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Temperature Dependence of the Intensity of Fluorescence of Poly(N-Vinylcarbazole) Films

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SUMMARY

The fluorescence spectra of thin films of poly(N-vinylcarbazole), PVCA, were measured at temperatures between 103 K and 535 K by constant excitation light intensity. Below 300 K, the corrected spectra were divided into bands belonging to different emitting species of PVCA. Temperature changes of the intensity of fluorescence of the two main excitation energy traps in PVCA are discussed using the simplified kinetic model of Johnson. Local anomalies on the curves of intensity of excimer fluorescence versus temperature measured at constant wavelength reflex the γ- and δ- relaxation regions in PVCA.

INTRODUCTION

The emission properties of PVCA are rather complex as may be seen from the recent sophisticated model of KLÖPFFER (1981) for PVCA films at 77 K. Accounting for only the main primary singlet energy processes, the model may be simpler (JOHNSON 1975). The excitation light quanta are absorbed by individual side groups of the polymer and the excitation energy migrates in the form of singlet excitons through the polymer by hopping between neighbouring pendant carbazolyl groups until it is trapped by one of the pre-formed excimer forming sites (EFS) from which it may be emitted as excimer I (EI) or excimer II (EII) fluorescence. The EI with emission band maximum at 420 nm may form at such sites on the chain where isotactic trans-trans conformational sequence allowing sandwichlike arrangement of two neighbouring carbazolyl side groups exists. EII with maximum of emission at 380 nm is believed to belong to an arrangement of the neighbours along the chain characterized by overlapped two phenyl rings only. No monomer emission of the PVCA films has been observed due to high efficiency of the migration. The concentration of EFS depends on the way of preparation of the polymer (ITAYA et al. 1976) and of the film but it remains constant below the glass temperature T_g of PVCA.

During the study of PVCA, luminescence properties at room temperature have often been compared with those at liquid nitrogen temperature, 77 K (e.g. JOHNSON and OFFEN 1971, KLÖPFFER and FISCHER 1973, JOHNSON 1975, KLÖPFFER and BAUSER 1976, ITAYA et al. 1976, RIPPEN and KLÖPFFER 1979). All these studies have revealed that at room temperature, the emission

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of PVCA consists mainly of EI fluorescence whilst at 77 K, the EII emission is commonly dominating. Only little attention has been paid to the study of the temperature dependence of the intensity of the two types of emission in a broad range of temperature. JOHNSON (1975) and recently ROBERTS et al. (1981) published data on such dependences for the solutions of PVCA but there has been only one paper dealing with the same dependence in thin films of PVCA. It is the paper of DAVID et al. (1972) who measured the intensity of fluorescence of PVCA films at temperatures between 77 and 425 K, divided the uncorrected spectra into two parts using the height of the maxima and interpreted the observed changes by the use of the monomer to excimer intensity ratio in the same way in which were treated excimers in solutions. As RIPPEN and KLÖPFFER (1976) using their iterative subtraction method and the results of ITAYA et al. (1976) were able to determine the shape of the two emission bands of PVCA, it was decided to perform a re-examination of the temperature dependence of the intensity of the two emissions in PVCA films, the results of which are presented below.

EXPERIMENTAL

Samples

Commercial LUVICAN 170 (M_w 10^6) supplied by BASF was purified by dissolving it in UV-spectroscopy grade benzene (LACHEMA,ČSSR))followed by precipitating it by methanol (LACHEMA, ČSSR). This was repeated four times.

Thin film samples were prepared on polished copper plates by casting a 0.1 Mole solution of PVCA in benzene followed by slow evaporation of the solvent at room temperature.

Apparatus

The samples were excited by the 313 nm Hg-line of a stabilized water-cooled high-pressure mercury discharge tube HBO 200. Having passed through the SPM 2 monochromator (Carl Zeiss,DDR), the excitation beam was focused on the sample at an angle of approx. 35^{o} to its surface. Fluorescence was analyzed at right angles to the excitation beam by another SPM 2 monochromator and detected by photomultiplier FEU-79 (USSR). All spectra have been corrected for the wavelength changes of the transmission of the apparatus and of the sensitivity of its detection part. The correction curve was constructed using an optical thermocouple (Hilger), the luminescence of standard solution of quinine bisulphate in H_2SO_4 (400 to 580 nm) and of Rhodamine 6G in ethanol (550 to 640 nm).

During the measurements, the samples were kept in vacuum of 1,3 Pa (10^{-2} Torr) in an optical cryostat. Temperature of the samples was controlled electrically and measured by a calibrated copper-konstantan thermocouple.

RESULTS

In Fig.1 are plotted the corrected spectra of a PVCA film detected during the first low-temperature cycle of the sample. First, the room temperature spectrum (curve 1) was detected. Then was the sample cooled to 103 K and further spectra were measured on the temperature rising branch of the

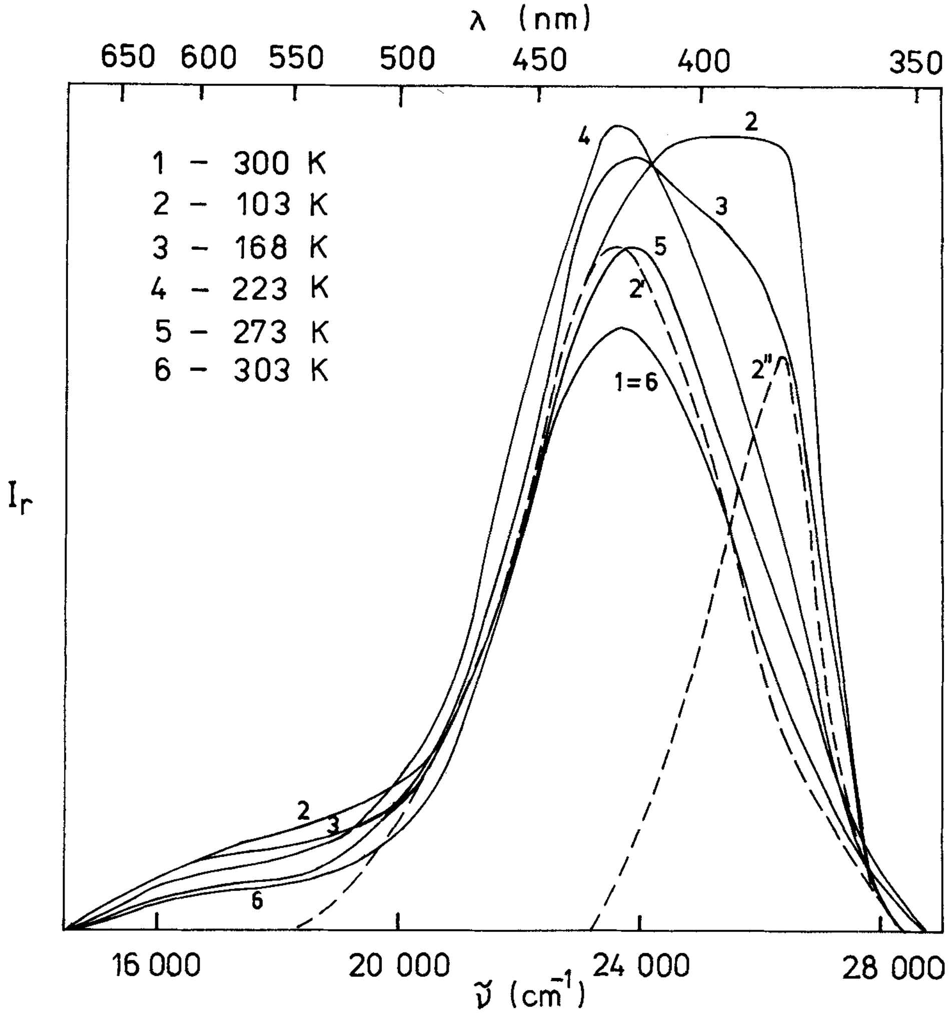

Fig.1. Relative intensity (arbitrary units) of fluorescence of a PVCA film at constant excitation intensity (at 313 nm) and at different temperatures. Corrected spectra. The dashed lines show the EI (2′) and EII (2′′) components of the spectrum 2 obtained by the use of the results of RIPPEN and KLÖPFFER (1979).

cycle. The spectra before and after cooling (curve 1 and 6) are identical. As seen from Fig.1, at the lowest temperature, the overwhole intensity is the highest as well as the relative contribution of the EII to the emission. All the shown spectra were divided into the two excimer bands by the aid of the results of RIPPEN and KLÖPFFER (1979). The integrated intensity of each band and the total of intensity (including the long-wavelength tale which will be discussed later) is plotted against temperature in Fig.2.

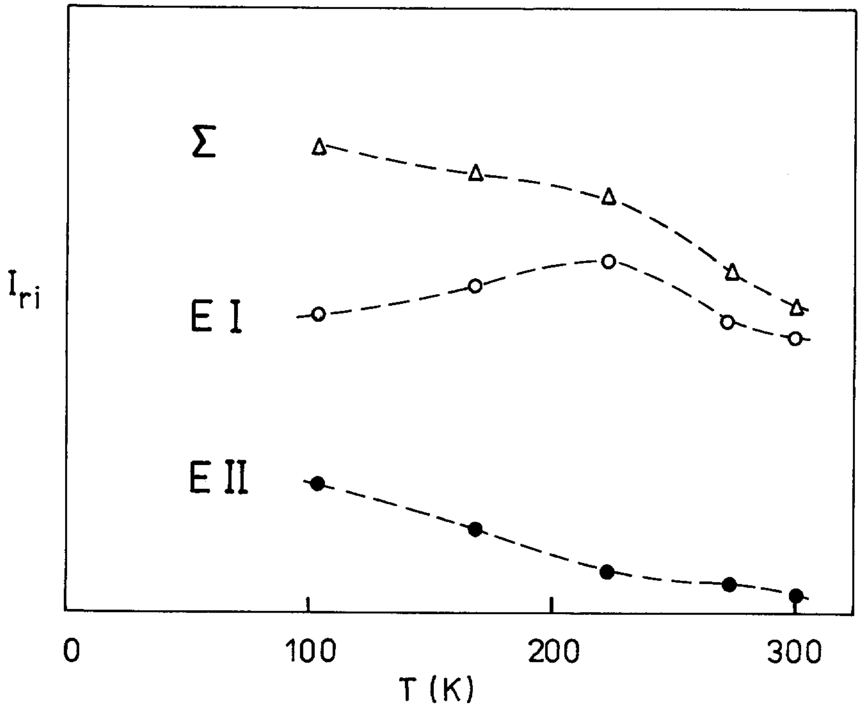

Fig.2. The dependence of integrated intensity of luminescence of the EI band, EII band, and of the total intensity of the PVCA film (arb.units) on temperature.

Interesting feature of this plot is the existence of a maximum on the curve of relative temperature changes of EI intensity.

After the low-temperature measurements, each sample was measured during its heating up to 535 K (glass temperature region of the material was around 470 K) and the following cooling to the room temperature. Because of the changes in the shape of the spectra and of irreversible rise of intensity of the emission around 600 nm, the division of these spectra into the separated parts could not be performed. The overwhole intensity of fluorescence behaved similarly to the intensity of fluorescence measured at 430 nm as a function of temperature in additional experiments which is plotted in Fig.3. In this figure is also plotted the same dependence of the emission measured at 375 nm which characterized, at least at low temperatures, the temperature changes of the EII band. The rise of intensity observed in both the spectral regions around the glass transition temperature of the material was irreversible. During the second temperature cycling of the samples, the overwhole intensity followed the upper branch of the curve for 430 nm emission in Fig.3., i.e. no further rise in intensity near T_g was observed.

The mentioned irreversible rise in intensity of the emission around 600 nm near T_g was observed only from those areas

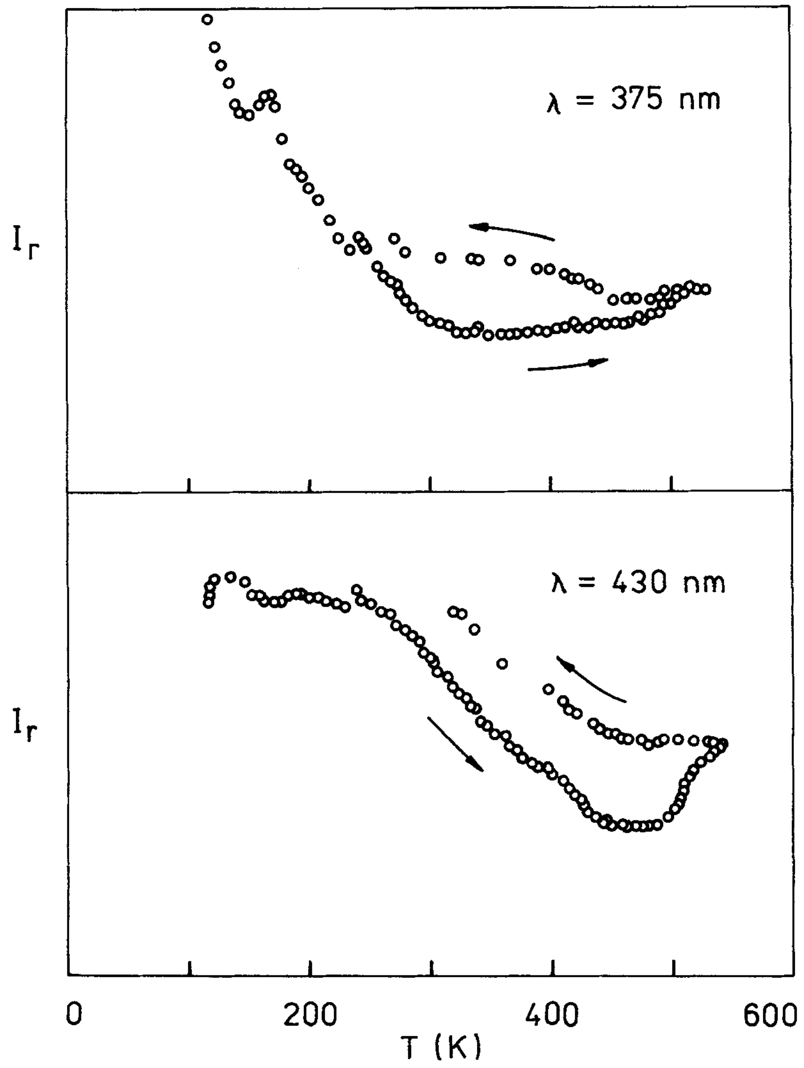

Fig.3. Temperature dependence of the relative intensity of fluorescence (arb.units) of PVCA film measured at 375 and 430 nm, resp., during the first heating-cooling cycle of the samples. Bandpass 4.5 nm.

of the samples which were irradiated by UV excitation light at high temperatures and was almost absent on places heated without irradiation. From this fact, it may be concluded that the emission around 600 nm is due to a product of a photoreaction rather than to a chemical impurity (the relatively poor vacuum in the cryostat may have supplied enough oxygen for such a reaction).

The local anomalies visible in both the curves in Fig.3 were present around 170 K and 235 K by all the measured samples during their first heating. They were absent in the second measuring cycles (i.e. after the heating above the T_g).

DISCUSSION

Local anomalies on curves in Fig.3.

It is known and was also checked in our laboratory (e.g. TRAN THI DUC 1978) that relaxation regions of polymers are reflected in changes of I_r vers. T curves of phosphorescence or delayed fluorescence of luminescent molecules present in the polymer. Here, we suggest that the observed anomalies in excimer fluorescence also reflect the relaxations of PVCA. In the dielectric resp. NMR relaxation studies of PVCA made by POCHAN and HINMAN (1975) resp. FROIX et al.(1975,1976), γ-relaxation of PVCA (rotation of the carbazolyl groups) was observed in the temperature region including the anomaly at 235 K in our measurements. Similarly, the anomaly around 170K may be connected with the δ-relaxation of PVCA (localized backbone motion) observed by them at lower temperatures. The mechanism of interaction of the luminescent centra with the moving parts of the polymer has not yet been understood.

High-temperature region.

The behaviour of PVCA films above room temperature is similar to that observed by FRANK and HARRAH (1974) and FRANK (1974) on films of poly(2-vinylnaphtalene), P2VN. In this material, monomer and excimer emissions are present. The authors observed irreversible rise of excimer emission after heating their samples above the T_g of P2VN and less rise with rising the casting temperature. For the explanation, they used the fact that the concentration of EFS is connected with the concentration of proper conformations on the chain. In films is frozen the equilibrium conformational distribution belonging to the solution of polymer at the casting temperature of the samples. This may be changed only by heating above T_g where conformational changes again may occur with equilibrium concentratinn of EFS higher than at the casting temperature. On following cooling of the sample, the number of EFS must remain the same as at T_g . This explanation is probably valid for the films of PVCA, too. There is still another possible cause of the observed behaviour connected with the supermolecular structure of the samples. Samples prepared at higher temperature are more densely packed than those prepared at lower temperature. This may lead to changes in the phonon spectrum which depress the radiationless deactivation processes in the luminescent centra and enhance the transfer of excitation energy along the chains.

Low-temperature region.

Here, a modification of the model of JOHNSON(1975) may be applied. The rate equations describing the kinetic behaviour of PVCA films are given in Eq.(1)

$$\begin{aligned} dM^*/dt &= I_0 - (k_M + k_{DM}D_1 + k_{DM}D_2)M^* + k_{MD1}D_1^* + k_{MD2}D_2^* \\ dD_1^*/dt &= k_{DM}D_1M^* - (k_{D1} + k_{MD1})D_1^* \\ dD_2^*/dt &= k_{DM}D_2M^* - (k_{D2} + k_{MD2})D_2^* \end{aligned} \tag{1}$$

The notation of the BIRKS(1970) type used here slightly differs from that of JOHNSON(1975) (mainly in numbering of the excimers). M^* denotes the concentration of excited monomer units, D_1^* and D_2^* that of EI resp. EII, and D_1 and D_2 the concentration of EFS for the two excimers. D_1 has been determined by KLÖPFFER(e.g.1981) to be 2×10^{-3}mole/mole basic unit, and we suppose, in agreement with JOHNSON(1975) that $D2 \gg D_1$. The rate constants k_M, k_{D1}, and k_{D2} include all the deactivation processes of the monomer, EI, and EII, resp. Rate constants k_{MD1} and k_{MD2} belong to the process of detrapping of the excitation energy from EI resp. EII, i.e. to its return to a monomer unit. In accordance with JOHNSON(1975), k_{DM}, the rate constant of transfer from a monomer unit to an EFS, is taken the same for both the types of traps in PVCA, as rapid migration along the chain is supposed to be the main mechanism of the propagation of the excitation energy (a mechanism which does not distinguish between the two types of traps). According to an estimate of energy migration rate along the chain of PVCA (KLIMOVIČ et al.1982) as well as to the transient fluorescence measurements (e.g.TAGAWA et al.1979, HRSTKA and KLIMOVIČ 1981), k_{DM} is very high and the corresponding propagation time must lie in the picosecond region. All the members describing the transformation of D_1^* to D_2^* and vice versa, used by JOHNSON(1975) in his treatment of PVCA solutions, were omitted here because the necessary conformational changes do not occur below T_g in the films.

So we suggest that the excitation energy migrates rapidly along the monomer centra and is almost immediately (after absorption) captured by the excimer traps. The amount of EI resp. EII emission at different temperatures is then influenced either by the trapping ability of the two types of traps or by the thermally activated redistribution of the excitation energy among them during the lifetime of the excitation. The monomer groups serve only as migration centra and the probability of monomer emission is, at least at low temperature, negligible. Under the above given supposals and photostationary conditions, the solution of Eg.(1) for 0 K gives

$$M^* = I_0/k_{DM}D_1 \qquad D_1^* = I_0/k_{D1} \qquad D_2^* = I_0 D_2/k_{D2}D_1 \tag{2}$$

Thus at 0 K, EII emission must be dominating. At higher temperatures, where detrapping of the shallow trap D_2^* becomes possible but D_1^* is stable, we obtain

$$\begin{aligned} D_1^* &= D_1 I_0(k_{D2} + k_{MD2})/\ k_{D1}(D_1 k_{MD2} + D_2 k_{D2}) \\ D_2^* &= D_2 I_0/\ (D_1 k_{MD2} + D_2 k_{D2}) \end{aligned} \tag{3}$$

Around the maximum of EI emission in Fig.2, k_{MD2} rate constant may be taken as dominating. Eq.(3) may be then simplified for the estimate of the activation energy of detrapping from D_2^* and of temperature quenching of the EI emission. This estimate gives 0.04 eV for E_{MD2} and 0.1 eV for E_{D1}. Until now, we used the assumption that excimers form spontaneously after the arrival of excitation energy at their EFS. This is probably true for EII at any temperature but there is a possibility that for the formation of EI additional activation energy is necessary. In that case, D_1 should be treated as temperature dependent and its activation energy would contribute to that estimated above. On the basis of the present experimental results, this question cannot be solved.

At still higher temperatures, detrapping from D_1 may occur. In that case, monomer emission should become detectable. And really, at temperatures above approx.400 K, we observed a shift of the short-wavelength edge of the spectra by several nm towards the shorter wavelengths.

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