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EXCIMER EMISSIONS OF SOME AROMATIC VINYLPOLYMERS

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The emission spectra of poly-3-vinylpyrene (PVPy), poly-3-pyrenylmethylvinylether (PPMVE), and poly-9-vinylacridine (PVAc) in solution were measured at room, dry-ice, and liq. N_2 temperatures. New observations of excimer fluorescences of these polymers could be obtained. Lifetimes of excimer fluorescences were measured in pulse method with excitation of N_2 gas laser; 160, 66, and 31 nsec for PVPy, PPMVE, and PVAc, respectively. Emission spectra of PVPy and PVAc almost exclusively consist of excimer fluorescences even at dry-ice temperature on the contrary to PPMVE.

It is well-known that aromatic vinylpolymers such as polystyrene,[1,2] polyvinylnaphtalene,[3] and poly-N-vinylcarbazole[4] exhibit excimer fluorescence in solution due to the interaction between nearby chromophores in the polymer chain. The detailed studies on emission spectra of not only above-mentioned polymers but also other aromatic vinylpolymers are expected to provide valuable informations in understanting the behaviors of excited states and conformational structures in solution as well as in solid film. In the search of high photoconductive vinylpolymers, we have already synthesized a series of aromatic vinylpolymers having large pendant π-electron conjugated systems and investigated the structure and electrical properties, especially of polymers such as poly-3-vinylpyrene (PVPy),[5] poly-3-pyrenylmethylvinylether (PPMVE),[6] poly-9-vinylacridine (PVAc),[7] and poly-N-vinylcarbazole.[8]

In the present letter, we would like to report new observations of excimer emissions of PVPy, PPMVE, and PVAc. The temperature dependence of the intensity and lifetime of the excimer emissions are also measured.

Emission spectra were measured with a Hitachi MPF model 3 spectrophotofluorometer, equipped with a xenon arc source and a R106F(S-19) photomultiplier tube. Spectra were uncorrected for either source output or detector response. Lifetime measurements were made in pulse method with excitation of N_2 gas laser (excitation; 337 nm, 5 nsec half-width pulse with 50 cycle repetitions). Fluorescence emissions through a spectrometer were detected with a 1P28 photomultiplier tube and fluorescence decays were determined from sampling oscilloscope traces. Except where indicated, samples of PVPy and PPMVE with the concentration of 8 x 10^{-4} mol/l in methyltetrahydrofuran - tetrahydrofuran (3 : 2), giving glasses at 77°K, were sealed under vacuum. In the case of PVAc chloroform - tetrahydrofuran (7 : 3) was used as a solvent because of its insolubility in other organic solvents.

In Figure 1 are shown emission spectra of PVPy at room, dry-ice, and liq. N_2 temperatures, respectively. At room temperature only a structureless broad emission band was obtained near at 480 nm. Since this band seems to locate in the wavelength region corresponding to that of excimer fluorescence of pyrene,[9] this broad structureless emission is identified with excimer fluorescence. The lifetime of this band is 160 nsec. In Figure 2 are shown fluorescence spectra of ethylpyrene (EtPy), a model compound of the monomeric unit of PVPy, for comparison. In concentrated solution, a broad emission band was observed in the 440 nm wavelength region. This band may be due to excimer formation as in the case of pyrene. In dilute solution (8 x 10^{-4} mol/l) only monomeric fluorescence was obtained, as can be seen in Figure 2.

In the case of PVPy, however, the concentration dependence of excimer fluorescence was quite differnt from EtPy, and even in 10^{-5} mol/l solution only excimer emission could be observed. This fact would provide a very interesting information in understanding the conformational stability of the polymer chain in solution. The concentration of 10^{-5} mol/l is low enough to neglect the interaction between two chromophores in different polymer chains. It may be, therefore, considered that excimer formation can easily takes place between nearby chromophores because of the rigid conformation of polymer chain.

In Figure 3 are shown emission spectra of PPMVE. In this case were observed not only excimer fluorescence with maximum at 470 nm but also structured monomeric fluorescence in the region of 400 nm with fairly large intensity. The excimer fluorescence of PPMVE had a lifetime of 66 nsec, which was much shorter than that of PVPy. In the case of PPMVE, excimer emission band decreases gradually in intensity with increase of monomeric emission as the temperature gets lower, and finally in glasses at 77°K excimer emission shows no appreciable intensity. On the contrary to PPMVE, emission spectrum of PVPy at dry-ice temperature (Figure 1) almost exclusively consists of excimer fluorescence. Sharp change takes place between dry-ice and liq. N_2 temperatures because of freezing of the molecular motions in the glass state at 77°K. It is interesting to make clear what kind of factors gives rise to the difference in the behaviors of excimer fluorescence between PVPy and PPMVE. Since in PPMVE the substituent pyrenyl groups are not connected directly to the skeletal chain of polymer, unlike PVPy, the formation of excimer sites becomes difficult with increase of internal rotation freedoms about the single bonds of side chain.

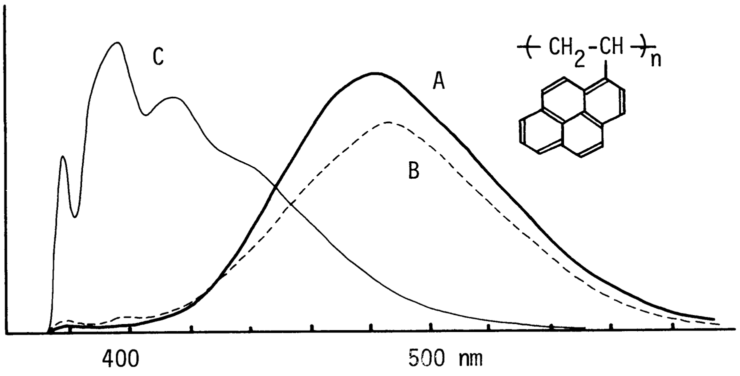

Figure 1. Emission spectra* of poly-3-vinylpyrene $8x10^{-4}$ mol/l solution in MTHF - THF.

A; room temperature

B; dry-ice temperature

C; liq. N_2 temperature

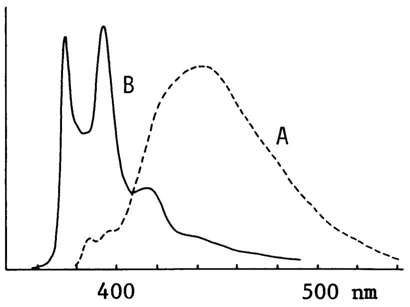

Figure 2. Emission spectra* of 3-ethylpyrene solution in THF.

A; concentrated solution

B; dilute solution, $8x10^{-4}$ mol/l

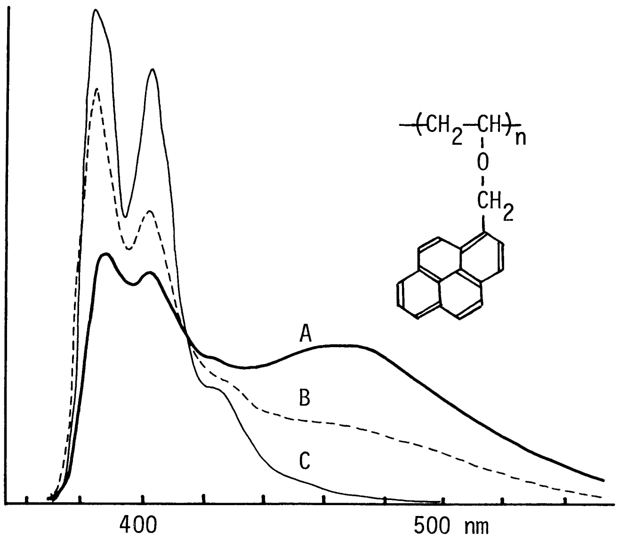

Figure 3. Emission spectra* of poly-3-pyrenylmethylvinylether $8x10^{-4}$ mol/l solution in MTHF - THF.

A; room temperature

B; dry-ice temperature

C; liq. N_2 temperature

* ; Emission spectra are drawn independently in arbitrary fluorescence intensity scale, respectively.

In Figure 4 are shown emission spectra of PVAc at room and dry-ice temperatures, together with emission spectrum of 9-ethylacridine (EtAc) as a model compound. In the case of PVAc, as in the case of PVPy, only excimer fluorescence could be observed in the fairly longer wavelength region of 525 nm with lifetime of 31 nsec. In film sample the same emission spectrum only consisting of excimer fluorescence was obtained. The temperature and concentration dependence is quite similar to those of PVPy. Taking these observations into account, PVAc may also take the rigid conformation even in solution. Unfortunately, emission spectrum at 77°K was not obtained because of the deposition of polymer at this temperature. It is interesting that EtAc gave only monomeric fluorescence even in high concentrations.

Further detailed studies on the variations of lifetimes of fluorescence emission with temperature are now in progress.

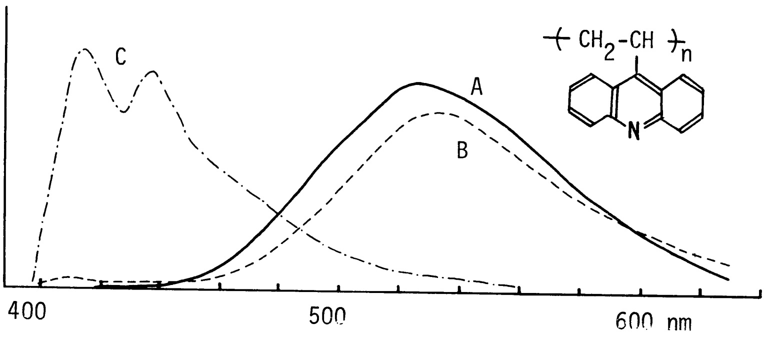

Figure 4. Emission spectra* of poly-9-vinylacridine and 9-ethylacridine.

A; 2x10^{-4} mol/l PVAc in $CHCl_3$-THF at room temperature.

B; 2x10^{-4} mol/l PVAc in $CHCl_3$-THF at dry-ice temperature.

C; 10^{-3} mol/l EtAc in THF at room temperature.

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