

TEMPERATURE-DEPENDENT FLUORESCENCE OF ACRYLIC POLYMERS CONTAINING BENZYL GROUPS

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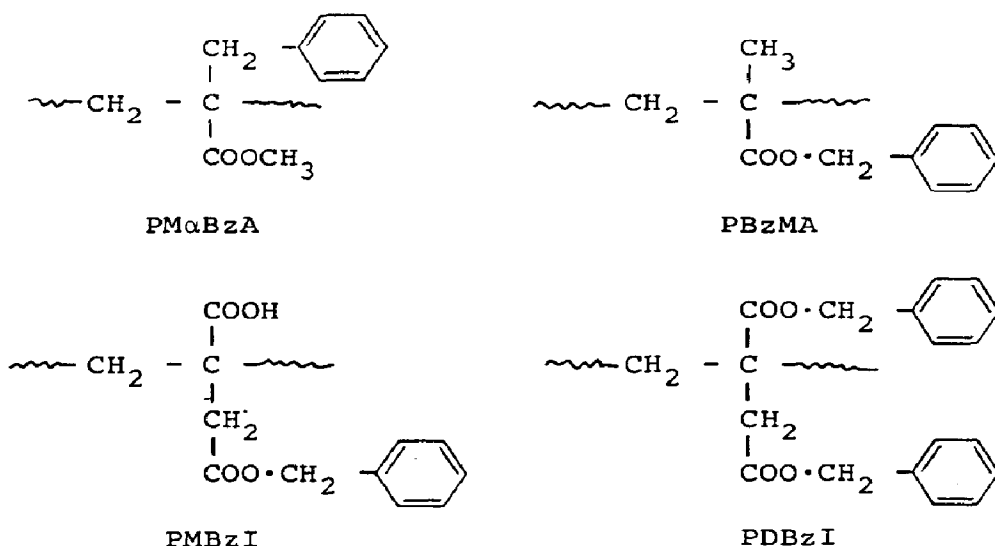
Summary

Fluorescence spectra were recorded as a function of temperature (10 - 60 °C) for dilute dioxane solutions of four homopolymers containing the benzyl group in different positions with respect to the backbone, poly(α -benzylmethyl acrylate), poly(benzyl methacrylate), poly(monobenzyl itaconate) and poly(dibenzyl itaconate). In all cases the intensity decreases with increasing temperature. Arrhenius plots show two lines with different slopes intercepting at a point which we ascribe to a transition temperature between two states of the coil characterized by different activation energy parameters. The transition temperatures are around 29 °C for all the systems except for poly(α -benzylmethyl acrylate) which gives simple linear behaviour without a transition. Activation energy parameters are compared for the different structures studied.

1. Introduction

The investigation of photophysical processes in macromolecules bearing aromatic groups is a matter of current interest and the mechanisms for intramolecular [1 - 5] and intermolecular [6 - 8] excimer formation deserve special attention. Studies of the temperature dependence of the fluorescence provide interesting information on radiationless processes involving excimers and excited state monomers [4 - 6, 9 - 13]. At temperatures close to room temperature, a discontinuity has been observed in Arrhenius plots of the emission intensity for small molecules [14 - 17] and chromophores anchored in a macromolecule [9, 11, 17]. Several arguments have been proposed in each case to explain such behaviour but in all cases the thermal activation of a new mechanism for non-radiative decay above a certain transition temperature was considered.

The aim of this work is to shed some light on the dependence of the mentioned transition of some chromophores on temperature. For this purpose, the temperature dependence of excimer and monomer emission from several vinyl homopolymers with benzyl groups was determined. Four polymers which have benzyl groups joined to the backbone in different locations (Scheme I) were considered to be of interest. The photobehaviour of these systems seems to be mainly determined by the mobility of the chromophore [18] and therefore a comparison between the results for similar structures will allow the determination of the different roles in polymer photo-physics played by the backbone and by the side-chain segmental mobility.



Scheme I.

2. Experimental details

The synthesis and the purification of monobenzyl itaconate and poly(monobenzyl itaconate) (poly(1-carboxy-1-benzoyloxycarbonylmethyl)ethylene) (PMBzI) have been reported previously [19]. The synthesis and the purification of dibenzyl itaconate and poly(dibenzyl itaconate) (poly(1-benzoyloxycarbonyl-1-benzoyloxycarbonylmethylethylene)) (PDBzI) were performed as described previously [20]. Both PMBzI and PDBzI were fractionated and their molecular weights were determined by gel permeation chromatography (GPC) to be 93.000 and 80.000 respectively [19, 20]. Poly(benzyl methacrylate) (PBzMA) was obtained by free-radical polymerization. It was also fractionated by precipitation, and the number average molecular weight M_n determined by osmometric measurements for the fraction employed here was 77.000 [21]. The synthesis of poly(α -benzylmethyl acrylate) (poly(1-methyloxycarbonyl-1-benzyl-

ethylene)) (PM α BzA) has been described previously [22]. The tacticities of these polymers do not differ significantly, and they are all atactic or slightly syndiotactic.

Cyclohexane and dioxane were from Carlo Erba S.A. for fluorescence and spectrophotometry respectively.

Fluorescence spectra were recorded with an LS 3 Perkin-Elmer spectrofluorometer. Excitation was carried out with light of wavelength 260 nm. The spectra were recorded in both air-saturated and oxygen-free solutions (N₂ purged). The Arrhenius plots for aerated solutions have slightly larger slopes but show the same transition temperature. The concentration of polymer solutions was maintained at below 5×10^{-3} M. Over this concentration range, the spectra were independent of concentration. Absorption spectra were recorded using a Shimadzu UV-240 spectrophotometer to check solvents and solutions.

3. Results and discussion

Fluorescence spectra for dioxane solutions of PBzMA, PMBzI, PDBzI and PM α BzA at room temperature are presented in Fig. 1. PMBzI, PM α BzA and PBzMA show only one emission whereas in the PDBzI spectrum there is

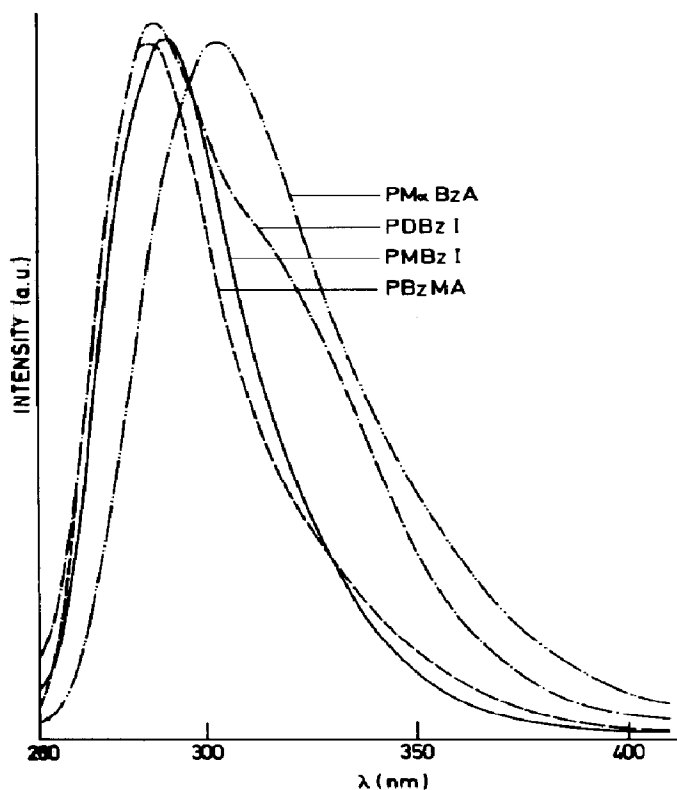


Fig. 1. Fluorescence spectra of dioxane dilute solutions of the four samples at room temperature (not drawn to scale).

a small shoulder corresponding to intramolecular excimer emission [18]. This has already been explained in terms of the different monomeric configurations, assuming that excimers can only be formed by chromophores in the same repeat unit [18]. It is interesting to note here that the naphthyl analogue (poly(2-naphthylmethyl methacrylate)) gives an excimer emission intensity similar to that of the monomer [23, 24]. This can be understood by taking into account that the naphthyl group has a longer lifetime than the phenyl group, and that therefore the probability of forming the sandwich conformation during the lifetime of the chromophore excited state is greater for the former.

In each case, the fluorescence quantum yield is very low and decreases with increasing temperature. In the case of PBzMA, the fluorescence quantum yield and the lifetime are smaller for the polymer than for the corresponding model compound, benzyl acetate [25]. Such behaviour is generally associated with intramolecular excimer emission. As this emission has not actually been observed, the behaviour has been attributed to the formation of non-emitting excimers [25].

The Arrhenius treatment of the monomer emission intensity I_M of PMBzI, PM α BzA and PBzMA

$$I_M = \frac{K_{FM}}{K_{FM} + K_{MNR}} \quad (1)$$

gives the activation energy for monomer non-radiative decay since the rate constant K_{FM} for radiative decay can be considered to be temperature independent and $K_{FM} \ll K_{MNR}$.

Arrhenius plots for the three polymers and for PDBzI monomer emission in dilute dioxane solutions are shown in Fig. 2. A linear dependence is observed for PM α BzA in dioxane and cyclohexane solutions, with the same slope being obtained in each case. It is clear from Fig. 2 that two linear portions with different slopes are observed for the other samples. Similar plots with two intercepting lines have previously been observed [14 - 17] but a single line is the most frequently reported result [26].

Table 1 summarizes the activation energies and transition temperatures T_t for the systems studied. It must be mentioned that the activation energy parameter obtained for I_M of PDBzI has a physical meaning different from that of the other polymers because excimer formation must be considered besides the non-radiative decay.

The transition temperatures are very similar for the three systems showing the slope change and they are very close to the conformational transition temperatures found for PDBzI and PMBzI in dioxane solution by viscometric and dielectric measurements [27].

It is also rather peculiar that the activation energy below T_t is the same for three structures so different as PM α BzA, PMBzI and PBzMA. This suggests that monomer deactivation involves the same segmental motion in each of the three cases and that it therefore corresponds to movement of the benzyl group, the group common to the three polymers.

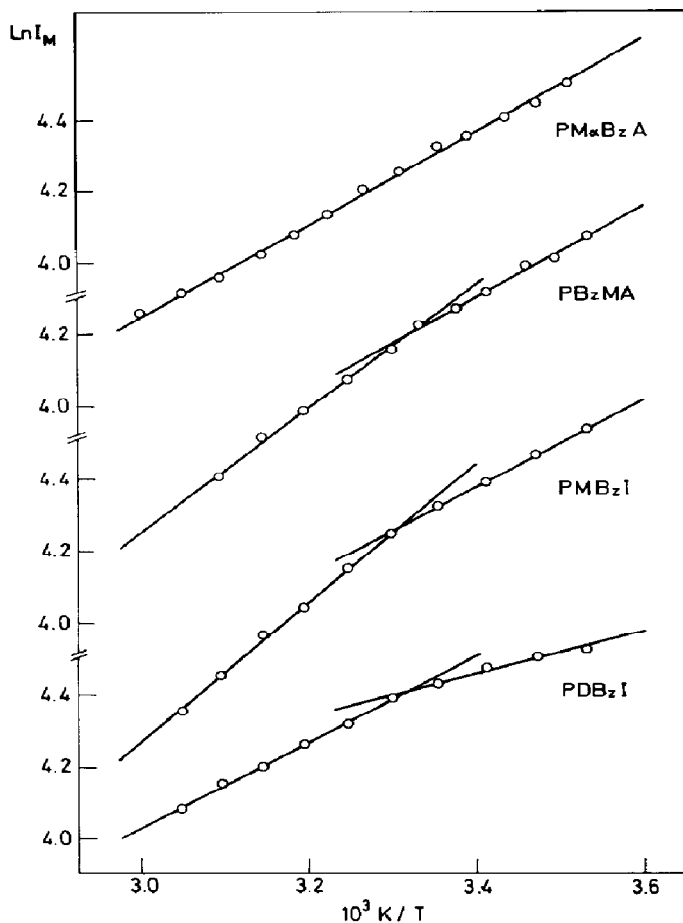


Fig. 2. Arrhenius plots for the monomer emission intensity of the four samples in dioxane solutions.

TABLE 1

Activation energy parameters ΔE_a obtained from I_M Arrhenius plots and transition temperatures T_t

Polymer	ΔE_a (kcal mol ⁻¹)		T_t (°C)
	$T < T_t$	$T > T_t$	
PM α BzA	2.57	2.57	—
PMBzI	2.41	3.83	29
PDBzI	1.15	2.38	28
PBzMA	2.57	3.44	29

Above T_t , the activation energy is larger for the systems showing transitions. This result can be interpreted in the sense that above T_t a greater number of segments are involved in the deactivation of the monomer excited state and that the activation energy therefore increases with respect to tem-

peratures below T_g . It is interesting to note that similar arguments were used to explain the viscometric behaviour [21]. In PM α BzA such behaviour is not possible because of the geometry of the main chain.

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