescence emission spectra of copolymer of methyl 3-vinylsalicylate and methyl methacrylate [poly(M3VS-co-MMA)] in cyclohexane/1,2-dichloroethane (1:1) solution. Concentration: 0.53 mg/mL.

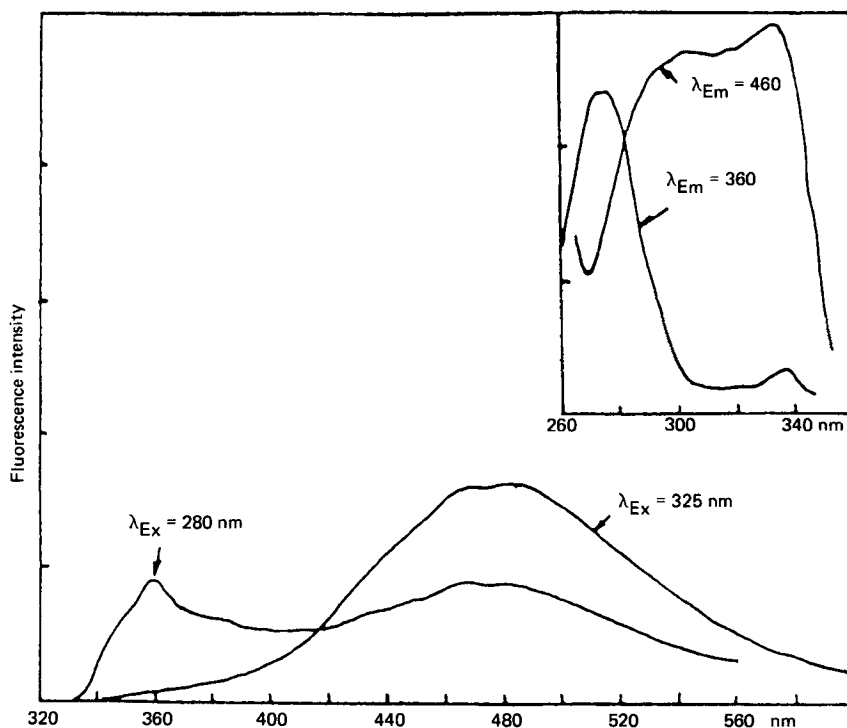


FIG. 9. Fluorescence emission spectra of copolymer of methyl 5-vinylsalicylate and methyl methacrylate [poly(M5VS-co-MMA)] in cyclohexane/1,2-dichloroethane (1:1) solution. Concentration: 0.53 mg/mL.

more electron energy transitions. The fluorescence emission spectrum of this compound, resulting from excitation with a λ_{\max} of 333 nm, is virtually identical with that resulting from excitation with a λ_{\max} of 270 nm.

It can be concluded that two states in the form of two tautomeric forms of methyl salicylates exist, apparently even in the monomeric form. These two forms seem to be exaggerated by exciting the ground state to the excited molecules. It seems that each tautomer is excited preferentially by wavelengths of the exciting radiation.

Polymers containing isomeric units of MS seem to behave like the low molecular compounds. As expected, there seems to be less structure in the λ_{\max} in the fluorescence and emission spectra of the MS units in the MMA copolymers.

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