

Triplet Exciton Annihilation Process on Two Dimensional Lattice of Naphthalene Choleic Acid Crystals

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A random walk simulation was used to determine the triplet exciton density and annihilation rate for a two dimensional lattice of naphthalene choleic acid with small amount of β -methylnaphthalene (BMN). The results demonstrate that energy transfer efficiency (α) increases as density increases and the annihilation begins to become significant at triplet exciton densities higher than 10^{-3} /sites. Another simulation was carried out to determine annihilation rate and unimolecular decay rate in the absence of BMN. The results indicate that the annihilation rate is equal to the unimolecular decay rate at the density of 1.2×10^{-3} /sites.

Introduction

It has been shown that the concepts of cluster distribution can describe energy transfer in multicomponent systems.^{1,2} Extensive studies of naphthalene-deuteronaphthalene crystals with β -methylnaphthalene (BMN) as an energy trap have been reported.³⁻¹⁰ Recently this system has been incorporated into a choleic acid crystal.¹¹ Energy transfer dynamics and the excitation density depopulation process in quaternary naphthalene choleic acid crystal ($C_{10}H_8/C_{10}D_8/BMN/DCA$) are studied monitoring sensitized phosphorescence and phosphorescence decay at 16 K and 4.2 K. Using deoxycholeic acid (DCA) as a crystalline matrix makes it possible to change the orientations and separations of the naphthalene molecules in the $C_{10}H_8-C_{10}D_8$ system and observe the effect on energy transfer. In these experiments both the deoxycholeic acid and the $C_{10}D_8$ serve as energy transfer insulators. The results pertain to triplet excitation energy transfer ($C_{10}H_8 \rightarrow BMN$) occurring after rapid relaxation to the lowest triplet state of $C_{10}H_8$. The lowest triplet state (T_1) is populated by intersystem crossing from the singlet. The triplet $C_{10}D_8$ relaxes rapidly by energy transfer to the $C_{10}H_8$, and transfer energy from $C_{10}H_8$ to BMN trap. Experimental results also reveal that there is no evidence of annihilation (exciter-exciter or exciton-trap) involved in decay process under the experimental condition. At low concentrations of naphthalene (5 mol %) when the $C_{10}H_8$ concentration is too low for energy transfer to occur, no phosphorescence is observed from BMN and unimolecular decay is the primary mechanism in the change of the excited triplet state density. With increasing naphthalene concentration, the triplet depopulation is controlled by both the unimolecular decay process and energy transfer to traps in early time (≤ 300 ms) until the density becomes too low for energy transfer to occur. At long times, unimolecular decay is the main mechanism for the triplet depopulation process.

The actual geometrical distribution of $C_{10}H_8$ clusters strongly influences the energy transport. The energy transfer rate is reduced by a factor of about 10^5 in naphthalene choleic acid relative to that in naphthalene crystals due to the larger distance between the molecules and the energy trans-

fer topology due to the change in molecular orientations and spacing.¹¹ Because of the slow rate for energy transfer and exciton annihilation in choleic acid, it appears possible to produce excited-state densities sufficiently high to allow excited-state structures of molecules to be determined.

It is of interest to understand the triplet exciton annihilation process for naphthalene choleic acid system. No exciton annihilation, however, was observed at the excited-state densities obtained under the experimental condition. Higher excited state density is needed to be able to observe the annihilation process. In this study, a computer simulation is carried out to obtain sufficiently high excited-state density, and to determine the triplet exciton density, and the annihilation rate under various conditions for naphthalene choleic acid system (NCA). The goal of the random walk simulation is to mimic the experimental results as well as possible in order to elucidate the energy transfer mechanisms and exciton annihilation process. The computational simulation methods are applied to treat an infinite lattice within the framework of a finite lattice. A crystal randomly distributed on a 1000×1000 square lattice is considered.

Determination of Cluster Distribution

First, we consider a two-dimensional lattice and determine the distribution of clusters of various size that occurs at different concentration of the occupying species. NCA has unit cell dimensions of $26.8 \times 13.6 \times 21.6 \text{ \AA}^3$ with a nearest neighbor guest-guest distance of 13.6 \AA along the b axis.¹² The characteristic of structural unit is the bilayer which extend into planes parallel to bc . The molecules along the c axis have the same orientation, and two adjacent bilayers are anti-parallel along the a axis. Since the distance of 21.6 \AA along the c axis is not significantly greater than the distance along the b axis, a consideration of two dimensional interaction for this system may be reasonable. A crystal randomly distributed on a 1000×1000 square lattice is considered, where the concentration is C . The probability that a randomly selected site is occupied by a $C_{10}H_8$ molecule is C .

To determine the cluster size, the cluster multiple labeling technique (CMLT)¹³ was used. CMLT technique is based on

the application of alternate labels to sites belonging to the same cluster. This technique is appropriate for the determination of the cluster distribution of a finite randomly mixed binary crystals. The practical algorithm is described in ref. 14. By inspecting the distribution of the cluster size, it can be seen that the cluster size increases gradually and cluster percolation is not observed in the concentrations between 5% and 20%. Since the stoichiometric ratio of NCA is 2 : 1 (*i.e.* 33% naphthalene choleic acid), this result is reasonable. In a two-dimensional system the percolation threshold is 0.59.^{14,22} For low concentrations, there are many isolated members, as well as many clusters of two, three, or four members. As the concentration increases, the distribution will contain more and more large clusters until several large clusters coalesce into a maxicluster, *i.e.* percolation occurs. Percolation may be viewed in analogy to phase transition, transition from a non-percolating state to a percolating state.¹⁵ Here "Phase transition" is not a physical phase transition, but is a purely geometric phenomenon in which clusters are clearly defined static object.

Random Walk Simulation

We consider the steady state condition. There is no walker on the lattice at $t=0$. The walkers are added at a constant rate, and the density of walkers increases from 0 to a constant average, a value which is referred to as the steady state density (ρ_{ss}). Some walkers will decay or annihilate and leave the system during the process of reaching the steady state, while newly produced ones will fill-in to maintain the total population. Figure 1 shows an example of a steady state reached by continuous excitation. Since continuous excitation was used, the required number of excitons are added at each step to the guest site at a constant rate and redistributed at each additional step. The adding process has two components: spatial distributions and reactions during the landing on the lattice. All sites in a lattice have equal probability for a walker to land. When a walker is added to a site occupied by another walker, the walker will react with the walker at that site. Periodic boundary conditions were used throughout the random walk simulation.

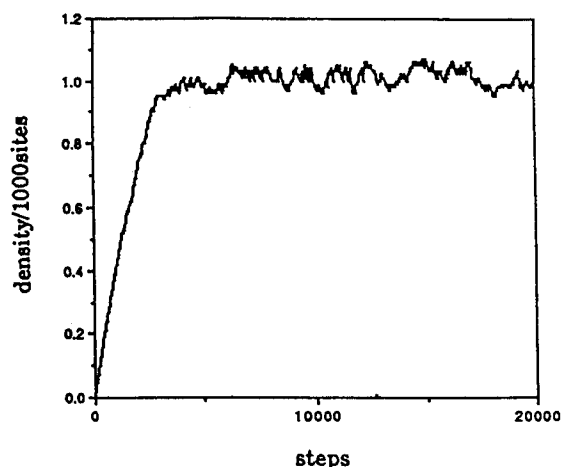


Figure 1. Approach to steady state for a random walk with continuous excitation.

The movement of walkers depends on the jump distance and the jump probability. Both factors vary from case to case. For an isotopic lattice in the absence of field, the motion of a walker is considered to be a random motion. The walker can move in any one of four directions, with a probability of 1/4. During the motion, some of the walkers will collide and annihilate while others are redistributed inside of system. In this work, we deal only with walks in which a walker randomly moves from a site to one of its nearest neighbor sites, because the time required to jump further than one site is longer than the lifetime of the walker; the nearest neighbor distance of NCA is 13.6 Å and the time required to jump this distance is estimated to be 10^{-3} second using Eq. (1)⁶

$$W(r) = \tau_{nn}^{-1} \exp[-\varepsilon(r/r_{nn} - 1)] \quad (1)$$

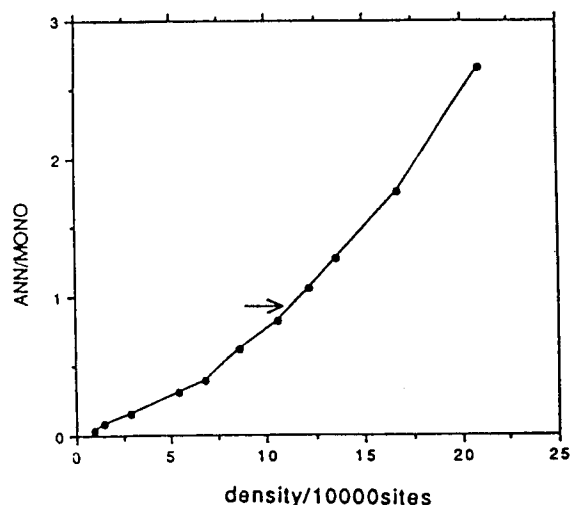
where τ_{nn} is the hopping time between nearest molecules, and r_{nn} is the nearest neighbor distance of naphthalene (5.1 Å)⁶. The nearest neighbor naphthalene triplet transfer time was found to be of the order of 10 to 100 ps, from the measurement of the delayed fluorescence for triplet excitons.¹⁷ A value of 100ps for τ_{nn} also was found from isotopic mixed crystal data and is in good agreement with the value obtained from diffusion measurement.¹⁸ The best fit with data was found⁶ using $\varepsilon=8.6$ and $\tau_{nn}=100$ ps. From this data, we can estimate a transfer time of about 1 ms. This estimate, however, neglects the orientation dependence of the interaction. The actual hopping time would be slightly slower due to the particular geometry of the naphthalene molecules in DCA system. For a jump the second-nearest neighbor (29 Å), the transfer rate is 10^7 times slower than at 14.7 Å, since the probability of the transfer goes as e^{-r} , as shown in Eq. (1). Thus the time required to jump to the next neighbor (29 Å) is in the order of 10^4 seconds, which is longer than naphthalene triplet lifetime (2.7s).¹⁰

We consider the two dimensional lattice of 33% naphthalene-choleic acid which is filled with naphthalene and small amount (4×10^{-4} mole fraction) of BMN. Only one species (the naphthalene excitation) is mobile, *i.e.* a walker, the other species (BMN) is stationary, *i.e.* a trap. Our reaction is assumed to be diffusion limited, *i.e.* the ratio of the number of reactive collisions to the number of total collision is 1. A walker moves along the lattice until it decays through one of following processes: (1) unimolecular decay, (2) trapping, (3) annihilation between molecules (*i.e.* meeting another walker at the same site). This partitioning has a large effect of the yield of phosphorescence. With BMN at a concentration of 4×10^{-4} mole fraction, the probability of direct excitation for BMN is low. Therefore, the BMN excited triplet state is formed by energy transfer from the donor (naphthalene) to acceptor (BMN). The emission from BMN therefore is termed sensitized phosphorescence. For unimolecular decay, we need to estimate the number of steps a walker makes within the lifetime of naphthalene. A walker decays unimolecularly on the average in 2.5×10^3 steps, if no trapping or annihilation occurs. To determine the maximum size cluster M_{max} an exciton can cover within its lifetime, the cluster distribution associated with the starting sites of the exciton that were trapped was determined by using CMLT. M_{max} was found to be 2330.

Table 1. The results of a random walk simulation for 10,000 steps (the time interval between steps is 9×10^{-4} second)

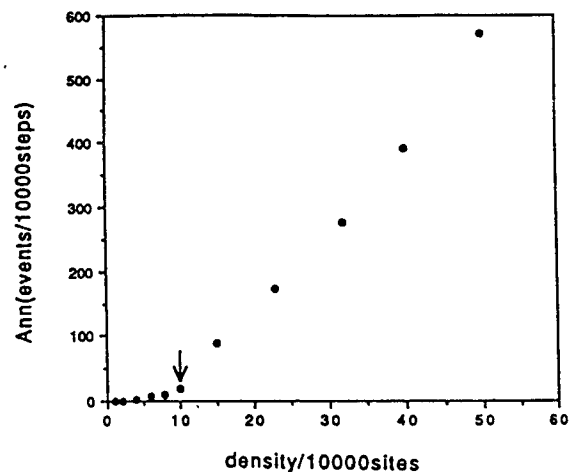
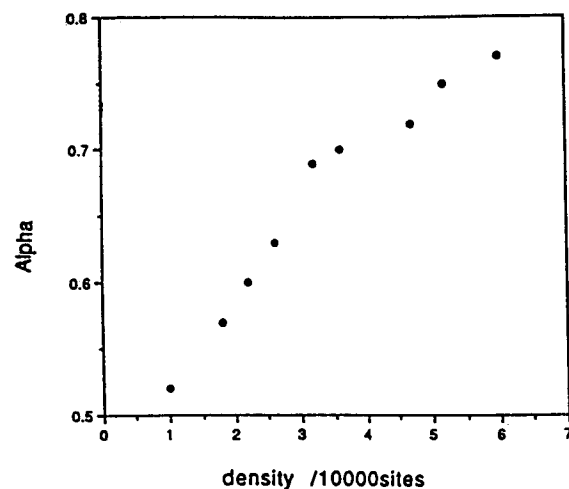
DEN	MONO	TRAP	ANN	α
1.0	111	122	0	0.52
1.8	196	252	1	0.57
2.2	226	334	1	0.60
2.6	236	402	3	0.63
3.2	242	552	4	0.69
3.6	258	640	5	0.70
4.7	276	710	9	0.72
5.2	285	855	13	0.75
6.0	330	1100	16	0.77

DEN: steady state density (10^{-4} /site). MONO: the number of unimolecular decays from $C_{10}H_8$. TRAP: the number of decays from trap. ANN: the number of annihilations.

**Figure 2.** The value of α for different triplet exciton densities.

Simulation Results

In the random walk simulation for a two dimensional lattice of 33% naphthalene choleic acid which is filled with naphthalene and a small amount (4×10^{-4} mole fraction) of BMN, the steady state triplet exciton density, the number of unimolecular decay from guest molecules, the number of decays from trap molecules, and the number of annihilation were recorded for 10000 steps, as shown in Table 1. The time interval between steps was 9×10^{-4} second.²⁰ This time interval was estimated using Eq. (1). By using data, the values of energy transfer efficiency (α) for different triplet exciton density are obtained as shown in Figure 2. In NCA system about 2330 sites are sampled, and α is reacted by these energy transfer dynamics. The results demonstrate that α increases initially with increasing density because larger clusters become more frequent. As density increases, the separation between molecules decreases, the intermolecular interaction increases, and the energy transfer becomes more efficient. The increase in α then flattens at higher density because of the limit set by M_{max} , which is the small number of sites that can be sampled by the exciton within a larger cluster. The results also show no abrupt transition.

**Figure 3.** The annihilation events that occurred in 10,000 steps for different triplet exciton densities. The results demonstrate that annihilation occurs at triplet exciton densities higher than 10^{-3} /sites.**Figure 4.** The ratio of annihilation rate to unimolecular decay rate, for different triplet exciton densities achieved by different addition rate, in the absence of traps.

The abrupt transition is characteristic of cluster percolation.^{1,14} Figure 3 shows the number of annihilation events occurring in 10000 steps for different triplet exciton densities. The results demonstrate the annihilation begins to become significant at triplet exciton densities higher than 10^{-3} /sites.

Another computer simulation was carried out to determine annihilation rate and unimolecular decay rate in the absence of BMN. The results indicate that the annihilation rate is equal to the unimolecular decay rate at the density N of 1.2×10^{-3} /sites or equivalently when 0.12% of the $C_{10}H_8$ molecules in the crystal are excited, as illustrated in Table 2 and Figure 4. Table 2 also illustrates the addition rate needed to produce different densities. It is of interest to determine the pumping rate required to achieve the density of 1.2×10^{-3} /site where the annihilation rate is equal to the unimolecular decay rate. This condition allows the annihilation rate constant (k_2) to be evaluated as $1.5 \times 10^{-18} \text{ cm}^3 \text{ s}^{-1}$ since $k_2 = k_1/N$, where k_1 is the unimolecular decay con-

Table 2. The unimolecular decay rate and annihilation rate for different densities achieved by different addition rates

INC	PUMP	DEN	MONO	ANN
30	1	1.00	228	7
20	1	1.46	325	28
10	1	2.85	612	102
5	1	5.44	1111	345
4	1	6.76	1301	523
3	1	8.66	1522	946
12	5	10.61	1696	1412
2	1	12.20	1835	1945
12	7	13.62	1696	2512
4	3	16.73	2112	3714
1	1	20.98	2163	5738

INC: increment of addition process in ms. PUMP: number of walkers added at each increment. DEN: steady state density (10^{-4} /site). MONO: number of unimolecular decays occurred in 10,000 steps. ANN: number of annihilation events occurred in 10,000 steps.

stant. The 2-dimensional unit cell of naphthalene choleic acid is $13.6 \times 21.6 \text{ \AA}^2$, therefore the density of 1.2×10^{-3} /sites corresponds to an exciton density N of $2.5 \times 10^{17}/\text{cm}^3$. The triplet-state population can be created indirectly by intersystem crossing from the singlet manifold. The oscillator strength is known to be 10^{-3} , and the triplet state quantum yield is in the range of $0.45 \sim 0.72$.²¹ With a molar extinction coefficient of 1,000 for the singlet absorption, e.g. at 250 nm, and an intersystem crossing quantum yield of 0.5, a light intensity of about 3.5×10^{15} photon/ cm^2s would be required to generate a triplet exciton density of $2.5 \times 10^{17}/\text{cm}^3$ in the first 0.01 cm of 1 cm^2 crystal with a uniform distribution. This light intensity can be attained with a continuous-wave (cw) laser at 250 nm producing $3 \text{ mW}/\text{cm}^2$ or a pulsed laser producing $0.3 \text{ mJ}/\text{cm}^2$ per pulse and 10 pulses/s.

Summary

Cluster distribution for different concentrations of C_{10}H_8 and C_{10}D_8 in naphthalene choleic acid (NCA) were determined by a computer simulation. The results of the simulation indicate that the cluster size increases gradually and cluster percolation is not observed in the C_{10}H_8 concentrations between 5% and 20%. A random walk simulation for a two dimensional lattice of 33% NCA which is filled with naphthalene and small amount (4×10^{-4} mole fraction) of BMN was carried out to determine the steady state triplet exciton density and annihilation rate under various conditions. By using data, the values of energy transfer efficiency (α) for different triplet exciton density are obtained. The results demonstrate that α increases as density increases (no percolation is observed), and the annihilation begins to become significant at triplet exciton densities higher than 10^{-3} /sites.

Another computer simulation was carried out to determine annihilation rate and unimolecular decay rate in the absence of BMN. The results indicate that the annihilation rate is equal to the unimolecular decay rate at the density of $1.2 \times$

10^{-3} /sites which corresponds to an exciton density of $2.5 \times 10^{17}/\text{cm}^3$. A light intensity of about 3.5×10^{15} photon/ cm^2s would be required to generate a triplet exciton density of $2.5 \times 10^{17}/\text{cm}^3$ in the first 0.01 cm of 1 cm^2 crystal with a uniform distribution.

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References

- Francis, A. H.; Kopelman, R. Exciton Dynamics in Molecular Solids. *Top. Appl. Phys.* **1981**, *49*, 241.
- (a) Kopelman, R.; Monberg, E. M.; Ochs, F. W. *Chem. Phys.* **1977**, *21*, 373. (b) Kopelman, R. *J. Phys. Chem.* **1976**, *80*, 2191. (c) Kopelman, R. Exciton Percolation in Molecular Alloys and Aggregates in *Topics in Applied Physics*; vol 15: Radiationless Processes in Molecular and Condensed Phase, ch. 5. (d) Hoshen, J.; Kopelman, R.; Monberg, E. M. *J. Stat. Phys.* **1978**, *19*, 219.
- Klymko, P. W.; Kopelman, R. *J. Phys. Chem.* **1983**, *87*, 4565.
- Ahlgren, D. C.; Kopelman, R. *J. Chem. Phys.* **1979**, *70*, 3133.
- Klymko, P. W.; Kopelman, R. *J. Phys. Chem.* **1982**, *86*, 3686.
- Gentry, S. T.; Kopelman, R. *J. Chem. Phys.* **1984**, *81*, 3014, 3022.
- Hanson, D. M. In *Molecular Electronic Devices*; Carter, F. L. Ed.; Marcel Dekker: New York, 1982; pp 89-111.
- Lipsett, F. R.; Macpherson, G. *Can. J. Phys.* **1966**, *44*, 1485.
- Hanson, D. M. *J. Chem. Phys.* **1969**, *51*, 5063.
- Ahlgren, D. C.; Monberg, E. M.; Kopelman, R. *Chem. Phys. Lett.* **1979**, *64*, 122.
- Kook, S. K.; Hanson, D. M. *J. Phys. Chem.* **1994**, *98*, 7239.
- MacNICOL, D. D. *Structure and Design of Inclusion Compounds: the Dexta-hosts and symmetry consideration*; in "Inclusion Compound" vol. 2: Structural Aspects of Inclusion Compounds Formed by Organic Host Lattice, edited by J. L. Atwood, J. E. Davies, D. D. MacNICOL, (Academic Press, London 1984) p 128.
- Hoshen, J.; Kopelman, R. *Phys. Rev.* **1976**, *B14*, 3438.
- Stauffer, D. *Introduction to Percolation Theory*; Taylor and Francis: London and Philadelphia, 1985; p 52.
- Essam, J. W. *Rep. Prog. Phys.* **1980**, *43*, 832.
- Rabek, J. K. *Mechanical of photophysical and photochemical Reactions in polymers*, John Wiley & Sons: 1987; p 31.
- von. Burg, K.; Altwegg, L.; Zschokke-Gränacher. I. *Phys. Rev.* **1980**, *B22*, 2037.
- Ern, V. J. *Chem. Phys.* **1972**, *56*, 6259.
- Kook, S. K.; Hanson, D. M. *J. Phys. Chem.* **1993**, *97*, 12339.
- Kook, S. K. Ph. D. Dissertation, Department of Chemistry, State University of New York at Stony Brook, 1991.
- (a) Ermolaev, V. L.; Svitasher, K. K. *Opt. Spec.* **1959**, *7*, 399. (b) Ermolaev, V. L.; Sveshnikova, E. B.; Saenko, E. A. *Opt. Spec.* **1967**, *22*, 86. (c) Li, R.; Lim, E. C. J.

Chem. Phys. 1972, 57, 605. (d) Karamos, G.; Kole, T.; Scribe, P.; Dalton, J. C.; Turro, N. J. *J. Am. Chem. Soc.* 1971, 93, 1032.

22. Park, C. H.; Song, C. Y.; Woo, H. G.; Choi, Y. K.; Kook, S. K. *Bull. Korean Chem. Soc.* 1995, 16, 630.

Raman Spectroscopic Characterization of a Rod-Coil Liquid Crystalline Oligomer-LiCF₃SO₃ Complex

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The interactions between a rod-coil liquid crystalline oligomer, ethyl 4-[4'-oxy-4-biphenylcarbonyloxy]-4'-biphenylcarboxylate with poly(ethylene oxide) (DP=12) (12-4) and LiCF₃SO₃ have been characterized by using Raman spectroscopy. Band assignments were made comparing the spectrum of 12-4 with those of the poly(ethylene glycol) monomethyl ether(PEGME) (Mw=550) and the ethyl-4'-hydroxybiphenyl-4-carboxylate (EHBPC), which are the coil and mesogen analogues, respectively. Analyzing characteristic bands of the 12-4-salt complex, we have found that the bands belonging to the coil and mesogenic units are changed in both intensities and frequencies. The spectral changes were interpreted from the viewpoint of the complexation between 12-4 and the Li⁺ ion. However, the possibility that the spectral changes in the mesogenic unit are not due to the complexation with the Li⁺ ion, but due to the conformational changes by the intercalation of nondissociated LiCF₃SO₃, is not ruled out.

Introduction

Polymer electrolytes complexed with alkali-metal cations have been studied for a long time because of their numerous applications such as solid state batteries and electrochromic devices.¹ These polymers are normally comprised of poly(ethylene oxide) (PEO), and to a lesser extent, poly(propylene oxide) (PPO) as a spacer group because PEO shows better solvating power for salt than the others do. The in-depth study of this PEO has provided rich information regarding the conformational and/or structural changes due to varying temperatures and salt concentrations.²⁻⁶ For example, a change in a conformational distribution corresponding to either *gauche* or *trans* isomerism is known to occur as temperature increases or as alkali-metal cations interact with the ether oxygens in the coil unit.

The liquid crystalline (LC) polymers which have aromatic moieties as a rigid mesogenic unit and polyethers as a flexible coil unit are of recent interest because the mesogenic unit provides variable structures while the coil unit contributes to an ionic conduction.^{7,8} Thermotropic polyesters are one of the most well-studied families in the area of main-chain LC polymers.⁹⁻¹¹ However, very little research has been done on rod-coil diblock systems containing PEO coil unit.

X-ray,^{12,13} ²³Na NMR,^{14,15} DSC,^{16,17} and Raman spectroscopy^{18,19} are techniques used to elucidate the relationships

between structure and ionic conductivity within ionic conducting polymers. Amongst these, Raman spectroscopy has proved to be one of the most powerful technique to characterize the conformational and/or structural changes of the LC polymers complexed with alkali-metal cations at the molecular level. However, most Raman works have concentrated on the spectral region of CH₂ rocking modes in order to investigate the conformational changes in the polymer backbone upon binding with alkali-metal cations. This is because the polymer chain plays a major role in the ionic transport in the amorphous regions.^{20,21}

It is reported that an increase in the rigid segment fraction in thermoplastic polyurethane (TPU) lowers the overall conductivity, even though ionic conductivity is normally the result of local segmental motions of a polymer chain.²² This implies that the interaction of mesogenic units with alkali-metal cations would reduce the conductivity of polymers. Thus, whether both segments are able to interact with salt or not is a matter of concern. In order to address this matter, it is, therefore, necessary to investigate not only the coil but also mesogenic units to see if the latter is involved in complexation with alkali-metal cations.

In this paper we report Raman spectroscopic studies of a rod-coil diblock liquid crystalline oligomer (12-4), where rod is ethyl 4-[4'-oxy-4-biphenylcarbonyloxy]-4'-biphenylcarboxylate and coil is poly(ethylene oxide) with the degree of polymerization of 12, and the complexes with 0.15 and 0.30 mols of LiCF₃SO₃ per 1 mol ethylene oxide unit in 12-

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