produce transients from model arylcarbamates and MDI-based polyurethanes. A thorough kinetic analysis of polyurethane laser flash photolysis based on these results will be published as a paper in the near future. In addition, detailed time-resolved decay profiles and radical decay times will be presented for all radical species discussed in this paper.

Acknowledgment. This work was sponsored in part by the Office of Naval Research. In addition, acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. Acknowledgment is also made to NSF for assistance in purchasing the laser flash photolysis unit (Grant CHE-8411829 Chemical Instrumentation Program).

Registry No. (MDI)(1,4-butanediol)(poly(tetramethylene glycol ether)) (block copolymer), 107678-92-2; BP-MDI, 60483-67-2; SiMe$_2$-MDI, 114944-06-8; aniline, 62-53-3; propyl *N*-phenylcarbamate, 5532-90-1.

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Structure and Photophysical Behaviors of Langmuir–Blodgett (LB) Films Containing Copolymers of Diethyl Fumarate with Vinylcarbazole and Acenaphthylene

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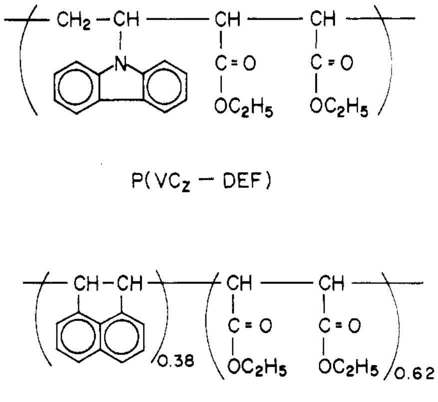
ABSTRACT: The copolymers of diethyl fumarate with vinylcarbazole and acenaphthylene gave stable monolayer films when they were mixed with stearic acid, though in the mixed monolayer films the phase separation in the copolymer and stearic acid phase occurred. The monolayer films could be transferred onto solid supports successively by the Langmuir–Blodgett (LB) method. In these multilayer LB films, acenaphthenyl or carbazolyl chromophore is incorporated as a polymer pendant group, excited energy-transfer and photoinduced electron-transfer processes were studied by adding amphiphilic dyes as acceptor molecules, and the efficiencies of the processes are discussed.

Introduction

The Langmuir–Blodgett (LB) technique provides ultrathin and molecularly ordered films which are now taking much attention from the viewpoint of microelectronic or optical devices.[1-7] So far, the LB films are formed with amphiphilic molecules, such as long-chain fatty acids and dyestuffs with long hydrocarbon chains;[8-10] however, a great deal of effort has been necessary to synthesize such amphiphilic compounds. Moreover, there are some cases where long hydrocarbon chains become a disadvantage. Some attempts to prepare LB films with lightly substituted or unsubstituted dyestuffs have occurred.[11,12]

In the present work, the LB films containing chromophores have been prepared in the form of a copolymer and fatty acid mixture. Acenaphthenyl or carbazolyl chromophore as a polymer pendant group can be incorporated into LB films without a long alkyl chain substituent. The monolayer structures at the air–water interface have been studied. Excited energy-transfer and photoinduced electron-transfer processes in the LB films have been studied using conventional amphiphilic dyes as an energy or electron acceptor.

Chart I


P(VCz – DEF)

P(AcNp – DEF)

Experimental Section

Acenaphthylene (AcNp)–diethyl fumarate (DEF) copolymer (P(AcNp–DEF)) and vinylcarbazole (VCz)–DEF copolymer (P(VCz–DEF)) were prepared in benzene by free-radical polymerization at 60 °C with 2,2′-azobis(isobutyronitrile) as a thermal initiator (Chart I). The copolymers were purified by several reprecipitations. The copolymer compositions were determined by elemental analysis; 38 mol % acenaphthylene for P(AcNp–DEF) and 50 mol % vinylcarbazole for P(VCz–DEF). The latter copolymer is an alternating copolymer.[13] *N*-Octadecyl-1-naphthaleneamide (NN) was synthesized from a reaction of 1-naphthoxy chloride and octadecylamine in chloroform. The

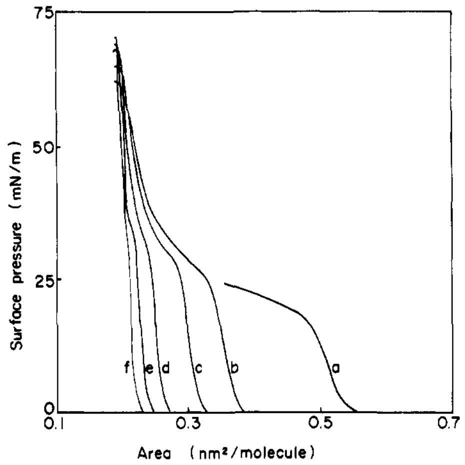


Figure 1. π–A isotherms of P(VCz–DEF)–stearic acid mixed monolayers: (a) copolymer:stearic acid = 1:0, (b) 1:1, (c) 1:2, (d) 1:5, (e) 1:10, (f) 1:20.

synthesis of *N*-octadecyl-9-anthramide (AN) is as follows: anthracene was reacted with oxalyl chloride in nitrobenzene and then reacted with octadecylamine in chloroform. The crude products were separated by column chromatography and purified by recrystallization. 1,1′-Dioctadecyl-4,4′-bipyridinium dibromide ($C_{18}V^{2+}$) was synthesized from a reaction of 4,4′-bipyridine and octadecyl bromide in ethanol and then purified by recrystallization. Distilled and deionized water was used. Chloroform used for spreading on the water surface was of fluorescence spectroscopy grade. Quartz, slides on which the multilayer was deposited were cleaned in boiling H_2SO_4–HNO_3 (2/1) solution and made hydrophobic with dimethyldichlorosilane. The surface pressure–area (π–A) isotherms were measured with an automatically working Langmuir trough (Kyowa Kaimen Kagaku HBM-AP using a Wilhelmy-type film balance). Fluorescence spectra were measured by a Shimadzu RF 503A spectrofluorophotometer.

Results and Discussion

Structure of Monolayers. A chloroform solution of a copolymer and stearic acid mixture was spread onto the surface of water containing 3×10^{-5} M $BaCl_2$ and 5×10^{-4} M $KHCO_3$. Figure 1 shows π–A isotherms at 17 °C for the mixture of P(VCz–DEF) and stearic acid in various molar ratios. All the isotherms showed a transition region in a range of about 20–35 mN/m, and the region decreased with increasing the molar ratio of stearic acid. The limiting surface areas were estimated from the isotherm curves by extrapolating the steepest region before the transition to zero surface pressure. In the isotherm for P(VCz–DEF) without stearic acid ((a) in Figure 1), the limiting area of repeating monomer unit (VCz monomer + DEF monomer) was about 0.55 nm². The surface area was estimated from the cross section of the P(VCz–DEF) monomer unit based on a polymer conformation from CPK models where the polymer main chain is laid on the water surface horizontally and the carbazole pendant group is oriented perpendicular to the chain. The value estimated is in a range of 0.5, which is close to the experimental data (0.55), to 0.9 nm²; the variation is due to the orientation of the diethyl ester group of DEF. It can be said that P(VCz–DEF) forms a monolayer on the water–air interface due to a hydrophilic character of DEF comonomer, and the copolymer monolayer is collapsed with a drastic conformation change (e.g., to random coils) at the surface pressure of the transition region. The copolymer layer, however, is not squeezed out, because the limiting area at the more condensed region after the transition does not become smaller than the area (0.2 nm²) of stearic acid. The limiting surface areas were plotted against the monolayer compositions, giving a straight line (Figure 2); the additivity of the surface area of P(VCz–DEF) monomer unit and that of stearic acid hold. In general, the plot of surface area against monolayer composition for mixed monolayers deviates upward or downward from a straight line, depending on intermolecular interaction. A linear relationship is observed in a situation where an ideal molecular mixing (like a mixing of ideal solutions) or a phase separation occurs. The straight line in Figure 2 can be explained by the phase separation in the copolymer and stearic acid phase. Similar isotherms were obtained with P(AcNp–DEF); the limiting surface area of the copolymer was found to be about 0.45 nm², and the area estimated with CPK models is in the range 0.4–0.7 nm². The monolayer of the copolymers and stearic acid with molar ratio of 1/10 (chromophore/stearic acid) could be transferred onto the solid supports in both downward and upward strokes (Y-type film) at a surface pressure of 15 or 20 mN/m and a dipping velocity of 5 mm/min. Although the phase separation occurs in the monolayer, the size of the copolymer domain by the phase separation would not be as large, because the monolayer can be transferred with a transfer ratio of 1. The neat P(VCz–DEF) copolymer monolayer could be also transferred onto the solid supports at the transition pressure. However, the transfer ratio was not constant. The first layer (downward stroke) was transferred with a ratio of about 3; however, the ratio decreases gradually with the deposition layers. These results show that the neat copolymer monolayer is not stable. The mixed monolayers with stearic acid give the stable LB films. DEF monomer can be copolymerized with monomers having various functional chromophores. Therefore, the present method is convenient to incorporate the desired functional groups into LB films.

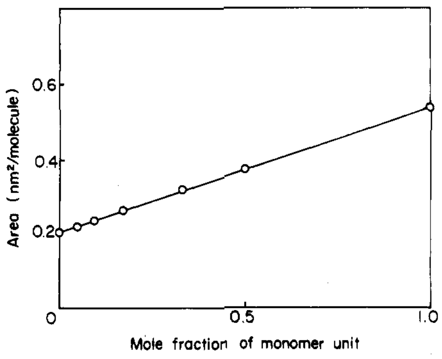


Figure 2. Plots of surface area vs mole fraction of P(VCz–DEF) monomer unit for P(VCz–DEF)–stearic acid mixed monolayers.

Energy Transfer and Electron Transfer. Energy-transfer and electron-transfer processes were studied with these LB films. Energy transfer from acenaphthenyl chromophore in AcNp–DEF copolymer to *N*-octadecyl-9-anthramide (AN) in the LB film was investigated from the fluorescence spectra in the presence and absence of AN acceptor. Energy transfer from *N*-octadecyl-1-naphthaleneamide (NN) to AN for comparison was also examined.

The fluorescence spectra could be measured when the LB film deposited only two layers on one side of the quartz slide, showing that the chromophores are dispersed molecularly into the copolymer domain of the LB films, even though the phase separation occurs. P(AcNp–DEF) in the LB film showed an excimer-like broad spectrum with a maximum peak at around 390 nm ((a) in Figure 3). NN also showed broad fluorescence with a maximum peak at 350 nm in the LB film ((a) in Figure 4). The broadening of the fluorescence spectra in the LB film suggests that the chromophore is fixed in various orientations and en-

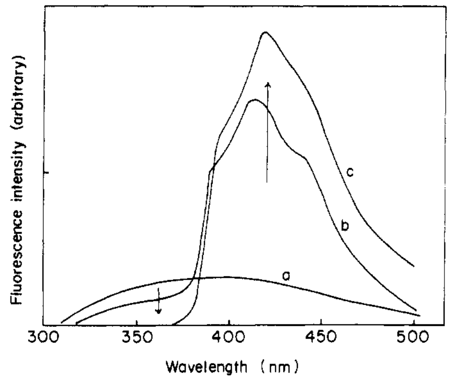


Figure 3. Change of fluorescence spectra of P(VCz-DEF)-AN-stearic acid mixed LB films with the composition (the number of layers: two layers on each side). (a) P(AcNp-DEF):AN:stearic acid = 1:0:10, (b) 1:0.03:10, (c) 1:0.1:10.

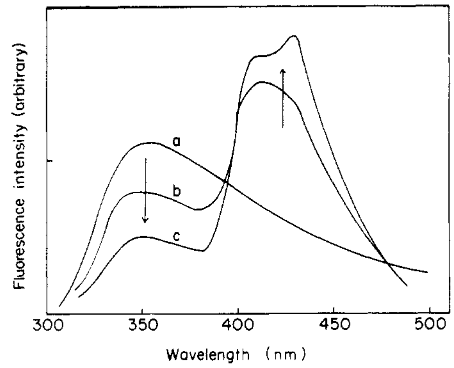


Figure 4. Change of fluorescence spectra of NN-AN-stearic acid mixed LB films with the composition (the number of layers: two layer on each side): (a) NN:AN:stearic acid = 1:0:10, (b) 1:0.0005:10, (c) 1:0.001:10.

vironments in the LB film. The fluorescence maximum (420 nm) of AN is separated from that of NN and AcNp. Figure 4 shows the energy transfer from NN to AN within the same layer (excitation: 290 nm). The fluorescence from AN by direct excitation at 290 nm can be negligible. When the molar ratio of AN increased, the fluorescence intensity of NN was decreased and that of AN was increased, showing that energy transfer from NN to AN occurs. The molar ratio of NN to stearic acid in the LB film is 1:10, where an energy migration between NN easily occurs. The efficient energy transfer from NN to AN in the LB film is attributable to the energy migration. For P(AcNp-DEF) also, the energy transfer to AN occurred (Figure 3). The chromophore (acenaphthene group) concentration was the same as that for NN (Figures 3 and 4). The efficiency for the energy transfer was compared by the fluorescence intensity of the acceptor (AN) (Figure 5). The statistical energy donor-acceptor separation distance (R) (abscissa in Figure 5) was defined from the area alloted to one AN molecule (total area/number of AN molecules). The energy-transfer efficiency is considerably small for the P(AcNp-DEF)-AN system. In the P(AcNp-DEF)-AN system, a higher acceptor (AN) density is necessary to obtain the same energy-transfer efficiency as in the NN-AN system.

Electron transfer from the excited carbazole in VCz-DEF copolymer to $C_{18}V^{2+}$ acceptor in the LB film (carbazole chromophore/stearic acid = 1/10) was studied by the fluorescence quenching method. The result is shown in Figure 6. The statistical electron donor-acceptor separation distance (R) was defined in a similar manner as above (total area/number of $C_{18}V^{2+}$ molecules). The statistical average separation distance (R_0), giving a half fluorescence intensity ($I/I_0 = 0.5$), was found to be about 2 nm. The obtained R_0 is of the same order of magnitude as seen in another electron-transfer system in which donor and acceptor molecules are assumed to be mixed homogeneously in a layer.[14-16] But, in this case, most of the donor chromophores (carbazolyl groups) must be separated from acceptor molecules ($C_{18}V^{2+}$) owing to the phase separation between P(VCz-DEF) and stearic acid. As for $C_{18}V^{2+}$, this molecule is highly mixed with stearic acid and would be located in a stearic acid phase. The mechanism of electron-transfer process can be considered as follows; the excited energy absorbed by carbazolyl group would be migrating within a P(VCz-DEF) domain, and when the excited energy arrived at the carbazolyl group neighboring to $C_{18}V^{2+}$, electron transfer would occur there.

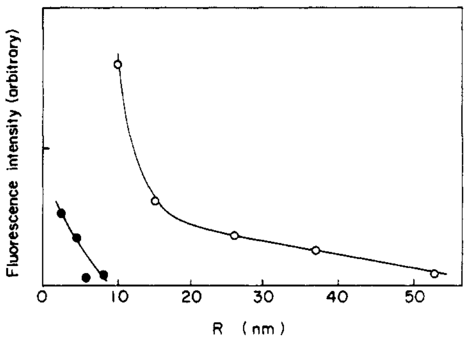


Figure 5. Dependence of fluorescence intensity of AN on statistical energy donor-acceptor separation distance (R): (○) NN-AN-stearic acid mixed LB film, (●) P(AcNp-DEF)-AN-stearic acid mixed LB film.

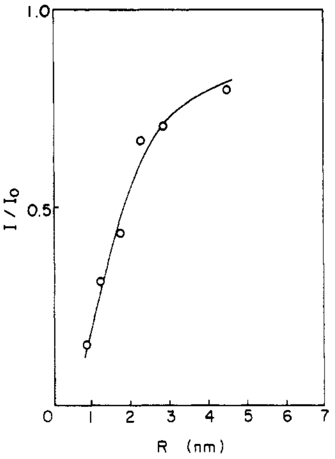


Figure 6. Dependence of I/I_0 on statistical electron donor-acceptor separation distance (R) in stearic acid mixed LB film with P(VCz-DEF) (carbazole chromophore:stearic acid = 1:10). I and I_0 indicate the fluorescence intensity in the presence and absence of $C_{18}V^{2+}$, respectively.

In conclusion, we could prepare the chromophore-containing LB films in the form of the mixture of DEF copolymers with fatty acid. This means that it is possible to incorporate the desired chromophores into LB films as a pendant group of the copolymer. Excited energy transfer and photoinduced electron transfer occurred in these mixed films. However, the efficiency of energy transfer was small compared to the usual LB films. As for photoinduced electron transfer, the efficiency corresponded to that of the usual LB films in regard to added acceptor molecules. However, the mechanism would be different from that of the usual LB films.

Registry No. (AcNp)(DEF) (copolymer), 114943-44-1; (DEF)(VCz) (alternating copolymer), 114943-45-2; AN, 114943-46-3; $C_{18}V^{2+}$, 90179-58-1; stearic acid, 57-11-4.

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Interaction of Polar Vinyl Monomers with Lithium Picrate in Dioxane

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ABSTRACT: The interaction of some polar vinyl monomers with lithium picrate (LiPi) in dioxane at 25 °C was studied by a competition technique using cross-linked poly(ethylene oxide) (PEO) as the insoluble ligand. The original competition method was modified for the case where the ionic solute forms more than one type of complex with the soluble and/or the insoluble ligand. The Langmuir–Klotz isotherm of LiPi binding to cross-linked PEO in the presence of monomer gave the apparent binding constant of the polymer gel when in competition with monomer. The formation constants of LiPi complexes with the monomer were then calculated from the apparent binding constant as function of monomer concentration. The nature of the polar group of monomer was found to be of paramount significance. The results were discussed in view of the possibility of complex formation between monomer and active centers in the anionic polymerization of polar vinyl monomers.

Introduction

Solvation[1,2] and complex formation phenomena are known to play an important role in ionic organic reactions in low polarity media. Special interest has been shown in processes involving anionic species, and many aspects of the chemistry of carbanions with *s*-metal counterions are now extensively documented and well understood.[3–5] Yet, certain problems of fundamental significance still remain unsolved. Among these is the occurrence of complex formation between monomer and the propagating centers in the anionic polymerization of polar vinyl monomers prior to monomer addition.[6]

The possibility of specific interaction with the monomer arises when ion pairing of the growing chain ends occurs to a considerable extent, a situation often encountered in ionic polymerization processes. Thus, conductivity measurements show that the anionic active centers of polar vinyl monomers exist predominantly as ion pairs or higher associates, even in THF,[7] the extent of chain propagation on free anions being negligible. On the other hand, the polar group of the monomer or the chain substituents is often a strong electron pair donor and can compete with the solvent for coordination of the counterion. Indeed, interaction of the active centers with neighboring monomer untis, e.g., the penultimate effect, is rather well-known.[8,9] Similar interactions with monomer are difficult to study in real polymerizing systems, even if they occur, since the reaction sequence is quickly completed by monomer addition to the growing chain end. No direct experimental evidence has been presented to prove complex formation.

Specific interaction between monomer and counterion in the chain propagation step is expected to have a profound effect on the reaction mechanism, especially in copolymerization processes. In certain systems, it may prove to be more important than monomer affinity for the free anion and give rise to reordering the apparent monomer reactivities. This possibility offers an indirect approach to checking the hypothesis of monomer coordination to the active centers in the anionic polymerization of polar monomers. It is the purpose of the present work to make the first step in this direction by providing a scale of relative affinities of some polar vinyl monomers for lithium counterions.

The interactions were studied in dioxane, a solvent of comparatively low cation affinity, since most of the common polar vinyl monomers are not typical electron donor ligands and cation binding is expected to be weak and hence solvent sensitive. Lithium picrate (LiPi) was selected as the reference salt since it does not initiate the polymerization of these monomers. The salt is poorly dissociated in dioxane, and mainly tight ion pairs are formed in solution. What must be avoided is the formation of free ions because their high reactivity will cause much of the reaction to proceed via the free ions instead of the ion pairs. Complex formation is most probable for lithium and magnesium counterions.[10] Finally, a simple method for the determination of the constants of alkali cation complex formation in solution was recently reported by Smid and Sinta for alkali picrates.[11] It utilizes polymer gels of known binding capacity for the ionic solute to compete with the solube ligand. In this study, cross-linked poly(ethylene oxide) (PEO) was used as the polymer gel. Both linear and cross-linked PEO are known to coordinate alkali picrates in solvents of low polarity,[12,13] and cross-linked PEO shows a very good swelling capacity in dioxane.

Experimental Section

Dioxane was refluxed over sodium–potassium alloy and distilled before use. Methyl isopropenyl ketone was prepared by aldol

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