

Formation of Luminescent Impurities During the Polymerization of Nylon 66

In earlier studies,¹⁻³ we reported on the fluorescence and phosphorescence emissions from nylon 66 polymer. Although the species responsible for the fluorescence could not be identified, the phosphorescence was attributed to the presence of carbonyl impurities present as separate compounds or as groups built into the polymer backbone. Further, the structure of the phosphorescence indicated that these carbonyls were conjugated with ethylenic unsaturation.⁴

TABLE I
Luminescence Changes During the Polymerization of Nylon 66^a

Cycle ^b	Excitation, λ/nm	Emission, λ/nm	Mean lifetime, sec	Emission band intensity (relative)
<i>Fluorescence^c</i>				
Salt	365 max	445 max	—	2.0
2	365 max	445 max	—	25
3	365 max	445 max	—	58
4 (Polymer)	365 max	445 max	—	100
<i>Phosphorescence^c</i>				
Salt	280 max 300	430 max —	1.0 —	2.0 —
2	280 300	425 480	1.6 0.44	16 10
3	280 300	415 460	2.12 0.50	55 24
4 (Polymer)	280 300	410 415, 460, 480	2.20 2.0, 0.5, 0.3	100 9, 46, 45

^a Contains no commercial additives.

^b Prepared as described in ref. 5.

^c Measured as given in earlier papers.¹⁻³

However, unlike that from most other light-sensitive commercial polymers, the phosphorescence emission from nylon 66 exhibits two distinct bands whose wavelength maxima (λ_{max}) and mean lifetimes appear to depend on the morphology of the polymer.^{1,4} Here, we report on both the fluorescence and phosphorescence from samples taken during consecutive stages of polymer manufacture in order to assess the effect on these emissions on the developing rigidity of the polymer matrix.

Weak fluorescence and phosphorescence emissions were initially observed from samples of the nylon salt used for polymer preparation. Both emissions were structureless, and their λ_{\max} values varied with the excitation wavelength (Table I).

After successive stages of the polymerization, using the method of White and Jones,⁵ examination of extracted samples showed that the intensities of both the fluorescence and phosphorescence emissions markedly increased (Table I), the latter exhibiting structure after cycles 3 and 4 (Fig. 1). A further interesting feature after polymerization was that the phosphorescence emission λ_{\max} had shifted to shorter wavelengths with an increase in its lifetime. The fluorescence λ_{\max} remained unchanged.

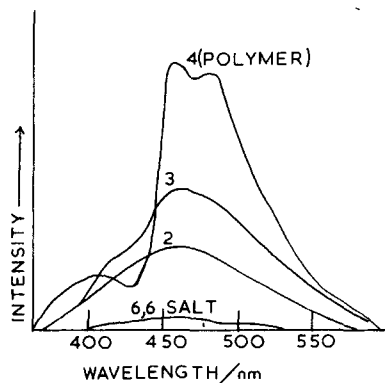


Fig. 1. Increase in phosphorescence emission intensity from nylon 66 after consecutive stages of its polymerization (measured at 77°K): excitation $\lambda = 310$ nm; bandwidth = 2 nm.

The observation of very similar fluorescence and phosphorescence from both nylon 66 salt and polymer suggests they are emitted from trace oxidation impurities. This conclusion is consistent with our earlier model system work⁶ which showed that only on oxidation of the amide was there a development of fluorescence and phosphorescence similar in type to that found here and reported on earlier.¹⁻³ Further, following each successive stage of polymerization, the resultant increase in the rigidity of the molecular environment and the restrictive effect that this would have on the rate of oxygen diffusion through the polymer matrix would thus explain both the increase in the phosphorescence emission and the λ_{\max} shift to shorter wavelengths.⁴

References

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