splits into two peaks, 4 and 4′. Peak 4 at 21.5 ppm is consistent with the CH_3(4) carbon resonance (21.3 ppm) in the solid-state spectrum of P(3HB) powder, while the chemical shift (20.2 ppm) of peak 4′ is approximately consistent with that (19.8 ppm) of the CH_3(4) carbon resonance in the solution spectrum of P(3HB) in chloroform. The relative intensity of peaks 4 to 4′ decreases with an increase in the fraction of 4HB units. In addition, the methylene carbon resonance of 3HB units splits into peaks 2 (43.1 ppm) and 2′ (41.4 ppm). The chemical shift of peak 2′ is almost identical with the value (40.8 ppm) of CH_2(2) carbon resonance in the solution spectrum of P(3HB) in chloroform. The relative intensity of peaks 2 to 2′ decreases with increasing 4HB fraction as well as the intensity of peaks 4 to 4′.

In the CP/MAS ^{13}C NMR spectrum C of sample 4 (49 mol % 4HB) the intensities of carbonyl carbon resonances (1 and 5) are very weak in comparison with those of other carbon resonances, indicating that the cross-polarization arising from ^{13}C–^{1}H dipole interaction is ineffective because of a high mobility of copolyester segments.

The P(3HB) polymer chain crystallizes as a left-handed 2_1 helix in the solid state.[32,33] The results of CP/MAS ^{13}C NMR analysis indicate that the crystallinity of the P(3HB-*co*-4HB) sample decreases with an increasing fraction of 4HB units. Peaks 4 and 2 in the CP/MAS ^{13}C NMR spectra of the P(3HB-*co*-4HB) samples arise from the CH_3(4) and CH_2(2) carbon species of 3HB units in the crystalline phase with a regular conformation of 2_1 helix. On the other hand, peaks 4′ and 2′ are likely to arise from those of 3HB units, which are poorly ordered with a high flexibility in the amorphous phase. The decrease of crystallinity in the P(3HB-*co*-4HB) samples was also suggested by the enthalpy of fusion, ΔH_m in table II. It is noted that the property of P(3HB-*co*-4HB) in the solid state is different from the solid-state property of P(3HB-*co*-3HV). Marchessault et al.[23] have shown that the P(3HB-*co*-3HV) samples have high crystallinities (>60%) throughout a range of compositions of 0–47 mol % 3HV.

In conclusion, new bacterial copolyesters are described that have a random sequence distribution of 3HB and 4HB units, and the crystallinity decreases with an increasing fraction of 4HB units.

Registry No. P(4HB) (SRU), 28728-97-4; P(4HB) (homopolymer), 114959-05-6; poly(4-chlorobutyric acid) (homopolymer), 114959-06-7.

References and Notes

(1) Schlegel, H. G.; Gottschalk, G.; Bartha, R. V. *Nature (London)* **1961**, *191*, 463.
(2) Lundgren, D. G.; Alper, R.; Schnaitman, C.; Marchessault, R. H. *J. Bacteriol.* **1965**, *89*, 245.
(3) Griebel, R.; Smith, Z.; Merrick, J. M. *Biochemistry* **1968**, *7*, 3676.
(4) Saito, T.; Fukui, T.; Ikeda, F.; Tanaka, Y.; Tomita, K. *Arch. Microbiol.* **1977**, *114*, 211.
(5) Suzuki, T.; Yamane, T.; Shimizu, S. *Appl. Microbiol. Biotechnol.* **1986**, *24*, 370.
(6) Henzle, E.; Lafferty, R. M. *Eur. J. Appl. Microbiol. Biotechnol.* **1980**, *11*, 8.
(7) Howells, E. R. *Chem. Ind. (London)* **1982**, *7*, 508.
(8) King, P. P. *J. Chem. Tech. Biotech.* **1982**, *32*, 2.
(9) Marchessault, R. H.; Coulombe, S.; Morikawa, H.; Okamura, K.; Revol, J. R. *Can. J. Chem.* **1981**, *59*, 38.
(10) Barham, P. J.; Keller, A.; Otum, E. L.; Holmes, P. A. *J. Mater. Sci.* **1984**, *19*, 2781.
(11) Barham, P. J. *J. Mater. Sci.* **1984**, *19*, 3826.
(12) Merrick, J. M.; Doudoroff, M. *Nature (London)* **1961**, *189*, 890.
(13) Senior, P. J.; Dowes, E. A. *Biochem. J.* **1973**, *134*, 225.
(14) Oeding, V.; Schlegel, H. G. *Biochem. J.* **1973**, *134*, 239.
(15) Fukui, T.; Yoshimoto, A.; Matsumoto, M.; Hosokawa, S.; Saito, T.; Nishikawa, H.; Tomita, K. *Arch. Microbiol.* **1976**, *110*, 149.
(16) Nishimura, T.; Saito, T.; Tomita, K. *Arch. Microbiol.* **1978**, *116*, 21.
(17) Holmes, P. A. *Phys. Technol.* **1985**, *16*, 32.
(18) Bloembergen, S.; Hamer, G. K.; Bluhm, T. L.; Marchessault, R. H. *Macromolecules* **1985**, *19*, 2865.
(19) Doi, Y.; Kunioka, M.; Nakamura, Y.; Soga, K. *J. Chem. Soc., Chem. Commun.* **1986**, 1696.
(20) Doi, Y.; Kunioka, M.; Nakamura, Y.; Soga, K. *Macromolecules* **1987**, *20*, 2988.
(21) Doi, Y.; Tamaki, A.; Kunioka, M.; Soga, K. *J. Chem. Soc., Chem. Commun.* **1987**, 1635.
(22) Doi, Y.; Tamaki, A.; Kunioka, M.; Soga, K. *Appl. Microbiol. Biotechnol. 1988*, *28*, 330.
(23) Bluhm, T. L.; Hamer, G. K.; Marchessault, R. H.; Fyfe, C. A.; Veregin, R. P. *Macromolecules* **1986**, *19*, 2871.
(24) Doi, Y.; Kunioka, M.; Nakamura, Y.; Soga, K. *Macromolecules* **1986**, *19*, 2860.
(25) Doi, Y.; Kunioka, M.; Tamaki, A.; Nakamura, Y.; Soga, K. *Makromol. Chem.*, in press.
(26) Owen, A. J. *Colloid Polym. Sci.* **1985**, *263*, 799.
(27) Fukuda, E.; Ando, Y. *Int. J. Biol. Macromol.* **1986**, *8*, 361.
(28) Ando, Y.; Fukuda, E. *J. Polym. Sci., Polym. Phys. Ed.* **1984**, *22*, 1821.
(29) Repaske, R.; Repaske, A. C. *Appl. Environ. Microbiol.* **1976**, *32*, 585.
(30) Doi, Y.; Kunioka, M.; Nakamura, Y.; Soga, K. *Macromolecules* **1986**, *19*, 1274.
(31) Randall, J. C. *Polymer Sequence Determination*; Academic: New York, 1977; Chapter 4.
(32) Cornibert, J.; Marchessault, R. H. *J. Mol. Biol.* **1972**, *71*, 735.
(33) Yokouchi, M.; Chatani, Y.; Tadokoro, H.; Teranishi, K.; Tani, H. *Polymer* **1973**, *23*, 694.

Laser Flash Photolysis of a 4,4′-Methylenebis(phenyl isocyanate) (MDI) Based Polyurethane and Model Carbamates

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Received December 7, 1987

ABSTRACT: Transient species in the laser flash photolysis of solutions of 4,4′-methylenebis(phenyl isocyanate) (MDI) based polyurethanes and small molecule models have been detected. One of the transient species, a substituted anilinyl radical, is not quenched by oxygen, while a second transient is extinguished by the introduction of oxygen. Based on the spectral results, a plausible mechanism is offered for the primary photochemical reactions of MDI-based polyurethanes.

The photolytic degradation of polyurethanes based on aromatic diisocyanates continues to receive a considerable amount of attention.[1–7] Indeed, there have been a number of schemes proposed to account for their photolytic degradation, each having its own merit.[1–7] This paper is designed to provide basic insight into the nature of the transient intermediates produced during the primary

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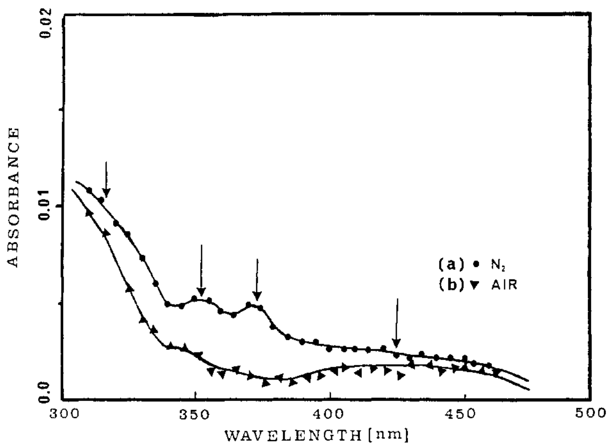


Figure 1. Transient absorption spectra (2.0 μs) of MDI–PUE in THF: (a) nitrogen saturated, (b) air saturated.

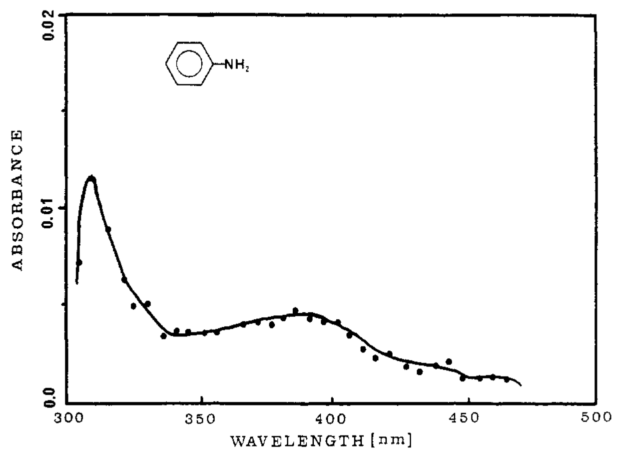


Figure 2. Transient absorption spectrum (2.0 μs) of aniline in nitrogen-saturated THF.

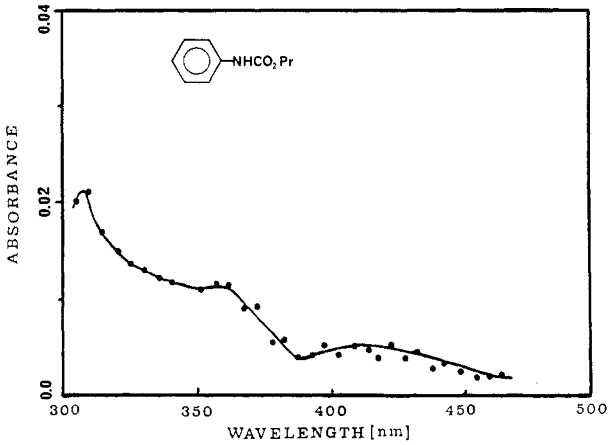


Figure 3. Transient absorption spectrum (2.0 μs) of propyl *N*-phenylcarbamate in nitrogen-saturated THF.

photochemical reactions of the aryl carbamate chromophores in a 4,4′-methylenebis(phenyl isocyanate) (MDI) based polyurethane in solution. The results for the MDI-based polyurethane are interpreted by comparison with appropriate mono- and biscarbamate small molecule models. The polyurethane used in this study (hereafter designated MDI–PUE) was prepared by reacting 4,4′-methylenebis(phenyl isocyanate) (MDI) with poly(tetramethylene glycol ether) (MW 1000) and then extending with 1,4-butanediol.

Figure 1 (curve a) shows the transient absorption spectrum of a nitrogen-saturated 5.5 × 10^{-3} g/dL solution of MDI–PUE in tetrahydrofuran (THF) obtained on an Applied Photophysics, Ltd., kinetics spectrometer at a delay time of 2.0 μs after firing a laser pulse from a krypton fluoride excimer laser (λ_{ex} = 248 nm; ~ 10-ns pulse width; 80 mJ/pulse). The ground-state absorbance of the polymer was 1.1 at 248 nm, and the transient spectrum was generated by analyzing transient decay curves recorded every 6 nm from 300 to 500 nm. The prominent features of the transient absorption spectrum in Figure 1, curve a, are the four bands with maxima at 310, 340–350 (broad), 370, and >390 nm (very weak diffuse absorbance band). Curve b in Figure 1 shows the transient spectrum of an air-saturated THF solution of MDI–PUE (5.5 × 10^{-3} g/dL). Oxygen completely extinguishes the peak at 370 nm but has less of an effect on the peaks at 310 nm and the absorbance band above 390 nm. The effect of air on the 340–350-nm band is difficult to interpret since it falls so close to the bands at 370 nm which are heavily quenched by oxygen. The oxygen effect at 370 nm is confirmed by lifetime quenching results which will be presented in a later paper.

Now we must ask, what species are responsible for the transient absorbance spectrum in Figure 1, curve a. This question can best be answered by first considering the laser flash photolysis of several small molecule models. The transient absorption spectra recorded 2.0 μs after the laser flash of both aniline (5.1 × 10^{-4} M) and propyl *N*-phenylcarbamate (5 × 10^{-4} M) in nitrogen-saturated THF are shown in Figures 2 and 3. [Essentially identical spectra were obtained in air-saturated THF.] For both aniline and propyl *N*-phenylcarbamate, a distinct peak is present at 310 nm as well as a broad band above 390 nm. In the case of propyl *N*-phenylcarbamate, an additional broadening is observed between 330 and 360 nm, with a maximum around 340–350 nm. Land and Porter[8] have assigned the strong peak at 310 nm and the weak band absorbance centered around ~400 nm in the flash photolysis of aniline in nonprotic solvents to the allowed and forbidden transitions of the anilinyl radical formed by N–H bond cleavage. Thus, the peak at 310 nm and the broad band above 390 nm in Figure 2 (aniline) and Figure 3 (propyl *N*-phenylcarbamate) can be assigned to an anilinyl radical which should be relatively nonreactive with oxygen, especially in a solvent with readily abstractible hydrogens. In the case of propyl *N*-phenylcarbamate, the anilinyl radical must be formed by direct homolytic cleavage of the nitrogen–carbon bond in the carbamate moiety. Based on the results for aniline and propyl *N*-phenylcarbamate, it is appropriate to ascribe the 310-nm and broad band absorbance above 390 nm in the transient spectrum of MDI–PUE (Figure 1) to an anilinyl-type radical. The detection of anilinyl radicals in the laser flash photolysis of MDI–PUE is in agreement with earlier identification[9] of an anilinyl radical (detected by ESR) in the photolysis of an MDI-based polyurethane. Our results are also consistent with formation of reported[1,2,4] photo-Fries and substituted aniline photoproducts which have been reputed to form by a primary N–C bond cleavage in the carbamate moiety followed by rearrangement and/or separation of the resultant radicals.

Identification of the species responsible for the band between 330 and 360 nm may be due, at least in part, to an ortho photo-Fries product. Other species may also contribute to the absorbance in this region. Assignments in this region require further analysis and are reserved for future studies.

Having furnished, based on model compounds, what seems to be a plausible assessment of two of the four bands in the transient absorption spectrum of MDI/PUE (Figure

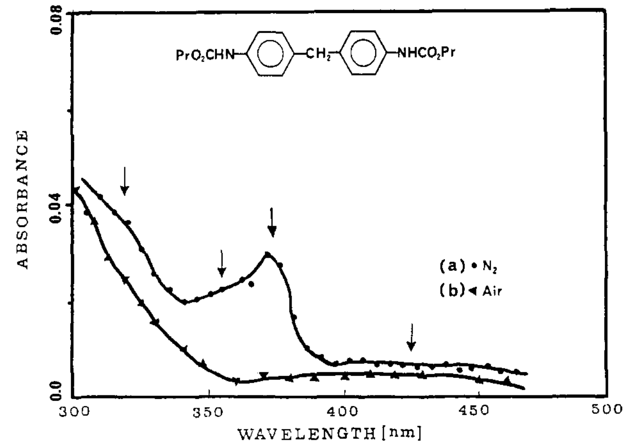
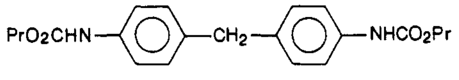


Figure 4. Transient absorption spectra (2.0 μs) of BP–MDI in THF: (a) nitrogen saturated, (b) air saturated.

1, curve a), identification of the 370-nm peak remains. Consider the bis(propyl carbamate) model (BP–MDI) of MDI shown below. It possesses, in addition to the two



BP-MDI

phenylcarbamate groups, a disubstituted methylene carbon. In addition, it should be noted that the transient spectra of propyl *N*-(*p*-tolyl)carbamate, although not shown, also has bands with maxima around 310 nm and above 390 nm. As in the case of propyl *N*-phenylcarbamate, the transient spectrum of propyl *N*-(*p*-tolyl)carbamate shows no maximum at 370 nm. Thus, any additional bands in the transient spectrum of BP–MDI can be attributed to the presence of the central methylene carbon. Bearing this in mind, the transient absorption spectrum of BP–MDI in Figure 4 (λ_{ex} = 248 nm; 2.7 × 10^{-5} M in nitrogen-degassed THF taken at a delay of 2.0 μs) shows a distinct peak at ~370 nm in addition to the structural features found in the transient spectrum of propyl *N*-phenylcarbamate (Figure 3). The 370-nm peak is completely quenched in the presence of oxygen. The possibility of the 370-nm transient resulting from an excited triplet was eliminated by failure to diminish its intensity with *cis*-piperylene, an effective triplet quencher. Although at this time we can offer no absolute identification of the species responsible for the 370-nm peak, we can conclude from its absorption maximum (well above 300 nm) that it results from a radical centered on an atom attached to the phenyl ring, for instance, a diarylmethyl radical ($Ar\dot{C}HAr$). Porter and Windsor (10) have shown that unsubstituted diphenylmethyl radicals have an absorbance maximum at 335 nm and are readily formed upon direct photolysis of diphenylmethane in paraffin solution by a C–H bond cleavage. We have reproduced on our instrument the transient absorption spectrum of the unsubstituted diphenylmethyl radical in THF and obtain an absorbance maximum around 340 nm. It is certainly plausible that substitution of carbamate groups at the para positions could red shift the absorbance maximum of the diphenylmethyl radical to around 370 nm. The following additional points are compatible with, although do not provide unconditional evidence for, a diarylmethyl structure:

1. Diarylmethyl radicals should react readily with oxygen: this is consistent with the results in Figure 1 (curve b).
2. The expected peroxy radical product between a diarylmethyl radical and oxygen should eventually, upon hydrogen abstraction from the solvent, yield a hydroperoxide. Such hydroperoxides centered on the diaryl-substituted methylene carbon have indeed been reported to form upon photolysis[1] of MDI-based polyurethanes.
3. Recent radical abstraction experiments in our lab[11] also strongly suggest the generation of a diarylmethyl radical.

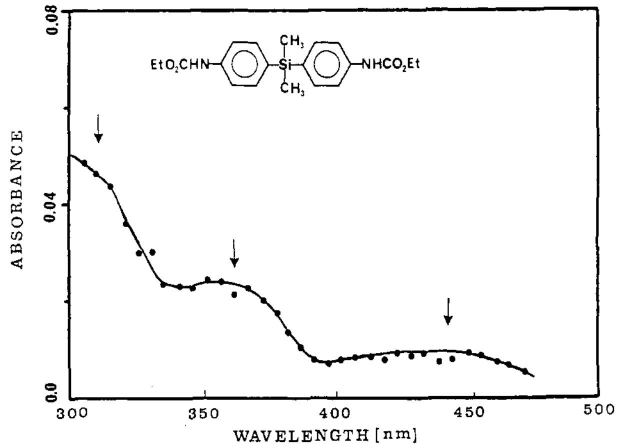
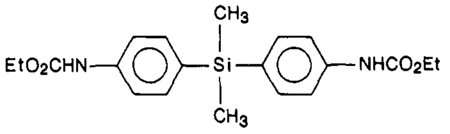


Figure 5. Transient absorption spectrum (2.0 μs) of $SiMe_2$–MDI in nitrogen-saturated THF.

In order to test the validity of assigning the 370-nm peak to a diarylmethyl radical, a dimethyl-substituted diarylsilane biscarbamate ($SiMe_2$–MDI) analogue of MDI was synthesized (see structure below). This compound cannot



$SiMe_2$-MDI

possibly form a diarylmethyl radical. In accordance with this expectation, the transient absorption spectrum (Figure 5) of this compound (λ_{ex} = 248 nm; 2.6 × 10^{-5} M in nitrogen-degassed THF taken at a delay of 2.0 μs) has no peak at 370 nm and thus provides additional support for assignment of the 370-nm peak in the transient spectrum of the model BP–MDI (Figure 4) and the polyurethane MDI–PUE (Figure 1) to the diarylmethyl radical. Results for a number of other model biscarbamates are also consistent with diarylmethyl radical formation.[11] Conclusive identification of the species responsible for the 370-nm peak is pendant on additional work in progress.

In summary, the transient absorbance spectra of the bis(propyl carbamate) model BP–MDI (Figure 4) and the polyurethane MDI–PUE in (Figure 1) are essentially identical. Combined with data for aniline and propyl *N*-phenylcarbamate models (Figures 2 and 3), a tentative mechanism has been postulated for at least a portion of the primary photochemical reactions of MDI-based polyurethanes in solution. Finally, it should be pointed out that care must be taken when extension of transient measurements in solution is made to polyurethane films since the lifetimes of radicals generated may be substantially altered. In addition, certain pathways for reactions of radicals in solution may be absent in the solid phase. Laser flash photolysis of polyurethane films will thus be the subject of a future investigation.

In order to substantiate the preliminary results presented in this paper, we recently completed a laser flash photolysis study in which independently generated hydrogen-abstracting *tert*-butoxy radicals are employed to 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.

References and Notes

(1) Gardette, J. L.; Lemaire, J. *Polym. Degrad. Stab.* **1984**, *6*, 135.
(2) Hoyle, C. E.; Kim, K. J. *J. Polym. Sci., Polym. Chem. Ed.* **1986**, *24*, 1879.
(3) Osawa, Z.; Nagashima, K. *Polym. Degrad. Stab.* **1979**, *2*, 311.
(4) Beachell, H. C.; Chang, L. C. *J. Polym. Sci., Part A-1* **1972**, *10*, 503.
(5) Schollenberger, C. S.; Steward, J. D. *J. Elastoplastics* **1972**, *4*, 294.
(6) Schollenberger, C. S.; Stewart, J. D. *Advances in Urethane Science and Technology*; Frisch, K. D., Reegen, S. L., Eds.; Technomic: Hartford, CT, 1973; Vol. II, p 71.
(7) Nevskii, L. V.; Tarkanov, O. G.; Belyakov, V. *Sov. Plastics* **1967**, *10*, 23.
(8) Land, E. J.; Porter, G. *Trans. Faraday Soc.* **1963**, *59*, 2027.
(9) Osawa, Z.; Cheu, E. L.; Ogiwara, Y. *J. Polym. Sci., Polym. Lett. Ed.* **1975**, *13*, 535.
(10) Porter, G.; Windsor, W. R. *Nature (London)* **1957**, *180*, 187.
(11) Unpublished results.

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

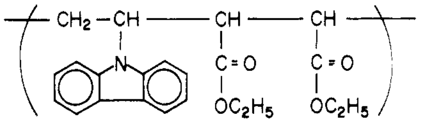
The Langmuir–Blodgett (LB) technique provides ultrathin and molecularly ordered films which are now taking much attention from the viewpoint of microelectronic or optical devices.[1-7] So far, the LB films are formed with amphiphilic molecules, such as long-chain fatty acids and dyestuffs with long hydrocarbon 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.

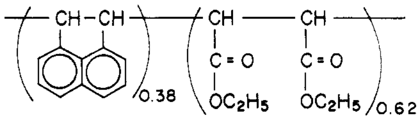
Experimental Section

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

Chart I



P(VCz – DEF)



P(AcNp – DEF)