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Intramolecular Excimer Formation of Poly(γ-(1-naphthylmethyl)-L-glutamate)

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Summary

Poly(γ-(1-naphthylmethyl)-L-glutamate) (PNLG) was synthesized and fractionated into samples with narrow molecular weight distributions. Absolute molecular weights of all the PNLG's used in this study were determined by a time-of-flight matrix-assisted laser desorption ionization mass spectrometry. The circular dichroism measurements of PNLG showed that all the PNLG's with a degree of polymerization larger than 7 had a right-handed helical structure in tetrahydrofuran (THF) solution. The effects of molecular weight on the photostationary and transient fluorescence of PNLG were examined in order to obtain information on excimer formation and singlet energy migration. Because the structure of a PNLG is rigid and regular, a one-dimensional random walk model can be used to describe singlet energy migration among side-chain naphthyl groups of PNLG. Consequently, the singlet energy migration coefficient of PNLG in THF was found to be more than $1.6 \times 10^{-5} cm^2 / s$.

Introduction

Many authors have reported intramolecular excimer formation in dilute solutions of homopolymers containing aromatic pendant groups.[1] An intramolecular excimer in a vinyl polymer system is formed between adjacent side-chain chromophores[2,3] and its formation needs two important processes: one is the formation of excimer conformations by local motion, and the other is the influx of excitation energy into the preformed excimer conformation by singlet energy migration.[4-6] Because the properties of a chromophore directly excited by absorbing light are identical with those excited by energy migration, it is not easy to obtain information on energy migration.

We felt that the molecular weight dependence of the efficiency of excimer formation should give important information on energy migration taking place in homopolymer with pendant aromatic chromophores. Then, we have studied the molecular weight dependence of excimer formation in some systems.[7-10] Each chromophore attached to a polymer molecule is assumed to be under the same environment whatever the molecular weight. Thus, if the molecular weight of a polymer is exactly determined, singlet energy migration can be examined by comparing excimer formation efficiencies of polymers with different molecular weights without introducing a new parameter. Actually we determined the singlet energy migration coefficient among side-chain phenyl groups in oligostyrenes to be $10^{-4} cm^2 / s$ by measuring the rates for excimer formation of styrene oligomers from dimer to tridecamer that were fractionated exactly.[7]

A helical polypeptide chain has been shown to be a good framework to support chromophores since its structure is rigid and regular.[11,12] Here we should be able to obtain information about the distance between chromophores, so we can determine quantitatively singlet energy migration by measuring the molecular weight dependence of excimer formation efficiency. It had been difficult to exactly determine molecular weight of artificial polypeptides prepared by organic synthesis. However, absolute molecular weights of such polymers can now be determined by using time-of-flight matrix-assisted laser desorption ionization mass spectrometry (TOF-MALDI-MS). In the present study, we took advantage of the determination of absolute molecular weight of PNLG by this measurement.

Some authors have studied the circular dichroism (CD) and fluorescence of poly(γ-(1-naphthylmethyl)-L-glutamate) (PNLG) as an example of artificial polypeptides having chromophores that effectively absorb uv light.[13-16] In particular, the CD spectra of PNLG demonstrated that there are some strong interactions between side-chain naphthyl rings.[14] In the present paper, we prepared PNLG's with a variety of molecular weights that were fractionated to samples with a narrow molecular weight distribution, and measured the molecular weight dependence of excimer formation in order to quantitatively determine singlet energy migration.

Experimental

Materials PNLG was synthesized according to Hatano et al.[13] except that bis(trichloromethyl)carbonate was used instead of phosgene. First, γ-1-naphthylmethyl-L-glutamate (NLG) was prepared by the reaction of L-glutamic acid with 1-naphthalenemethanol in dioxane using p-toluenesulfonic acid as a catalyst according to the previous paper[14] (see Scheme 1). Then, NLG was polymerized by the conventional N-carboxyanhydride (NCA) method in tetrahydrofuran (THF) with n-butylamine as an initiator. The NCA of NLG was prepared by dissolving 10 g NLG and 4.2 g bis(trichloromethyl)carbonate in 100 ml dry THF and heating at 45°C after the method of Daly and Poché.[17] The ratio of NCA to the initiator was either 20 (PNLG-1) or 100 (PNLG-2). After two weeks, the precipitated PNLG was collected, dissolved in THF, and repeatedly reprecipitated by pouring the THF solution into methanol, and then into n-hexane. The gel permeation chromatography (GPC) curves of the crude PNLG's showed that the polydispersities of the polymers were wide. Thus, we repeatedly fractionated crude PNLG's by GPC: the GPC experiments were carried out at 40°C on a Tosoh HLC-8120 GPC system equipped with a TSK gel α-3000 column using N,N-dimethylformamide (DMF) including 30 mM lithium bromide as an eluting solvent. The flow rate was 0.6 mL/min. The column was found to work correctly because each GPC curve of a fractionated PNLG was different and adequate. Each fraction sample was first dialyzed against DMF to remove salt and then repeatedly against THF. Samples were stored in a concentrated solution of THF.

The molecular weight of each PNLG was determined using a Perseptive Biosystems Voyager-DE STR MALDI-MS. An electron multiplier was used for detection, and the signal was recorded by a Tektronix TDS 540B 500-MHz digitizing oscilloscope. The method used here was after Belu et al.[18] Tab. 1 summarizes the molecular weights and their distributions of PNLG samples used in the present study. PNLG15-1 and PNLG15-2 were fractionated from different crude PNLG (PNLG-1 and PNLG-2) samples synthesized, but they have nearly same molecular weight. Consequently, we could not

obtain any PNLG's with a degree of polymerization larger than 22. High molecular weight PNLG molecules were assumed to become insoluble during the polymerization process of the NCA.

Measurements Uv absorption spectra were measured on a Shimadzu UV-2200. Fluorescence spectra and fluorescence excitation spectra were measured on a Hitachi F-4500 spectrofluorometer at 20°C. Fluorescence decay curves were obtained by using a Horiba NAES550 single photon counting machine with a nanosecond flash lamp. An excitation wavelength of 288 nm was selected by use of an interference filter. The emission decay was measured at 20°C through an interference filter of 330-, 340-(monomeric singlet), or 390-nm (excimer). We analyzed fluorescence decay curves by the deconvolution method after O'Connor and Phillips,[18] using the Durbin-Watson factor (DW)[19,20] to assess the validity of the trial fitting function. DW is calculated from

$$DW = \sum_{i=2}^{N} (R_i - R_{i-1})^2 / (\sum_{i=1}^{N} R_i^2) \qquad (1)$$

where the weighted residual $R_i = (Y_i - F_i)/Y_i^{1/2}$, Y_i is the value of the experimental data and F_i is the value of the trial calculation value corresponding to the time channel i, and N is the number of experimental points. For the best fit, the value of DW approaches 2.0. Absorption and fluorescence measurements were carried out in aerated THF that was freshly distilled. Circular dichroism (CD) spectra were measured on a JASCO J-720 circular dichroism apparatus. The CD measurements were carried out in THF with different concentrations, each of which was determined by uv absorption spectra.

Results

The CD spectra of the PNLG's in THF were identical with those of PNLG in dichloroethane reported by Ueno et al,[14] which showed two negative bands at ~215 and 232 nm. The molar ellipticity values of all the PNLG samples were found to agree with one another (-2×10^{-4} *M* at 215 nm) and also with the values of PNLG in dichloroethane. The values did not change at concentrations between 4 and 60 mg/L. Consequently, all the samples used in this study have a right-handed helix structure in THF solution as Ueno et al. pointed out.

Fig. 1 shows the fluorescence spectra of PNLG22 at different concentrations in aerated THF solution. All of the spectra are normalized to the peak. The peaks near 330 and 400 nm have been assigned to the naphthyl monomer singlet and excimer emission, respectively. In fact, the excitation spectra for the fluorescence between 330 and 450 nm of all samples were almost identical. They were also identical with their absorption spectra. Fig. 1 demonstrates that no concentration dependence was observed for the fluorescence spectra of the PNLG below 3 μM, meaning that (1) all the excimers contributing to the fluorescence spectra in Fig. 1 are formed intramolecularly, and (2) PNLG molecules do not aggregate at all in THF.

We also measured the fluorescence spectra of the other PNLG's at various concentrations and confirmed the above finding that there was no concentration dependence of PNLG fluorescence in THF. Fig. 2 shows the fluorescence spectra of PNLG's with different molecular weights in aerated THF solution. Each fluorescence spectrum shown in Fig. 2 was obtained by averaging 4~6 fluorescence spectra of PNLG at different concentrations. PNLG15-1 and PNLG15-2 are the samples that were fractionated from different crude PNLG samples, although they have nearly same

molecular weight. The fluorescence spectra of PNLG15-1 and PNLG15-2 were almost identical with each other, indicating that the fractionation went well.

Fig. 2 demonstrates that excimers are more readily formed in higher molecular weight PNLG. Fig. 2 means that (i) the intensity ratio of excimer fluorescence, I_E, and monomer fluorescence, I_M, increases with an increase in degree of polymerization up to 22 and (ii) we failed to obtain the degree of polymerization above which I_E/I_M should level off, because the fluorescence spectra must be identical with one another if I_E/I_M is constant.

In order to examine the kinetics of excimer formation, we measured the transient fluorescence of all the PNLG samples in aerated THF. The monomeric fluorescence of each of the PNLG samples closely fit the sum of dual exponentials with time constants of 3~5 ns (τ_1) and ~20 ns (τ_2) as Eq. 2.[22]

$$I_M(t) = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} \quad (A_1 + A_2 = 1) \tag{2}$$

On the other hand, the excimer fluorescence was found to rise single-exponentially with a time constant of τ_1 and decay single-exponentially with a time constant of τ_2:

$$I_E(t) = A_3 e^{-t/\tau_2} - A_4 e^{-t/\tau_1} \tag{3}$$

Because the fluorescence near 400 nm was overlapped with monomer fluorescence, A_3 was not equal to A_4. The values of τ_2 obtained from excimer fluorescence are confirmed to be almost identical to those obtained from monomer fluorescence. The time profiles of each PNLG in THF are summarized in Tab. 2.

Since the excimer dissociation of polystyrene and oligostyrenes is neglected,[7,24,25] the monomer fluorescence of polystyrene should decay single-exponentially. However, their monomer fluorescence is much weaker than the excimer fluorescence and the excimer fluorescence overlaps the monomer fluorescence region. Then, their apparent decay curves are sums of two exponentials. In the case of PNLG, the monomer fluorescence at 340 nm is very strong while the excimer fluorescence is negligible at this wavelength. Thus, it can be concluded that a component of the long time constant (τ_2) is due to monomeric fluorescence decay.

The kinetics of intramolecular excimer formation in many polymer systems having side-chain aromatic chromophores has been reported to obey the conventional model shown in Scheme 2. Under conditions where excimer dissociation cannot be neglected, monomer fluorescence and excimer fluorescence should decay according to Eqs. 4 and 5.

$$I_M(t) \propto \frac{\tau_1\tau_2 X - \tau_1}{\tau_2 - \tau_1} e^{-t/\tau_1} + \frac{\tau_2 - \tau_1\tau_2 X}{\tau_2 - \tau_1} e^{-t/\tau_2} \tag{4}$$

$$I_E(t) \propto e^{-t/\tau_2} - e^{-t/\tau_1} \tag{5}$$

where

$$\frac{1}{\tau_1}, \frac{1}{\tau_2} = \frac{X + Y \pm \sqrt{(Y - X)^2 + 4k_{EM}k_{ME}}}{2} \tag{6}$$

$$X = k_{FM} + k_{IM} + k_{EM} \tag{7}$$

$$Y = k_{FE} + k_{IE} + k_{ME} \tag{8}$$

Because the fluorescence of PNLG was found to decay according to Eqs. 4 and 5, it can be concluded that excimers of PNLG dissociate at room temperature.

By substituting the values of k_{FM} and k_{IM} for naphthalenemethanol in aerated THF (τ=12.6 ns; $k_{FM} + k_{IM} = 7.94 \times 10^7 s^{-1}$), the rate constants for excimer formation, k_{EM}, and dissociation, k_{ME}, could be determined. The values calculated are summarized in Tab. 2. Although the values are not always monotonously proportional to the degree of polymerization, the transient results show that the rate at which PNLG's form excimers increased with an increase in degree of polymerization despite the relatively large value of k_{ME}.

Discussion

The experimental results obtained by measuring the CD and fluorescence spectra can be summarized as follows: (i) all the PNLG used in this study have a right-handed helix structure in THF solution, and (ii) the rate for excimer formation of PNLG increases with an increase in degree of polymerization.

Fitzgibbon and Frank developed a strictly one-dimensional random walk model to describe singlet energy migration in isolated chains of aromatic vinyl polymers and explained the molecular weight dependence of I_E/I_M for poly(2-vinylnaphthalene) (P2VN).[26] Their model gave I_E/I_M values of P2VN at low temperatures that were close to experimentally determined values. In the model, the molecular weight dependence of the I_E/I_M values was based on both the average concentration of excimer forming sites, q, and the probability that the excitation energy is deactivated without hopping to another chromophore. However, their values of q, which were calculated based on rotational isomeric state theory, are 15 times larger than the concentration of meso tt, which is the main excimer conformation. Their large values of q are probably due to the fact that, in the case of atactic vinylpolymers in the random-coil state, the relaxation time of local molecular motion depends on the molecular weight. We have previously demonstrated this by measuring ^{13}C NMR spin-lattice relaxation of poly(α-methylstyrene).[27] Because the structure of a helical polypeptide is rigid and regular, polypeptides with side-chain chromophores are some of the best model molecules for satisfying the conditions of a one-dimensional random walk model. Each side-chain chromophore is thought to be under nearly the same conditions because the side chains are in a helical array.

In the case of polypeptides having side-chain chromophores, an intramolecular excimer is formed between two chromophores separated from each other by one pitch of the helical array.[28] Although a distance between two chromophores should be less than 0.33 nm in order to from an excimer,[29] two side-chain chromophores are usually further separated from each other in an α-helical polypeptide consisting of α-amino acid residues, because one pitch of an α-helix polypeptide is 0.54 nm with 3.6 units of amino acid residues.[30] In this case, if the side-chains are short, it is impossible for side-chain chromophores to form an excimer. In fact, poly(L-naphthylalanine) (PLNA) does not exhibit excimer fluorescence at all.[31] Thus, in the case of α-helical polypeptides, a long side chain is needed to form an excimer.

Here are two probable mechanisms by which two side-chain chromophores separated by one pitch can form an excimer: (i) an excited chromophore moves and encounters another chromophore in the ground state, and (ii) excitation energy migrates along side-chain chromophores and reaches a preformed excimer conformation site. In general, the motion of a side chain of a polypeptide becomes more restricted with an increase in molecular weight. Thus, the increase of excimer formation with increasing

molecular weight is mainly due to (ii). The value of q appears to be nearly constant in the case of a helical rod such as PNLG in THF, although it is possibly dependent on the molecular weight in the case of P2VN, which has a random-coil, atactic structure, and whose segmental motion and local motion may change with molecular weight. Then, if excitation energy can migrate among side-chain chromophores of a whole PNLG molecule, the rate of excimer formation is thought to increase with increasing degree of polymerization (N) up to a number, because the expected value for the excitation energy to encounter an excimer site is Nq, and must increase with an increase in N.

Unfortunately, we could not obtain higher molecular weight PNLG's whose rates of excimer formation are independent of molecular weight because their degrees of polymerization are larger than the number of naphthyl units that excitation energy can migrate across during the lifetime of a singlet excited naphthyl group. However, we can assume that the excitation energy hops around all the side-chain naphthyl groups of PNLG22 in THF, and calculate the value of the singlet energy migration coefficient, Λ, for PNLG22. This value can be presented as the minimum value of Λ for PNLG. When energy migration along the side-chain naphthyl groups of PNLG is treated as a one-dimensional random walk, the expected distance, L, that excitation energy will migrate is expressed as,

$$L = \sqrt{2\Lambda\tau_M} \qquad (9)$$

where τ_M is the fluorescence lifetime of excited naphthyl monomer. One pitch of a normal polypeptide consisting of α-L-amino acids is 0.54 nm and contains 3.6 units. An x-ray diffraction diagram of PLNA obtained by the powder method showed a peak corresponding to a distance of 0.55 nm.[31] The authors realized that this distance is nearly identical with the pitch of typical α-helical polypeptides, but they did not rule out the possibility that it was due to some other explanation. Assuming the usual value of 0.54 nm, we calculated the value of L for PNLG22 to be 3.32 nm. Then, Λ can be calculated to be $1.6\times10^{-5} cm^2/s$ using τ_M = 3.5 ns. This value is close to the value of $1.2\times10^{-5} cm^2/s$ obtained by the quenching method for PNLG30 in dichloroethane by Ueno et al.[16] The quenching method is not always valid for obtaining the singlet energy migration coefficient, but this correspondence indicates that both the quenching method and our method are valid in the case of PNLG whose structure is rod-like.

Values of Λ for many polymer systems have been reported[32]: most vinylpolymers having side-chain aromatic groups have values of Λ on the order of $10^{-4} cm^2/s$. Thus, $10^{-5} cm^2/s$ appears to be a little smaller than the average value. Another polymer having the nearly same Λ value as PNLG is poly[2-(2-naphthyl)ethyl methacrylate)[33] whose naphthyl groups are very far from the main chain.

Let us discuss the mechanism of the energy migration taking place in PNLG22. On the basis of a one-dimensional random walk, Λ is also expressed as Eq. 10 using a rate constant for singlet energy migration, k_{mig} which shows the rate for the excited energy to transport from one naphthyl group to another.

$$\Lambda = (n/2)k_{mig}R^2 \qquad (10)$$

where R is the average distance between two naphthyl groups, and n is the number of naphthyl groups for an excitation energy to transfer: n is 2 under the first approximation. In the case of poly(γ-benzyl-L-glutamate),[34] the distance is around 0.7 nm between the helix axis and the center of phenyl group projected onto a plane

perpendicular to the helix axis. Thus, the closest naphthyl group from one naphthyl group is not the side-chain group in the adjacent unit but in every third naphthyl group which is in the same direction of the helical rod. This distance can be approximated to be the distance of one pitch, namely 0.54 nm. In this case, the value of k_{mig} is calculated to be $5.5 \times 10^9 s^{-1}$.

On the other hand, excitation transportation depends on the coupling strength of a donor and an acceptor: energy transport due to Coulombic resonance interactions was developed by Förster[35,36] and Galanin.[37] Their theory is based on the assumption that the leading term in the interaction is the dipole transition moments between a donor and an acceptor. Here the rate constant for energy transfer, k_{et}, is expressed as a function of the distance between the donor and the acceptor, r, such as Eq. 11.

$$k_{et} = \frac{1}{\tau_M}\left(\frac{R_0}{r}\right)^6 \qquad (11)$$

where R_0 is a critical radius referred to the Förster radius: when $r=R_0$, the value of k_{et} is identical with that of the reciprocal of donor fluorescence lifetime. In the case of 1-methylnaphthalene, R_0 is 0.825nm.[38] Thus, we can calculate the value of k_{et} as the rate constant for the singlet energy migration between two nearest naphthyl groups of PNLG by using r=0.54 nm and τ_M = 3.5 ns: the value of k_{et} is $3.6 \times 10^9 s^{-1}$. The value of k_{et} is found to be almost identical with that of k_{mig} in spite of not taking into account the most stable arrangement of the long side-chain. This result suggests that the main mechanism of singlet energy migration is the Förster one.

In the present paper, we have obtained information on singlet energy migration among side-chain naphthyl groups of PNLG by taking advantage of the naphthyl groups being in an α-helix arrangement.

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Tab. 1

Characterization of PNLG

sample name	M_w	M_n	M_w/M_n	degree of polymerization
PNLG22	5960	5400	1.10	22
PNLG15-1	4070	3540	1.15	15
PNLG15-2	3970	3670	1.08	15
PNLG8	2240	2150	1.04	8.3
PNLG7	1980	1920	1.03	7.3

Tab. 2

Fluorescence decay profiles of PNLG in aerated THF. A_1, A_2, τ_1, and τ_2 were obtained from decay curves of monomer fluorescence.

sample	A_1	τ_1 (ns)	A_2	τ_2 (ns)	k_{EM} (s^{-1})	k_{ME} (s^{-1})	$k_{FD}+k_{ID}$ (s^{-1})
PNLG22	0.40	3.47	0.60	16.7	7.18×10^7	5.61×10^7	1.97×10^8
PNLG15-1	0.52	4.82	0.48	15.9	5.87×10^7	2.65×10^7	1.32×10^8
PNLG15-2	0.48	4.71	0.52	17.0	5.31×10^7	3.17×10^7	1.39×10^8
PNLG8	0.47	5.14	0.53	24.6	3.36×10^7	4.03×10^7	1.22×10^8
PNLG7	0.55	5.22	0.45	27.2	4.25×10^7	3.61×10^7	1.06×10^8

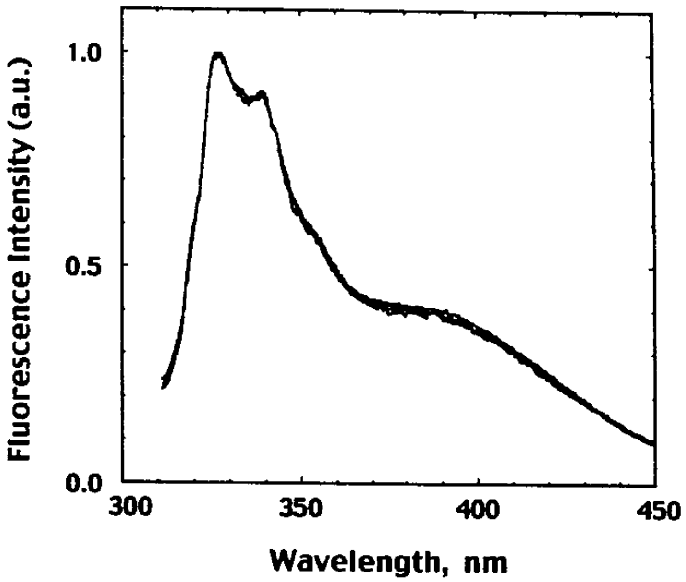


Fig. 1

Concentration dependence of fluorescence spectra of PNLG22 in aerated THF solution: [PNLG] = 4, 2, 0.7, and 0.2 μM. All the spectra are normalized to the peak. The excitation wavelength is 282 nm.

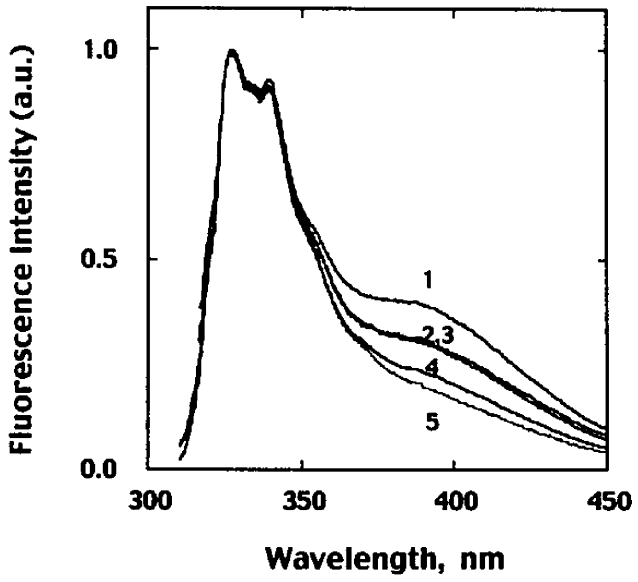
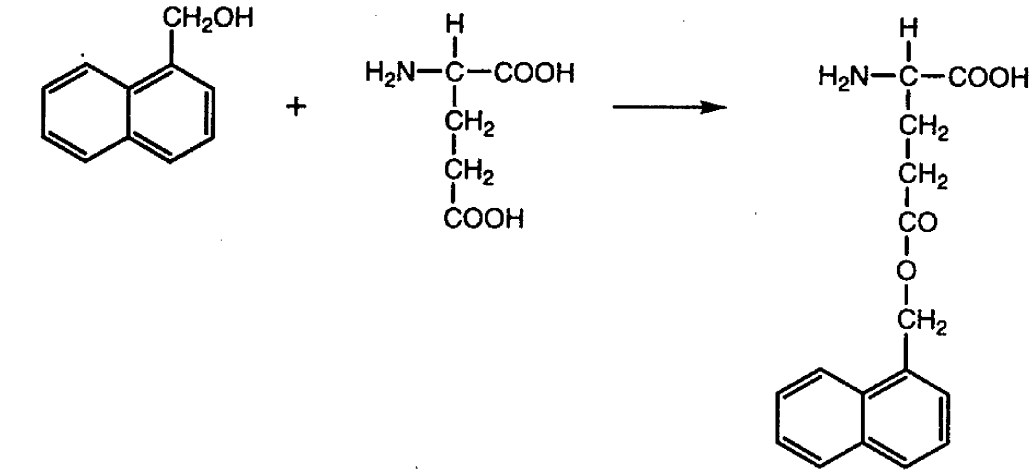


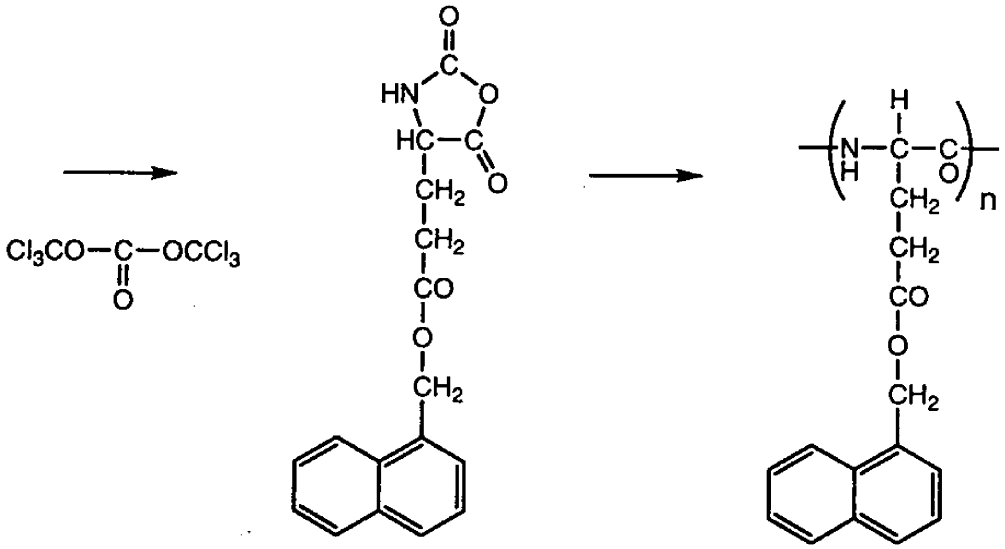
Fig. 2

Fluorescence spectra of PNLG in aerated THF: 1, PNLG22; 2, PNLG15-1; 3, PNLG15-2; 4, PNLG8; 5, PNLG7. All the spectra are normalized to the peak. The excitation wavelength is 282 nm.

Scheme 1 Preparation of PNLG



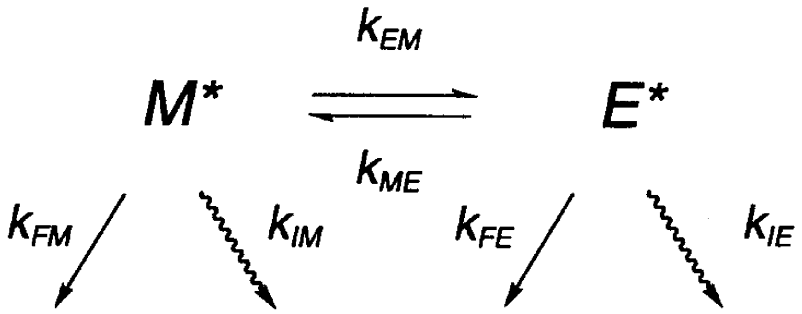
NLG



PNLG

Scheme 2

Kinetic Scheme for Excimer Formation in PNLG[a]



[a] M^* and E^* are monomer singlet and excimer, respectively. k_{FM} and k_{FE} are the rate constants for the radiative deactivation from excited monomer and excimer state, respectively. k_{IM} and k_{IE} are those for the nonradiative deactivation, and k_{EM} and k_{ME} are those for excimer formation and dissociation, respectively.