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Energy Migration and End-to-End Distance Relation in Copolymers of Acenaphthalene

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انتقال الطاقة في بوليميرات الأسينافثالين التشاركية وعلاقتها بمتوسط نهاية- نهاية سلاسل البوليمر

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إمتصاص الأشعة بواسطة نظام البوليمرات التي تحتوي على وحدات أروماتية تنتج حالات مثارة ضوئيا. هذه الظاهرة ولدت بحوثا لها أهمية بالغة وخاصة أن نظام البوليمرات يمكن استخدامه في مجال انتقال وتجميع الطاقة، ومنها الطاقة الشمسية.

امتصاص الأشعة فوق البنفسجية بواسطة الكروموفورات العضوية المتصلة بسلسلة البوليمر وكذلك انتقال الطاقة بواسطة الأكسيتون (وحدة طاقة) تعتبر موضوع البحوث النظرية. في هذا البحث تم تحضير سلسلة من البوليمرات المشاركة مع وحدات أخرى من بوليمر الأسينافثالين ومونيمرات الأكريلونيتريل، و2-فاينل نفثالين، وميثل أكريلونيتريل بالبلمرة الأستحلابية. وقد تم تقدير متوسط الأوزان الجزيئية بطريقة اللزوجة. الأطياف الفلوريسينية وضحت نوعين من المقذوفات المونوميرية عند 350 نانومتر والأكسيميرية عند 480 نانومتر. كما تم حساب أطوال انتقال الأكسيتون (وحدة الطاقة) في البوليمرات سالفة الذكر بوساطة تقنية التثبيط باستخدام الأكسجين وكذلك استخدام علاقة ستيرن-فولمر. ونظرا لصلابة بوليمر الأسينفثالين والتي بدورها تعرقل تكوين (الأكسيمر) ما عدا في التركيبة الحلزونية للبوليمر. عليه تم تحسين مرونة البوليمر بإضافة المونيمرات ألعضوية المذكورة لتشكل بوليمرات تشاركيه على طول سلسلة البوليمر لكي تسمح عملية التركيبة البوليمرية تكوين الأكسيمر بنسب تراكيز مئوية عديدة في البوليمر.

كانت أطول أبعاد انتقال الطاقة في البوليمر المحتوي على نسبة 53.5% تساوي 93 أنجستروم . تم حساب أبعاد انتقال هذه الطاقة كنسبة من المسافة بين طرفي البوليمر. العلاقة بين أبعاد انتقال الطاقة ونهاية- نهاية مبلمر مشارك تمت مقارنتها لتوضيح أقصى مدى لانتقال الطاقة في البوليمر التشاركي.

Abstract: *The absorption of radiation by polymeric systems containing aromatic units produces photo-excited states. This phenomenon has generated considerable research interest since polymeric systems may be used for energy collection and transmission. Ultra-violet absorption by fluorophores attached to a polymer chain and the subsequent energy migration by a way of exitations are subjects of theoretical interest. A series of copolymers of acenaphthalene (ACN) with acrylonitrile (AN), 2-vinylnaphthalene (2-VN), methylacrylonitrile (MAN), by emulsion polymerization, has been prepared. Fluorescence spectra showed both monomeric (350 nm) and excimeric (480 nm) peaks. Exciton migration lengths were calculated by quenching techniques using oxygen and Stern-Volmer relationship.* $L = (ksv / 2\pi R_o N_o)^{1/2}$ *. Chain rigidity in poly (ACN) hinders excimer formation except for the helix*

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conformation. Introduction of flexible (AN), (MAN) and (2-VN) units along the chain allows excimer formation of different %ACN concentration. Copolymer containing 53.5% ACN had the longest migration distance (93Å). The energy migration lengths, as a percentage of the end-to end distance, were calculated. The relation between the energy migration (L) and the end-to-end distance $(r^{-2})^{1/2}$ has been compared for the three different copolymers.

INTRODUCTION

The absorption of radiation by fluorophores attached to a polymer chain and the subsequent energy migration by way of excitons are subjects of theoretical interest [1-3]. Other coworkers [4] have described polymers containing pendent chromophores as antenna polymer which may function as energy gathering devices or allow singlet energy to proceed to a trap. More fundamental question are the exact mechanism of energy migration between fluorophores, the required orientation and maximum distance remain unanswered for many systems. An excited states in poly acenaphthalene (PACN) and in a random copolymers of acenaphthalene with the following comonomers 2-vinylnaphthalene (2VN), acrylonitrile (AN), methacrylonitrile (MAN) [5,6] have been studied. Two types of copolymers of (ACN) were investigated. The first type contains (ACN) units separated by photo-inactive groups in the main chain such as (AN), or (MAN). This permits a comparison of the homopolymer (PACN), to the copolymers containing smaller numbers of (ACN) chromophores, where monomer being randomly spaced by photo-inactive groups along the polymer chain. The second type is a copolymer of (ACN) and another monomer containing different chromophore which is photo-active groups such as (2VN). In the first type only excited singlet, A^*, and excimer $(AA)^*$ are important states while in the second type two excimers, $(AA)^*$ and $(BB)^*$, also the exciplex $(AB)^*$ are possible.

If A and B is different chromophore then excimer and exciplex formation are formed as:

$$ {}_1A^* + {}_oA \rightarrow {}_1(A \ldots\ldots A)^* \quad \text{EXCIMER} $$

$$ {}_1B + {}_oB \rightarrow {}_1(B \ldots\ldots B)^* \quad \text{"} $$

$$ {}_1A^* + {}_oB \rightarrow {}_1(A \ldots\ldots B)^* \quad \text{EXCIPLEX} $$

Energy migration along a polymer chain may occur from excited singlet, excimer or exciplex as follows:

Excited singlet migration $ {}_1S_i^* + {}_oS_j \rightarrow {}_oS_i + {}_1S_j^* $

Excimer migration $ {}_1D_i^* + {}_oD_j \rightarrow {}_oD_i + {}_1D_j^* $

Exciplex migration $ {}_1exp_i^* + {}_oexp_j \rightarrow {}_oexp_i + {}_1exp_j^* $

Poly (ACN) has a rigid chain structure and it can form excimers with alternate units along the chain [7], or by stacking in a helical conformation. Excimer formation has been reported for alternate copolymers of (ACN) with styrene [8] and for (ACN) with maleic anhydride [9]. The situation is different for 2-vinylnaphthalene since alternating copolymers of 2VN with methylmethacrylate or methacrylic acid did not form excimer. In the random copolymers of the same system showed excimer fluorescence [10]. In this study a series of copolymers of acenaphthalene with acrylonitrile poly (ACN-CO-AN), have been prepared by emulsion polymerization while copolymers of acenaphthalene with 2-vinylnaphthalene poly (ACN-CO-2VN), and methylacrylonitrile, poly (ACN-CO-MAN) were prepared by solution polymerization.

Quenching was carried out using oxygen or carbon tetrachloride and nitro methane [11] to obtain steady state fluorescence spectra. Fluorescence spectra showed both monomeric (350 nm) and excimeric (480 nm) peaks. Then energy migration lengths were calculated by quenching techniques using the Stern-volmer relationship. [12]

$$ L = (K_{sv} / 2\eth R_o N_o)^{1/2}. \qquad (1) $$

Where the singlet energy migration lengths, (L), are related to the Stern-Volmer constant, K_{sv}, and the F□rster encounter radius, R_o, and Avogadro's number N_o.

An arbitrary comparison between the migration and the polymers end-to-end distance was made. Since the migration length is based on a one dimensional random walk, a more meaningful comparison is between migration lengths in copolymers and homopolymers.

The energy migration lengths as a percentage of end-to-end distances $(r^{-2})^{1/2}$, were calculated using Flory relationship. [13]

EXPERIMENTAL METHODS

Copolymers of (ACN) and (AN) were prepared with varied compositions, by emulsion polymerization in water-ethanol (4:1) by volume, degassed with nitrogen. A surfactant such as detergent (Ivory soap) was added and potassium persulfate was used as initiator. Polymerization was carried out at 90°C for 24 hours. Copolymers were precipitated into methanol and purified by subsequent dissolution in benzene and precipitation into methanol. poly (ACN-CO-2VN) was prepared by solution polymerization in benzene at 60°C reflux for 36 hours, Azobis-isobutyronitrile (AIBN) was used as initiator.

All acenaphthalene samples, used in the polymerizations, were recrystallized from methanol-pentane mixture (3: 1). (AN) and (MAN) were distilled prior to use. Copolymers of (ACN) and (MAN) were prepared by solution polymerization in benzene at 60°C for 36 hours using (AIBN) as initiator, and the polymer was isolated by precipitation into 600 ml of methanol followed by precipitation from benzene into methanol .

Copolymers composition and the percentage of (ACN) in the copolymer of poly (ACN-CO-AN) and poly (ACN-CO-MAN) were determined by ultraviolet absorption method [14]. Data are listed in Table 1, using the measured optical density for (ACN) in (PACN) at 310 nm in 1, 2-dichloroethane as a solvent. For poly (ACN-CO-2VN), the compositions were checked by NMR spectroscopy (300MHZ). In all cases, conversions were held to 30% or less in order to avoid drift in copolymer composition.

Steady state fluorescence spectra were obtained on an Amino-Bowman J4 instrument using Hg-Xe light source. Samples were prepared in 1, 2-dichloroethane immediately before use. Several excitation wave lengths 290, 325 and 353 nm were tried with each series of (ACN) copolymers to obtain emission bands of highest intensity, for the experiments to measure quenching intensity using oxygen as a quencher. Samples were degassed with nitrogen, air and oxygen in a sequence to give a quencher concentration in order of zero, 2.3 and 12.9 x 10^{-3} molar [15].

Table 1. The molecular weights and intrinsic viscosity of polyacenaphthalene and poly(ACN– CO-MAN).

Mole % ACN	$[\eta]_{intrinsic}$ (dl/g)	Molecular weight (M_v x 10^{-4})
5	0.055	0.11
7	0.150	0.48
14	0.128	0.38
100 *	0.100	1.17

* Benzene used as solvent.

RESULTS AND DISCUSSION

The molecular weight of the polymers were calculated by using Mark-Houwink-sakurada equation $[\eta] = (kM_v^a)$, where k = 3.0 x 10^{-4}, a = 0.594 for benzene solvent and k = 3.25 x 10^{-4} , a = 0.72 for N, N-dimethyl formamide (DMF) solvent. η is the intrinsic viscosity and (M_v) is the viscosity average molecular weight of the polymer. The viscosity of all polymers was measured in an Ostwald viscometer. Temperature was controlled between 29 and 30°C. The solution was made by dissolving 50 mg of copolymers in 25 ml dry benzene or DMF as required. $\eta_{relative} = t_x/t_o$ where t_x is the efflux time of solution and t_o is the efflux time of solvent. $\eta_{inherent} = \ln \eta_{relative}/C$, where C is the concentration of polymer in g/dl. Then the intrinsic viscosity can be obtained by, : $\eta_{intrinsic} = \text{Lim}_{c \to o}\ \eta_{inherent.}$

The results of intrinsic viscosity η and the molecular weights of poly (ACN) and poly (ACN-CO-MAN) are shown in Table 1.

Similar calculation of the molecular weights was made for the other copolymers.

The polymer chromophore in the ground state ($_oS$) absorbed energy (hν) and promoted to the excited singlet state ($_1S^*$). The chromophore in the excited state either return to the ground state by emitting energy in the form of fluorescence or interact with other chromophores to form an excimer ($_iD^*$). The excimer may exhibit fluorescence and return to the ground state ($_oS$), or the energy can migrate to form a new excimer ($_jD^*$) which is a preformed site. Excited singlet, which do not form excimer, can follow the same process exhibiting fluorescence and return to the ground state, or an exciton can migrate to another chromophore giving a new excited singlet ($_jS^*$). Energy migration continues until fluorescence occurs or an energy trap is encountered. [16,17]

These can be interpreted using the following mechanisms:

Absorption of energy $\quad {}_oS + h\nu \rightarrow {}_1S^*$

Internal conversion $\quad {}_1S^* \rightarrow {}_oS + \text{heat}$

Emission (fluorescence) $_1S^* \rightarrow {}_oS + h\nu$

Excimer formation $_1S^* + {}_oS \rightarrow {}_iD^*$

Quenching $_1S^* + {}_oQ \rightarrow {}_oS + {}_1Q^*$

In this work a convenient method to study energy migration involves the determination of quenching parameters. The electronically excited state aromatic units attached to the main chain of the polymers was quenched by small molecules of oxygen. Then the Stern-Volmer. Equation relates fluorescence intensity to quencher concentration is:

$$F_o/F = 1 + K_{sv}[Q] \qquad (2)$$

Where F_o and F are the fluorescence emission intensity (intensities of excimeric fluorescence) at zero and different concentration of quencher respectively. K_{sv} is the Stern-Volmer constant and [Q] is the concentration of the quencher in mole/ litre. The energy migration lengths (L) were calculated from the Stern-Volmer relationship number (1).

The Stern-Volmer constant is calculated by equation (2) using the measured intensity of fluorescence at three different concentration of oxygen. Stern-Volmer curve of poly(ACN-CO-MAN) shows excimer emission at 405 nm. (Fig. 1). However, Stern-Volmer curve for poly (ACN-CO-2VN) shows excimer emission at 388 nm and 403 nm as shown in Figure 2.

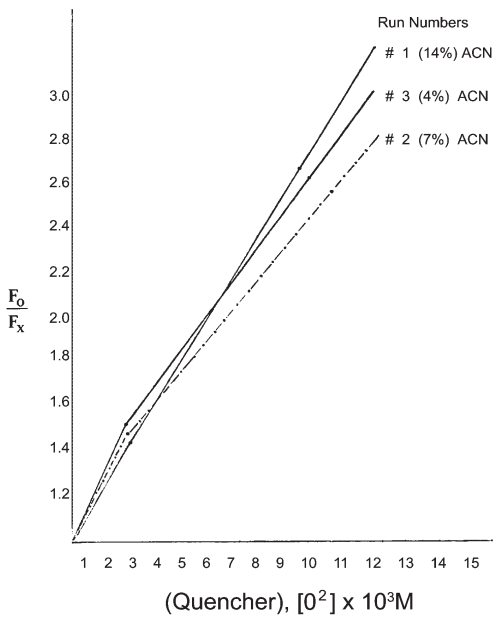


Fig. 1. Stern-Volumer curve of poly (ACN-CO-MAN), excimer emission at λ̂= 405 nm.

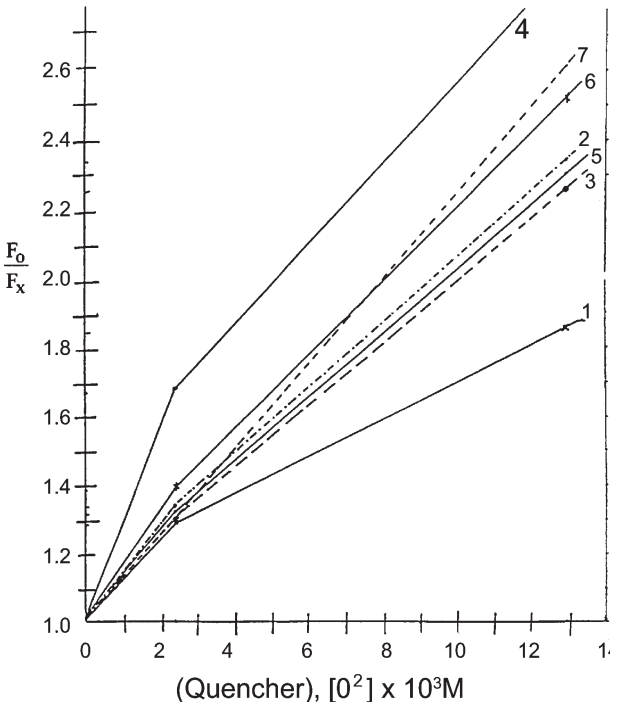


Fig. 2. Stern-Volmer curves of poly (ACN-CO-2VN), excimer emission at λ̂= 405nm. No.on curve for ACN % as 1 (5.5%) 2(17.3), 3(41.7), 4(53.5%), 5(59.8), 6(80.3), 7(94.5%).

Energy migration lengths are compared to the calculated end-to-end distance of polymers obtained from Flory's relationship.

$$[\eta] = \Phi \langle r^{-2} \rangle^{3/2} / M \qquad (3)$$

Φ is the Flory's constant which is equal to 2.1 x 10^{21} dl / (g mole cm^3), $[\eta]$ is the intrinsic viscosity, $\langle r^{-2} \rangle^{1/2}$ is the end-to-end distance and M is the viscosity average molecular weight of the polymer.

Copolymers in which energy migration lengths (L) equal or exceeds the end-to-end distance $\langle r^{-2} \rangle^{1/2}$ are needed for efficient energy collection and transmission.

Migration lengths in random copolymers of (ACN) with (AN) are not greatly affected by composition. Copolymers containing 47% and 80% ACN had the longest migration length of 70 Å compared to 63 Å for poly (ACN) obtained by equation (1) under similar condition. The above percentages correspond to an overall monomer composition of 2:8 and 6:4. Other parameters which may be important are molecular size and chain conformation. The incorporation of photo-inactive units such as (AN) or (MAN) in the copolymer increase chain flexibility and allow more excimer formation.

Random poly (ACN-CO-AN) showed monomer

and excimer fluorescence at 355 nm and 405 nm. (Fig. 3). Energy migration lengths and end-to-end distance are listed in Table 2**.**

The migration lengths in copolymers of Poly(ACN-CO-MAN) are greatly effected by composition. Copolymers containing 5% ACN had the longest migration length of 88 Å comparing to 63 Å in Poly(ACN) calculated under similar condition. It is clearly shown that energy migration lengths and excimer formation for a series of copolymers of Poly(ACN-CO-MAN) are effected by the percentage amount of (ACN) chromophore which is limited to five , seven and fourteen percent as shown in Table 3.

Other important results are the comparison between energy migration lengths and end-to-end distance of the copolymers calculated by Flory relation. A copolymers of poly(ACN-CO-MAN) containing 5% ACN had the longest energy migration distance 88 Å which exceeds end-to-end distance of 31 Å. The migration lengths decreased as the ACN content increased from 5 to 14% but in all cases were longer than the end-to-end distances.

The fluorescence spectra of poly (ACN-CO-MAN) show monomer emission at 346 nm and excimer emission at 405 nm. (Fig. 4). The intensity of excimer emission band decreased as the percentage of (ACN) decreases from 14 to 5% and shifts to longer wavelength 412 nm (Fig. 5).

In copolymers of (ACN) and (2VN) the maximum migration lengths of 93 Å is obtained with a copolymer of 53.5% ACN or 1:1 composition. This ratio favors exciplex formation and may indicate that

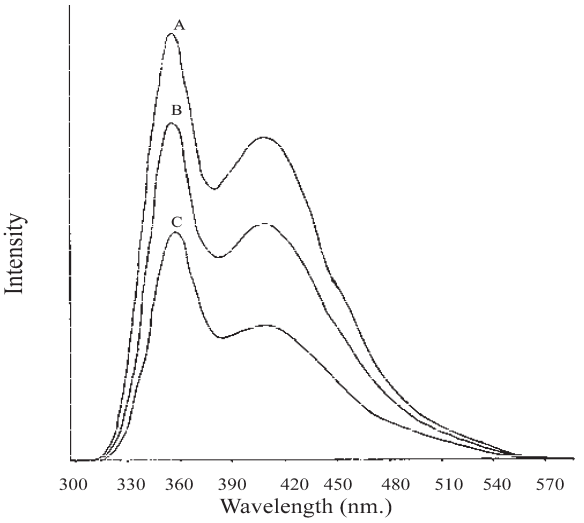


Fig. 3. Fluorescence spectra of poly (ACN-CO-AN), C=0.1 g/l. In 1,2-dichloroethane, 298k°, 36% ACN in the copolymer.

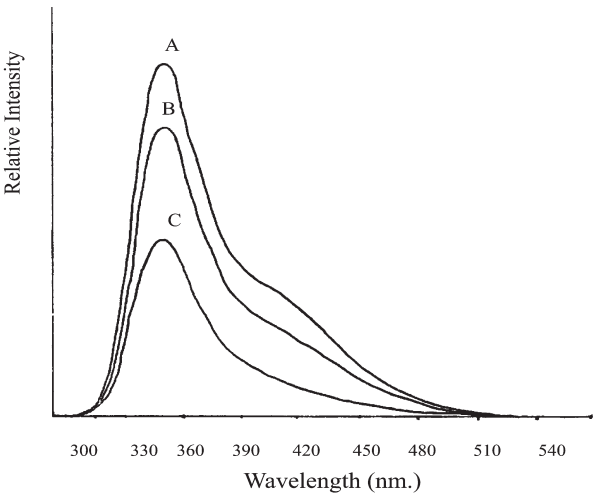


Fig. 4. Fluorescence spectra of poly (ACN-CO-MAN) C=0.19g/1 in 1,2-dichloroethane, 298°K, 14% ACN in the copolymer.

Table 2. Composition, end-to-end distances and migration lengths in poly (ACN-CO-AN).

Mole % ACN in the copolymer	Stern-Volmer K_{sv} M^{-1}	Calculated $\langle r^{-2}\rangle^{1/2}$ (Å)	Energy migration lengths (L) Å	100 L / $\langle r^{-2}\rangle^{1/2}$ in Å
36	157	39.4	68	173
47	168	41	70	171
66	134	144	63	44
76	113	119	58	61
78	139	96	64	54
80	168	61	70	114
95	138	103	64	63
100	137	96	63	65

Table 3. Composition, end-to-end distances $\langle r^{-2}\rangle^{1/2}$ and energy migration fo poly (ACN-CO-MAN).

Mole % ACN in the copolymer	Stern-Volmer K_{sv} M^{-1}	Calculated $\langle r^{-2}\rangle^{1/2}$ (Å)	Energy migration lengths (L)Å	100 L / $\langle r^{-2}\rangle^{1/2}$ in Å
5	261	31	88	284
7	204	70	78	112
14	165	62	69	111
100	137	103	63	61

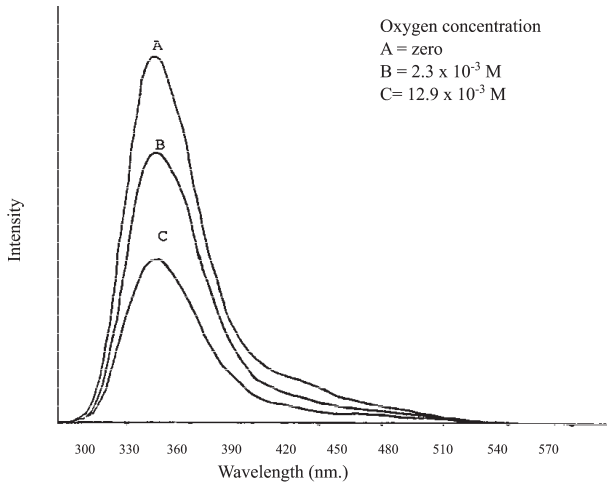


Fig. 5. Fluorescence spectra of poly (ACN-CO-MAN), C=0.1.g/1 in 1,.2-dichloroethane, 298kº, 5% ACN in the copolymer.

exciplexes provide an adventitious pathway for energy migration. Copolymers of other composition, both greater than and less than 50% ACN, give approximately 61 to 70 Å for migration lengths.

A regrouping of fluorophores may occur during exciton migration in the 1:1 copolymer. Such an effect might be expected to be temperature dependent, no studies in this area were attempted.

Å

$$B\,(A\,B)_i^{*}\,A\,B \xrightarrow{\text{Migration}} B\,A\,(B\,A)_j^{*}\,B$$

Calculated energy migration lengths and k_{sv} values for Poly (ACN-CO-2VN) are given in Table 4.

CONCLUSION

1. Poly (ACN-CO-AN) polymerized by emulsion polymerization to yield varied composition. The copolymer was evaluated as a carrier for energy on irradiation at different wave lengths namely 325 and 353 nm.

2. The migration lengths in copolymers of ACN and AN are not greatly effected by composition. A copolymer of 47% ACN has a migration length (L) of 70 Å compared to 69 Å for 80% ACN composition under similar conditions.

3. A copolymer of 47% ACN had the longest excemeric migration length. This indicates that a poly (ACN-CO-AN) allow the fluorophores to interact.

4. For Poly (ACN-CO-MAN) with a copolymer composition varied from 5 to 14 % ACN have an energy migration lengths 88 Å correspond to the copolymer of 5% composition and 69ú correspond to the copolymer of 14% composition. This indicates that excimers can be formed at low percentage composition of fluorophore; the migration lengths are all longer than the calculated end-to-end distances with copolymers of low ACN content (5% to 14%).

5. The poly (ACN-CO-MAN) system showed that excimer can be formed at low composition of fluorophore and energy transfer to copolymer containing 50% or more fluorophore.

6. In a series of copolymers of ACN and 2VN with a composition varied from 5.5% to 94.5% ACN, a copolymer containing 53.5% ACN had the longest migration distances 93 Å. Which indicate that energy from an exciplex may transfer to an exciplex-forming site.

7. The energy migration lengths (L) in both copolymers of Poly(ACN-CO-AN) and Poly(ACN-CO-MAN) with the above mentioned %ACN contents exceeds the end-to-end distances, This close agreement indicates that the above copolymers may be useful for energy collection and transmission.

8. In copolymers of ACN and 2VN the maximum migration length of 93 Å is obtained with a copolymer

Table 4. Composition, quenching constants end-to-end distances and migration lengths i poly (ACN-CO-2VN) .

Mole % ACN in the copolymer	Stern-Volmer K_{sv} M/1[a]	Energy migration lengths (L) Å	Calculated $\langle r^{-2}\rangle^{1/2}$ (Å)	100 L / $\langle r^{-2}\rangle^{1/2}$ in Å
5.5	126	61	114	54
17.3	148	66	125	53
41.7	130	62	149	41
53.5	291	93	136	68
59.8	139	64	138	46
80.3	165	70	126	55
94.5	130	62	132	47

(a) K_{sv} for excimer emission at 405 nm.

of 53.5% ACN composition. This ratio favors exciplex formation and thus indicates exciplexes provide a lower energy pathway for exciton migration.

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