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Photophysical studies of amorphous solids of bisphenol A polycarbonate

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The fluorescence properties of bisphenol A polycarbonate (PC) solids were studied in detail as a function of casting and annealing temperatures (40–180°C), resulting in the establishment of a method to measure the pure fluorescence spectrum of PC solids. The spectrum was subject to contamination by a photoproduct of PC, which was assumed to have a similar structure to 2,2′-dihydroxydiphenyl. The existence of an excimer, formed between intermolecular phenyl groups in the PC main chain, was ascertained, showing that some main chains are located with a distance of 0.35 nm between one another in the amorphous area of PC solids.

(Keywords: bisphenol A polycarbonate; fluorescence spectrum; excimer formation)

INTRODUCTION

Recently, the photophysical properties of macromolecules have been studied intensively and extensively from both fundamental and practical points of view[1–11]. Particularly outstanding is the introduction of the use of luminescent probes as tools to investigate microstructures and motions of polymer molecules. Since use of the luminescent method guarantees high sensitivity, it could be employed for monitoring small chemical and physical changes in materials. We have come to realize through an extensive literature survey that characterization of the fluorescence properties of luminescent materials has focused on very few polymers such as polystyrene and poly(vinyl carbazole).

Bisphenol A polycarbonate (PC) is an important plastic known for its excellent transparency and high impact resistance. When non-u.v.-stabilized PC is exposed to sunlight outdoors, its surface becomes noticeably yellow and exhibits evidence of photodegradation, prompting many authors to investigate the photochemical properties of PC[12–31]. However, no fluorescence spectra of pure PC films have been reported so far due to defects, impurities and the photoproducts of PC. The fluorescence technique has been effectively applied to studies of PC in only a few cases[16,30].

In this paper we report the fluorescence properties of PC films, resulting in a description of the PC microenvironment. In particular, we describe the excimer formation between phenyl groups in the PC main-chain backbone. This provides valuable information on main-chain aggregation.

EXPERIMENTAL

The bisphenol A polycarbonate (PC) sample used in the present study was purchased from Science Polymer Products ($M_w = 28\,800$) and purified by repeated dissolution and precipitation with tetrahydrofuran (THF) and methanol, respectively. PC films for the fluorescence measurements were prepared on quartz discs using a spin-casting method from a 10% THF (Wako Chemicals, spectrosol grade) solution, and dried by extensive pumping under vacuum for > 3 days at a constant casting temperature (T_{cast}). Quenching of the films was done by the influx of dry nitrogen gas into the oven. More than three films were prepared to ascertain the reproducibility. The films were left on the quartz discs for ease of handling during subsequent measurements. The glass transition temperature of PC films prepared by the same method was determined to be 149 ± 1°C using a Perkin–Elmer DSC7.

Fluorescence spectra were measured on a Hitachi F-3000 spectrofluorometer at ~25°C. Films on quartz discs were set at 45° to the exciting beam. The emission signal was digitized and transferred into an NEC personal computer system. The emission spectrum of the quartz disc, measured as a control, exhibited scattered light which was subtracted from each fluorescence spectrum of PC to yield a corrected spectrum. Fluorescence measurements for the concentrated solutions of PC and their model compounds were carried out in a 1 mm (optical path length) quartz cell set at 45° to the exciting beam.

RESULTS AND DISCUSSION

Determination of method to obtain fluorescence spectrum of PC film

Figure 1 shows fluorescence spectra of a PC film cast at 40°C, as well as the spectrum from a dilute THF solution of PC. Several characteristic points concerning the PC fluorescence shown in *Figure 1* can be noted: (1) the fluorescence peak of the PC film shifts to a longer wavelength (298 nm) compared with that of PC in THF

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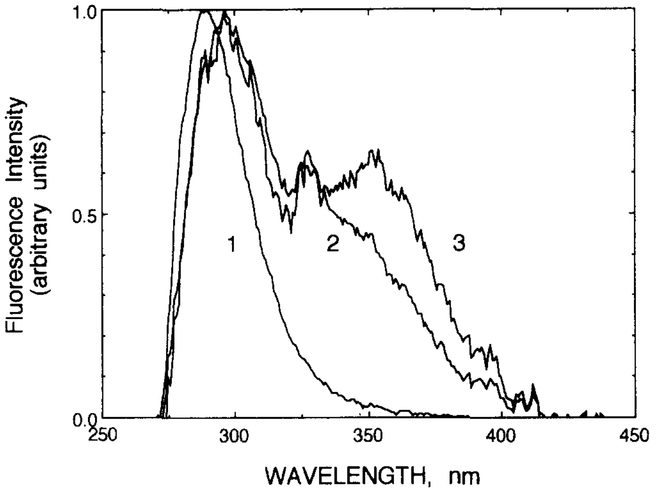

Figure 1 Fluorescence spectra of PC in THF (1) and of PC films cast at 40°C (2, the first measurement; 3, the fourth measurement): excitation wavelength is 250 nm. The spectra are normalized at the peak

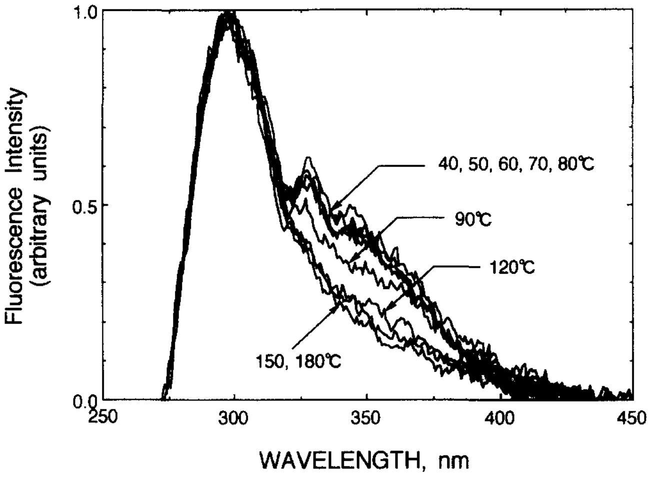

Figure 2 Casting temperature (T_{cast}) dependence of fluorescence spectra of PC films that were not annealed above T_g (normalized at the peak): excitation wavelength is 250 nm

(288 nm); (2) the fluorescence spectrum of PC film exhibits an emission with structure at ~330 nm; and (3) the emission at ~360 nm increases with the number of sequential runs of the fluorescence spectrum for the same PC film. Spectrum 3 in *Figure 1* corresponds to the fluorescence spectrum of PC film produced after 5 min irradiation by 250 nm light through the 3 nm bandpass in the spectrofluorometer. Thus PC is subject to photodegradation even by the very weak light in the fluorometer. Therefore the first necessary condition (I) to obtain the inherent fluorescence spectrum of a PC film is to minimize the total amount of light exposure. The following conditions are established: (i) the measurement should be done only once per PC film; (ii) the bandpass of the excitation light should be narrow (3 nm for our measurement); and (iii) the scanning speed for the fluorescence measurement should be fast (240 nm min^{-1} between 250 and 450 nm). Although it is difficult to quantify the value of the photon flux for the excitation, the total amount of photons given to the sample films is considered to be constant. The reproducibility of the spectra was ascertained by measuring five PC films cast at 40°C under the above conditions.

Figure 2 displays fluorescence spectra of PC films at several casting temperatures, T_{cast}. The results can be summarized as follows: (1) the fluorescence spectra of PC films cast at temperatures of $<80°C$ agree well with one another and have structured emission near 330 nm; (2) the structured emission at ~330 nm decreases with increasing casting temperature up to 150°C; and (3) the spectra of PC films cast at temperatures of $>150°C$ agree well with each other and the 330 nm structure completely disappears. These results suggest the existence of an impurity with a structured emission peak at 330 nm and that this compound can be excluded by extensive pumping under vacuum, especially at temperatures higher than the glass transition, T_g, of the PC film. Thus, in addition to measurement condition I, we impose an additional condition (II) for measuring the fluorescence spectrum of pure PC solids: the films should be annealed above T_g while applying a vacuum.

Next we measured the dependence of PC film fluorescence on the casting temperature (T_{cast}), having established the measurement conditions I and II. Each film was held at T_{cast} for 3 days, followed by annealing at 170°C overnight. *Figure 3* shows that the fluorescence spectra of PC films so treated agree perfectly with one another and that the emissions at 330 and 360 nm observed in *Figure 1* are not inherent to PC solids. *Figure 3* is presumed to show the fluorescence spectra of pure PC films, since the fluorescence excitation spectra between 290 and 370 nm coincide with the absorption spectrum.

The characteristic points of the fluorescence spectra of PC solids are now summarized: (1) the fluorescence peak of PC film shifts to a longer wavelength (298 nm) compared with that of PC in THF (288 nm); (2) a broad structureless band appears in the longer wavelength region of the fluorescence spectra; and (3) a dependence of the fluorescence spectra on T_{cast} is not observed. We next make an assignment of the impurity compounds in PC films, followed by a discussion of the photophysical properties of PC films.

Possible fluorescent impurities in PC film

In *Figure 1*, the fluorescence spectra of PC films were found to change during sequential fluorescence measurements of the same sample. In this section, we investigate

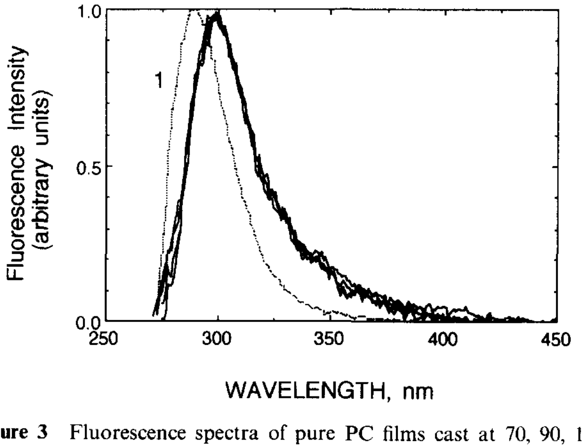

Figure 3 Fluorescence spectra of pure PC films cast at 70, 90, 110 and 170°C under the measurement conditions established in the present paper (I and II), together with the spectrum from a dilute THF solution of PC (1) (normalized at the peak): excitation wavelength is 250 nm

the run number dependence of fluorescence spectra of PC films cast at 150°C, which have no initial 330 nm emission impurity. As shown in *Figure 4*, the intensity of the phenyl fluorescence at 298 nm decreases with increasing irradiation time, while that of a new fluorescence at 360 nm increases. The observation of an isoemissive point near 340 nm demonstrates that the compound with 360 nm emission is a photoproduct of PC generated photolytically. Thus, we must conclude that PC fluorescence spectra may be complicated by the emission of two impurity species: (i) one with a 330 nm emission peak present upon casting PC films (no vacuum applied), and (ii) one with a 360 nm emission peak generated photolytically. We will next try to identify the photoproduct (ii) by comparing its fluorescence spectra with those of several model compounds.

The photochemical processes of PC have been studied extensively and the main pathways for decomposition appear to be well established. One primary pathway for degradation is the photo-Fries reaction resulting from formation of aryloxyl and aryloxycarbonyl radicals produced by the initial excitation. The photo-Fries reaction is well documented with regard to both PC[12,13,16,17,20] and appropriate model compounds[32–35] in solution. Another important degradation pathway reported in the literature is the photooxidation reaction[15,18,19,21–27]; the site subject to oxidative attack is the gem dimethyl groups and the aromatic groups not only of bisphenol A units but also of photoproducts[21,24,25] formed by the photo-Fries reaction. The photodegradation process of PC is summarized in *Figure 5*[27].

The photoproducts possibly formed by way of the photooxidative pathway in *Figure 5* would be expected to have either nearly the same fluorescence as bisphenol A or no fluorescence; compounds with benzoyl group are non-fluorescent. Thus, we first examined the photophysical properties of the model compounds possibly produced by way of the photo-Fries pathway in *Figure 5*. *Table 1* summarizes the peak wavelengths of both u.v. absorption and fluorescence bands of photoproduct model compounds (**I** to **V** in *Figure 5*) in THF solution, together with their spectral intensities. The fluorescence of 2,2′-dihydroxydiphenyl (DHDP) peaks at 345 nm is the longest wavelength observed in all the model compounds except the very weak emission of phenyl salicylate. Since (1) the fluorescence yield of DHDP is very high and (2) the linkage of the main chain with the phenyl group of DHDP would induce a red shift of the fluorescence spectrum, we conclude the compound responsible for the 360 nm emission in *Figures 1* and *4* has a similar structure to that of DHDP, and that it is formed by way of the reaction scheme shown in *Figure 6*.

Figure 4 demonstrates that the concentration of the DHDP-type product ultimately reaches a peak, probably due to the high inherent reactivities of 2,2′-dihydroxydiphenyls. Hence, we conclude that fluorescence analysis is an extremely sensitive tool for observing, at a very early stage, the photochemical change in PC films. Interestingly, no spectral changes could be observed in the same photolysed PC films by *FT*i.r. measurements.

With regard to the 330 nm impurity emission, there is a possibility that it is a derivative of phenoxyphenol. However, we have no data to support this supposition. In any case, the 330 nm impurity emission contaminates PC from the beginning and its elimination is not achieved by the usual repeated dissolution and precipitation

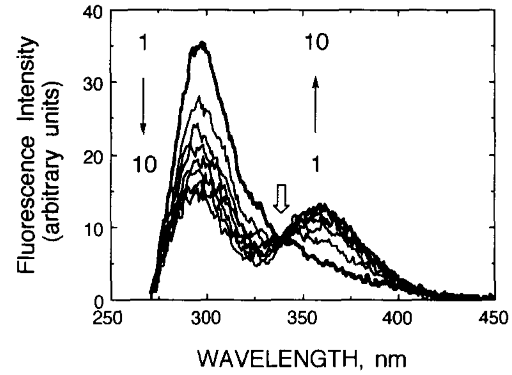

Figure 4 Irradiation time dependence of fluorescence spectra of PC films cast at 150°C: excitation wavelength is 250 nm. The numbers show the running time of the fluorescence measurement. Arrow shows the isoemissive point

Table 1 Spectroscopic properties of model compounds of PC and its photoproducts in aerated THF solutions[a]

Sample	Model[b]	Absorption peak wavelength (nm)	Molar absorption coefficient, ε, of absorption peak	Emission peak wavelength[c] (nm)	Emission peak intensity[d]
Bisphenol A polycarbonate		264	1100	290	1
Bisphenol A	PC	280	4400	303	6.2
Diphenyl carbonate	PC	259	480	282	0.56
Phenyl salicylate	**I**	310	5500	477	0.058
2,2′-Dihydroxybenzophenone	**II**	337	5700	–	0
2,2′-Dihydroxydiphenyl	**III**	285	7500	345	16
4-Phenoxyphenol	**IV**	279	2900	322	4.2
3-Phenoxytoluene	**IV**	272	1900	294	3.6
Diphenylether	**IV**	272	2000	290	2.6
4-Hydroxytoluene	**V**	281	1800	303	10

[a] The error of wavelength is ±1 nm; the intensity of absorption and fluorescence was obtained to two significant figures

[b] See *Figure 5*

[c] Excitation wavelength is the absorption peak

[d] Each emission intensity was measured for solutions with the same optical density (0.050) at the absorption peak wavelength. It is normalized in such a way that the emission intensity of PC is 1.0

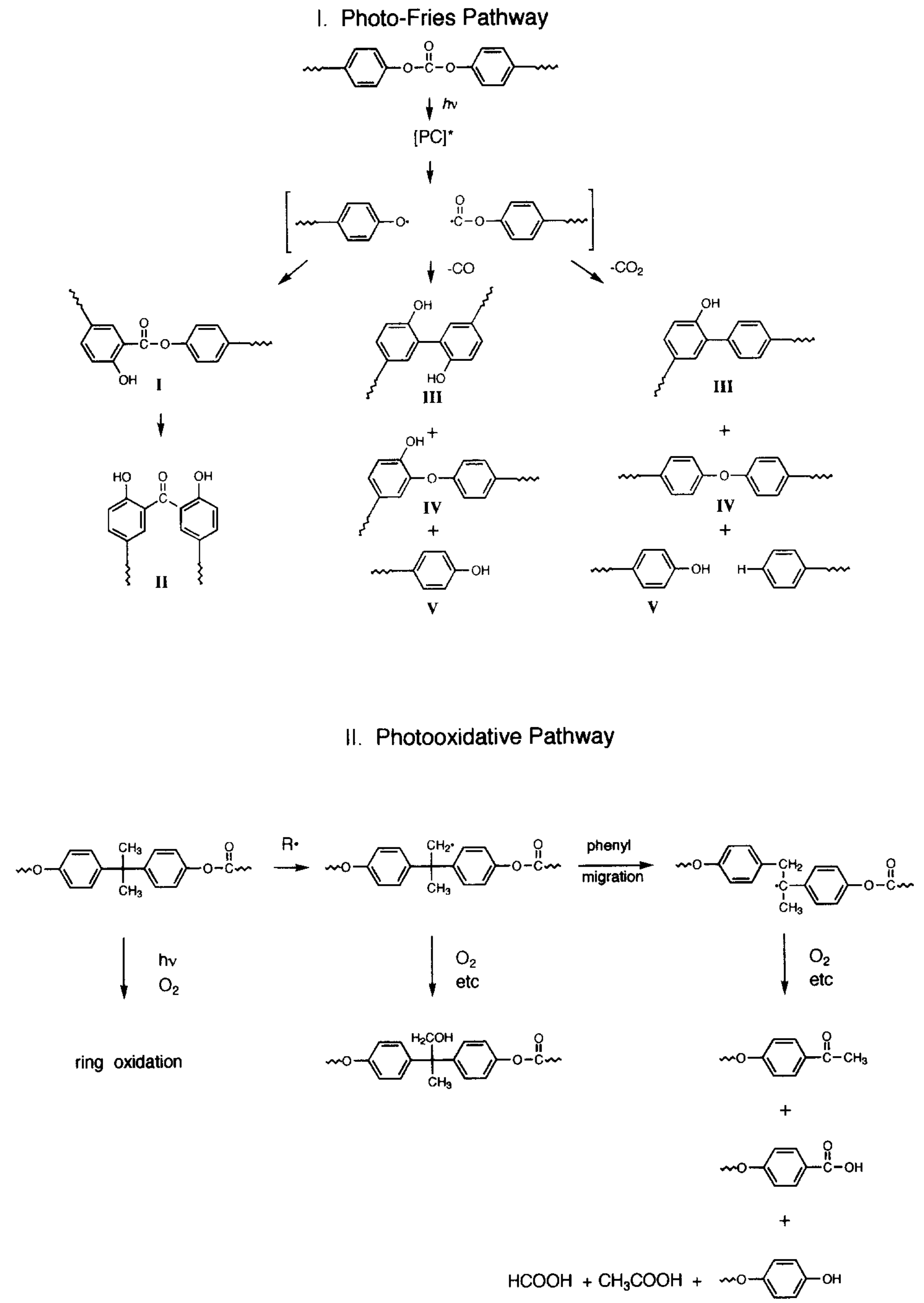

Figure 5 Scheme of possible photochemical reactions in PC solids[27]

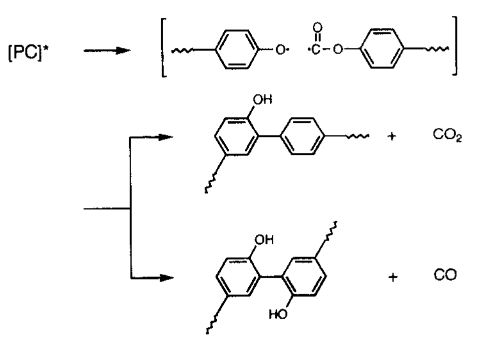

Figure 6 Possible photochemical reaction scheme in PC solids to produce the photoproduct whose emission peak is around 360 nm

method, although it can be eliminated from PC films under vacuum at temperatures higher than 150°C. We project that the impurity is a small aromatic molecule perhaps capable of hydrogen bonding with bisphenol A units; however, this is strictly supposition.

Microenvironment in PC films estimated from fluorescence behaviour

As previously discussed, *Figure 3* demonstrates that a structureless fluorescence band appears in the longer wavelength region by comparing the spectrum of PC films with that of PC in THF. Since the excitation spectrum of the broad structureless emission tail agrees well with the inherent PC absorption spectrum, this fluorescence in the longer wavelength region must be an integral part of PC films. In order to examine whether this emission is due to an intermolecular excimer, we measured the concentration dependence of the fluorescence spectra of PC and its model compounds in THF solutions.

Figure 7 suggests that intermolecular excimer is formed between the phenyl groups in the main chain of PC, because the PC solutions with higher concentrations exhibit higher intensities of the red-shifted emission above 330 nm, although the formation efficiency is not high. In fact, the ratio of the fluorescence intensity at 330 nm to that of the peak maximum is found to be proportional to the PC concentration. We measured the spectra of concentrated solutions of both bisphenol A (BA) and diphenyl carbonate (DC), which are model compounds of PC. The fluorescence spectra of BA do not change significantly with concentration, although the fluorescence intensity in the longer wavelength region increases slightly with an increase in concentration. An apparent dependence on concentration can be observed in the fluorescence spectra of DC as shown in *Figure 8*. This suggests that the DC model compound can also form intermolecular excimer at high concentrations.

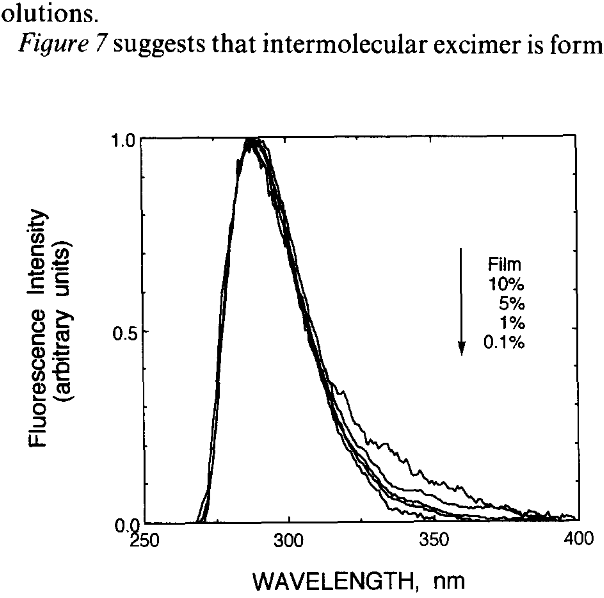

Figure 7 Concentration dependence of fluorescence spectra of PC in aerated THF solutions together with spectrum of a PC film (normalized at the peak): excitation wavelength is 250 nm. The concentrations are 0.39 base M (10% (w/w)), 0.18 base M (5%), 0.035 base M (1%) and 0.0035 base M (0.1%). The spectrum of PC film is superimposed by shifting it to arrange its peak at 298 nm

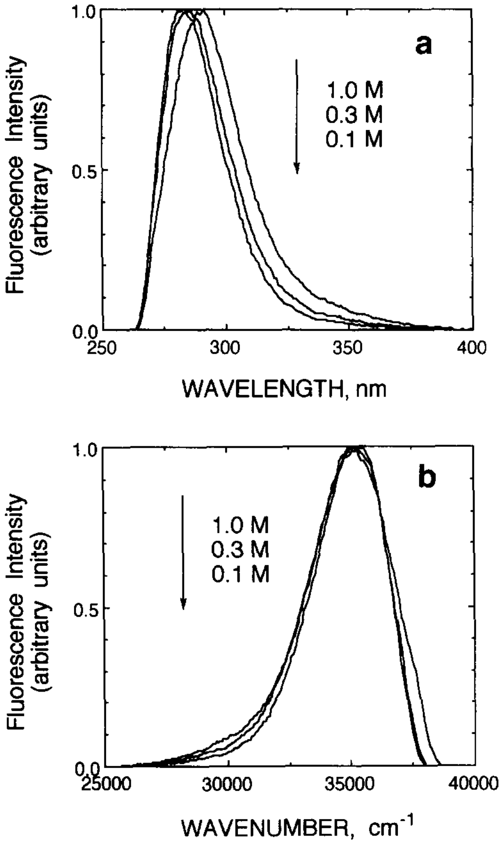

Figure 8 Concentration dependence of fluorescence spectra of diphenyl carbonate in aerated THF solutions: excitation wavelength is 250 nm. (a) Real spectra normalized at the peak; (b) all spectra superimposed by shifting them to arrange their peaks at constant wavenumber

The fluorescence behaviour of the concentrated solutions of PC, BA and DC demonstrates that the intermolecular excimer can be formed between interactive groups in the main chains of PC molecules. Since the equilibrium separation of the molecules in a typical aromatic excimer[36] is 0.33 nm, we conclude that some main chains in PC solids are located close together, with a distance of 0.35 nm. The fraction of interactive excimer forming repeat units is limited and independent of T_{cast} (*Figure 3*).

SUMMARY

The present paper is the first to show the pure fluorescence spectrum of PC film. The usual fluorescence measurements of commercial PC solids are subject to contamination by impurities and/or photoproducts of PC. This is why the pure fluorescence spectrum of PC solids has not been reported so far. We have established the method to obtain reproducible spectra in this paper: (I) the exposure of films to the light should be kept to a minimum (e.g. measurement should be done only once per film) and (II) the films should be annealed under vacuum above T_g in order to eliminate impurities. The pure fluorescence spectrum of PC film is found to show excimer fluorescence. This excimer is formed between the phenyl groups in the main chains of different polymer molecules, indicating that there is a close contact of main chains, within 0.35 nm, in the amorphous area of PC solids. Thus we conclude that we can investigate the microenvironment of PC molecules in the amorphous area of PC solids by means of fluorescence measurements. It must be stressed that this method could be employed for monitoring small chemical and physical changes in PC products in factories.

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