Enhancement of Intramolecular Photocycloaddition of Bichromophoric Compounds via Inclusion in Low-Density Polyethylene Films

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The photocycloaddition of tetra- and penta(ethylene glycol) labeled at the chain terminals with 2-naphthoyl groups (N-P$_n$-N; $n = 4$ or 5) and tetra(ethylene glycol) terminated by 7-(4-methylcoumarinyl) groups (C-P$_4$-C) has been investigated in hexane solutions and in low-density polyethylene (LDPE) films. At loading levels less than 1×10^{-2} mol/g-film, irradiation of the compounds in LDPE leads to formation of intramolecular photocyclomers to the exclusion of intermolecular products. Irradiations in hexane containing 1×10^{-3} M of a bichromophoric compound produce large amounts of oligomeric material. The difference between the results in solution and the film is explained in terms of the compartmentalization of the guest molecules in the LDPE amorphous regions. Cold-stretching the LDPE films significantly increases the relative efficiency of the intramolecular photocycloadditions due to reduction of the free volume at the reaction sites. This work reports a new approach to synthesize large-ring compounds in high chemical yields at relatively high substrate concentrations.

Introduction

The construction of macrocyclic compounds continues to be an important topic in synthetic organic chemistry.[1,2] A molecule with two reactive groups separated by a flexible link may undergo either intramolecular or intermolecular reactions. Intramolecular reaction gives macrocyclic ring-closure products, while intermolecular reaction results in dimers, oligomers, and polymers. Thus, cyclization suffers from the competition from intermolecular reactions. The rates of the latter are dependent on substrate concentration, while those of the former are not, since the *effective* concentration for intramolecular reaction is constant by virtue of the tether between the two functional groups. Hence, in normal solutions where diffusion is rapid, high substrate concentrations favor polymerization while cyclization occurs in good chemical yields only at low concentrations.

The working definitions of "high" and "low" concentration ranges are also dependent upon solvent viscosity (i.e., solute diffusion rates). In a certain reaction medium, if the rates of translational diffusion (which is a prerequisite for intermolecular reactions) of the substrate molecules can be attenuated much more than those for rotational diffusion and conformational changes (which is a prerequisite for intramolecular reactions), it is possible to synthesize large-ring compounds in high yields under high substrate concentrations. We find that the sizes and shapes of reaction cavities of low-density polyethylene (LDPE) films can accommodate our bichromophoric substrates and allow relatively free rotational/conformational changes while retarding translational diffusion. Thus, intramolecular reaction can occur without competition even at high loading levels since individual reaction cavities prefer to include only one substrate molecule and diffusion between cavities is slow on the molecular reaction time scale.

LDPE is a very complex family of materials that consist of ca. 50% of crystalline regions (wherein chains are tightly and regularly packed) and ca. 50% of amorphous or interfacial regions (wherein chains are in somewhat random conformations).[3] The glass transition of the amorphous part occurs near −30 °C, and the melting transition is >100 °C.[4] A wide variety of organic molecules can be incorporated into LDPE by soaking its films in a swelling solvent containing the guest. It has been established that guest molecules are excluded from the crystalline portions of LDPE at temperatures below the melting transition. Their principal locations are the amorphous parts and the interfacial regions between crystalline and amorphous domains.[3b,d] Due to its aniso-

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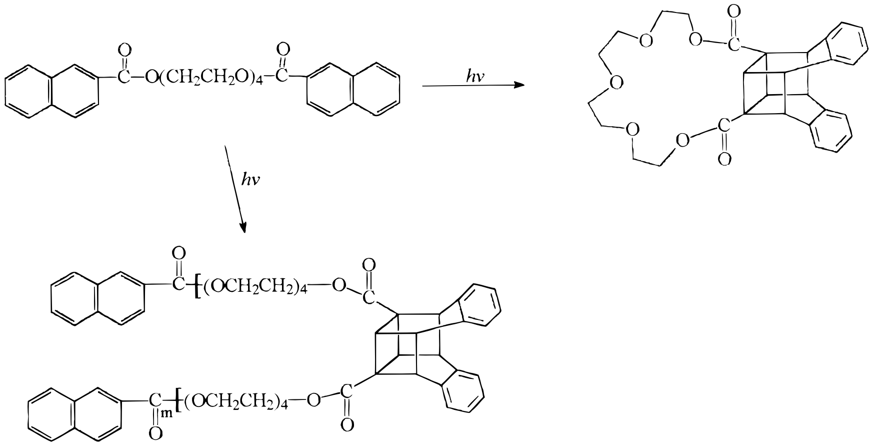
Scheme 1



tropic nature, LDPE has been used as a reaction medium to control the reaction pathways of a variety of guest molecules.[5,6] Although several interesting examples in this topic have appeared,[5−7] we are aware of only one example in which it is used to enhance the formation of large-ring compounds.[7a] The sites where guest molecules reside need not resemble those in the native polymer. The swelling process by which species are introduced "opens" the network of polymethylene chains in the amorphous and interfacial regions; when the swelling liquid is removed, the nearby chains move into van der Waals contact with the reactive guest molecules that have been left behind. In this way, the free volume of the reaction sites can be made sufficiently large[8] to accept a molecule with two reactive groups linked by a flexible chain,[9] yet small enough to force the two terminal groups in proximity. Furthermore, according to a Poisson distribution, there is less than a 5% probability to find two guests in one cavity if the loading level is less than one guest molecule per 10 reaction cavities. As long as this condition is met and the rate of site exchange by guests is slower than that of conformational changes of the guest molecule, intermolecular reactions should be inhibited, while intramolecular reactions still can occur.[10] We report that this is indeed the case for the photocyclizations of tetra- and penta(ethylene glycol) terminated by 2-naphthoyl groups (N-P$_n$-N) or tetra(ethylene glycol) terminated by 7-(4-methylcoumarinyl) groups (C-P$_4$-C).[11]

$$\text{Np-COO-}(\text{CH}_2\text{CH}_2\text{O})_n\text{-OC-Np}$$

$$\text{N-P}_n\text{-N}, (n = 4, 5; \text{Np} = \text{2-naphthyl})$$

$$\text{Cu-O}(\text{CH}_2\text{CH}_2\text{O})_n\text{-Cu}$$

$$\text{C-P}_4\text{-C}, (\text{Cu} = \text{7-(4-methylcoumarinyl)})$$

Results and Discussion

General. LDPE films, from Du Pont of Canada, have been characterized in detail.[12] Incorporation of a substrate into a film was achieved by soaking in a chloroform solution. After several hours, the solvent was removed, and the film was washed with methanol (a nonswelling liquid) to remove surface-occluded substrate. Loading levels of ca. 1×10^{-3} mol/g-film for N-P$_n$-N and 1×10^{-2} mol/g-film for C-P$_4$-C were attained. The films were then transferred to a Pyrex vessel and irradiated under a nitrogen atmosphere. Generally, to complete the conversion required 5 h of irradiation for N-P$_n$-N and 10 h for C-P$_4$-C; in hexane, the conversions of analogous molar concentrations and absolute numbers of moles were accomplished after about 3 h irradiation for N-P$_n$-N and 5 h for C-P$_4$-C. After irradiation in the films, the products were extracted with chloroform and analyzed by HPLC. Material balance in general was greater than 90%.

Photocycloaddition of N-P$_n$-N. Irradiation of alkyl 2-naphthoates is known to yield a "cubane"-like photocyclomer as the unique product (Scheme 1), although six isomeric cyclomers are formally possible.[11,13] This selectivity originates from two restrictions. First, the photocycloaddition occurs only between the substituted rings. Second, in the cyclomer, the substituents are in a head-to-tail orientation. Irradiation of N-P$_n$-N in organic solvents, such as hexane, can lead either to intra- or

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[10] Assuming that the substrate molecules are randomly distributed over the *reaction cavities* in an LDPE film (but not the total volume), their distribution can be expressed by the Poisson equation.

$$P(n) = \lambda^n \exp(-\lambda)/n!$$

λ is the ratio of the number of substrate molecules to the number of occupiable cavities, and $P(n)$ is the probability of n substrate molecules being in a cavity. In the case of one substrate molecule per 10 cavities ($\lambda = 0.1$), $P(1)$ and $P(2)$ are 0.09 and 4.5×10^{-3}, respectively. Thus, the probability to find one substrate molecule in one cavity is 20 times that to find two substrate molecules in one cavity. It follows that, on a purely statistical basis, the amount of intermolecular photodimer will be less than 5% of the intramolecular cyclomer.

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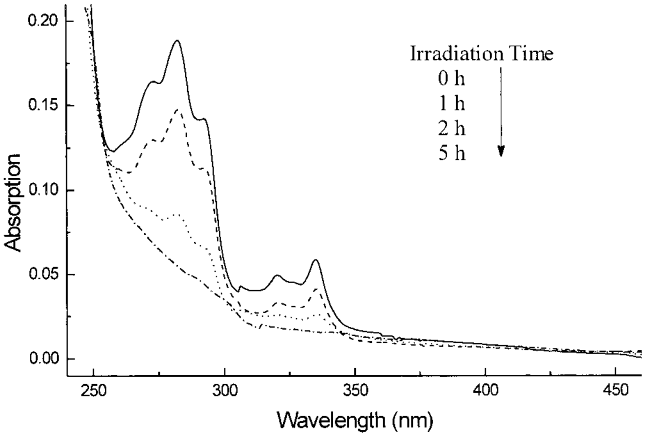


Figure 1. Absorption spectra of N-P_4-N in LDPE as a function of irradiation time. Loading level: 1×10^{-3} mol/g-film: —, 0 h; - - -, 1 h; •••, 2 h, -•-, 5 h.

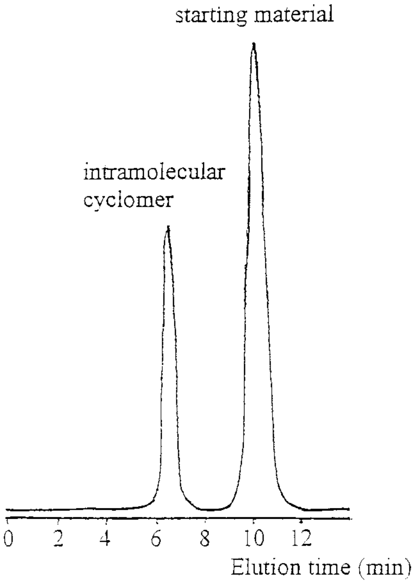
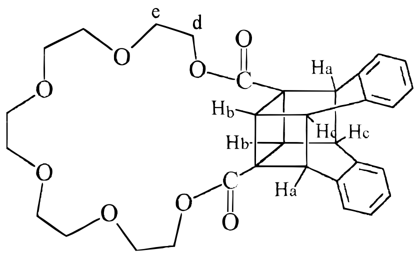


Figure 2. HPLC chromatogram of N-P_4-N after 2 h irradiation in LDPE.

intermolecular cycloadditions. At concentrations higher than 1×10^{-3} M, the main product is intermolecular photocyclomers.

By contrast, irradiation of N-P_n-N in LDPE films yields only intramolecular photocyclomers. The progress of the photocycloadditions was followed by UV absorption spectroscopy. Figure 1 shows changes in the absorption spectra of N-P_4-N as a function of irradiation time; similar results were obtained when N-P_5-N was the guest molecule. Evidently, after 5 h of irradiation, the conversion approached 100%. The products were extracted from the LDPE film with chloroform and analyzed by HPLC. Figure 2 is the HPLC profile of the products during irradiation of N-P_4-N. Only the intramolecular ring-closure photocyclomers were evident; no intermolecular products were detected. The isolated yields of intramolecular products were >90% on the basis of consumption of the starting materials.

Table 1. ^{1}H NMR Data and Structural Assignments of N-P_5-N



Cyclomer of N-P_5-N

δ (ppm)	peak multiplicity	integration	assignment
6.95−7.00	m	8H	Ar
4.52	d	2H	H_a
4.39	dd	2H	H_c
4.25	m	4H	H_d
3.86	d	2H	H_b
3.6−3.8	m	16H	H_e

The conclusion that the photoreactions are almost exclusively intramolecular is based on the observation that *m*/*z* values of the molecular ions in the mass spectra of photoproducts are identical to those of the corresponding starting materials. Furthermore, no protons assignable to the naphthyl group were detected in the ^{1}H NMR spectra of the products. The structure proposed for the cubane-like photocyclomer rests mainly on its ^{1}H NMR spectrum, which is similar to that reported.[11,13] The spectral details and assignments for the intramolecular photocyclomer of N-P_5-N are given in Table 1, and those for N-P_4-N are given in the Experimental Section.

Due to the immiscibility of the polyether chains of the N-P_n-N with polyethylene, the maximal loading of N-P_n-N in LDPE film we could reach was ca. 1.2×10^{-3} mol/g-film. Since the LDPE films employed are 42% crystalline,[12] the actual volume in which the guest molecules reside is only ca. 60% of the total. As a result, the true concentrations in the amorphous regions are at least 1.7 $\times$ 10^{-3} mol/g-film. Despite this, the exclusive formation of intramolecular photocyclomers suggests that each occupied site contains one molecule of N-P_n-N.

To obtain further information on the cavities experienced by the N-P_n-N, their fluorescence spectra were examined. At the loading level of 1×10^{-3} mol/g-film, the N-P_n-N show monomeric and weak excimer emissions. A model compound, ethyl 2-naphthoate, gives only monomer emission under analogous conditions. The excimer/monomer fluorescence intensity ratios for the N-P_n-N are independent of concentration, indicating that the excimer is intramolecular. Since the rate of translational diffusion of the naphthoate groups in the LDPE films is slow on the time scale of the decay of the excited singlet states,[5,8,14] the excimers probably form from chromophores that are at or near excimer-like conformations prior to excitation. On the basis of the relative weakness of the intramolecular excimer emissions, we propose that only a small fraction of N-P_n-N molecules have their naphthoyl groups in an excimer-like conformation in the ground state at any given time; the chromophores of most N-P_n-N molecules do not overlap and provide monomer fluorescence upon excitation. However, two naphthoyl groups may diffuse into proximity on longer time scales. When one of them is excited, intramolecular photocycloaddition occurs. In this way, long-term irradiation of N-P_n-N in a film can eventually lead to complete conversion.

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Table 2. Conversion of N-P$_4$-N in Stretched and Unstretched LDPE Films as a Function of Irradiation Time (Loading Level: 1 × 10^{-3} mol/g-film)[a]

	conversion (%)		
	1 h	1.5 h	2 h
stretched film	24.7	37.9	48.3
unstretched film	17.6	27.4	33.5
efficiency ratio for stretched to unstretched samples	1.40	1.38	1.44

[a] Averaged on five samples; error limits were ca. 5%.

The effect of stretching LDPE films doped with N-P$_4$-N on its photochemical reactivity was also examined. It has been found previously that even when one type of LDPE is employed reproducible results are limited to films that share the same history.[5,7] Thus, we cut a doped film into several pieces, half of which were stretched manually to 4.5 times their original length. The relative reactivities for intramolecular photcycloadditions of the N-P$_4$-N in stretched and unstretched samples are indicated in Table 2. The results indicate that dimerization efficiency in the stretched films is ca. 1.4 times greater than in the unstretched ones. This observation has ample precedent.[7] The product ratios from competitive intramolecular Paterno−Buchi photocyclization, and intermolecular photoreduction of 10-undecenyl benzophenone-4-carboxylate have been employed to probe the free volume changes that occur at guest sites when LDPE films are stretched.[7a] A remarkable increase in the relative yield of the photocyclization product was observed when the films were stretched to ca. 500% their original length. Aviv and coworkers studied the photodimerization of tetraphenylbutatriene in LDPE films and compared the reactivity in stretched and unstretched samples.[7c] A 3-fold increase in quantum efficiency for photodimerization of the substrate upon stretching the LDPE films was reported. The interpretation advanced to explain these results is that film stretching decreases the average free volume of guest sites by aligning partially the polymethylene chains that constitute the cavity walls. Therefore, the two photoreactive groups of our substrates will reside, on average, closer to each other in stretched films than in unstretched ones; intramolecular photocycloaddition will be enhanced.

Photocycloadditons of C-P$_4$-C. The photochemistry of coumarin and its derivatives has been the subject of numerous investigations, mainly as a consequence of its importance in biological systems.[15] Direct irradiation of coumarin itself in solution results in highly inefficient formation of the syn head-to-head and syn head-to-tail cyclomers as the major and minor products, respectively; triplet sensitization is more efficient and yields the anti head-to-head cyclomer as the major product (Scheme 2). De Schryver and co-workers[16] found that irradiation of 7,7′-polymethylenedi(oxycoumarin)s at low concentrations yields only syn head-to-head and head-to-tail intramolecular cyclomers. Steric factors introduced in the corresponding molecule by methyl groups at the 4-positions of the coumarins led predominantly the syn head-to-tail cyclomer. At higher concentrations, the amounts of intermolecular photoproducts increase as expected.

C-P$_4$-C can undergo intra- and intermolecular photoreactions. Irradiation of $<5 \times 10^{-4}$ M C-P$_4$-C in an organic solvent such as benzene results primarily in intramolecular syn head-to-tail cyclomer (Scheme 2), as demonstrated by mass spectral and NMR analyses. The m/z value of the molecular ion of the product is identical to that of C-P$_4$-C, and there are no protons assignable to coumarinyl in the ^{1}H NMR spectrum. The syn head-to-tail nature of the cyclomer is based on comparison of its ^{1}H NMR spectrum (Figure 3 and Table 3) with those of related molecules.[16] Upon irradiation of more concentrated solutions, a large amount of oligomeric material was formed. For example, at a concentration of 1×10^{-3} M, ca. 20% of oligomers were present in the product mixture.

As observed in the case of the N-P$_n$-N, irradiation of 1×10^{-2} mol/g-film C-P$_4$-C in LDPE resulted in conversion to intramolecular cyclomer. Generally, the conversion was close to 100% after 10 h of irradiation. The products were extracted from the LDPE films and identified by their spectral properties and by comparison with authentic samples. As in the case of irradiations in homogeneous solutions, only the syn head-to-tail cyclomer was detected. Since the material balance was >90%, any unidentified products must be minor. Thus, at loading levels $<1 \times 10^{-2}$ mol/g-film, each reaction cavity in LDPE must contain no more than one C-P$_4$-C molecule: intermolecular reaction is inhibited and intramolecular reaction is enhanced.

We also examined the effect of stretching the LDPE film on the photochemistry of C-P$_4$-C. Films doped with C-P$_4$-C were stretched manually to 4.5 times their original length and then irradiated. Again, at 1×10^{-2} mol/g-film C-P$_4$-C, only the intramolecular syn head-to-tail cyclomer was obtained. However, compared with the unstretched sample, the efficiency of the photocycloaddition is increased 1.2 times. This observation is consistent with the hypothesis that film stretching decreases the free volume of the reaction cavities[6,7] and, thereby, enhances intramolecular reactions by forcing the reactive groups to reside nearer each other.

Conclusions

Low-density polyethylene can incorporate bichromophoric molecules composed of oligo(ethylene glycol) chains terminated by naphthyl or coumarinyl groups. At loading levels $<1 \times 10^{-2}$ mol/g-film, host reaction cavities are singly occupied, allowing the substrate molecules to be isolated from each other. As a result, irradiation of our guest molecules produces intramolecular photocyclomers exclusively; no intermolecular products could be detected. Consistent with the hypothesis that stretching LDPE films reduces the free volume of their reaction sites, the time required to achieve full conversion of the guest molecules in stretched films was shorter than the period in unstretched ones.

Further comments on the nature of the reaction cavities are appropriate.[6] The intrinsic size of guest sites in LDPE should preclude any of the bichromophoric

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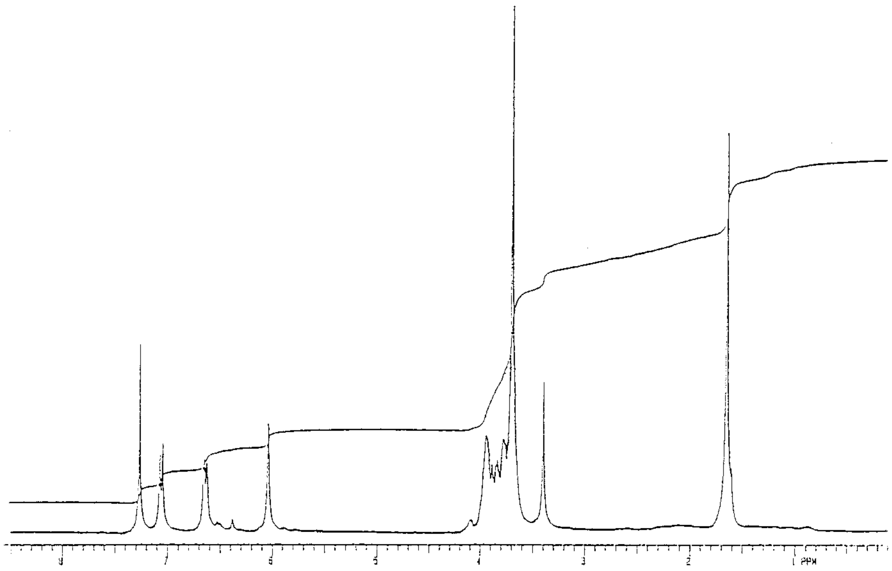
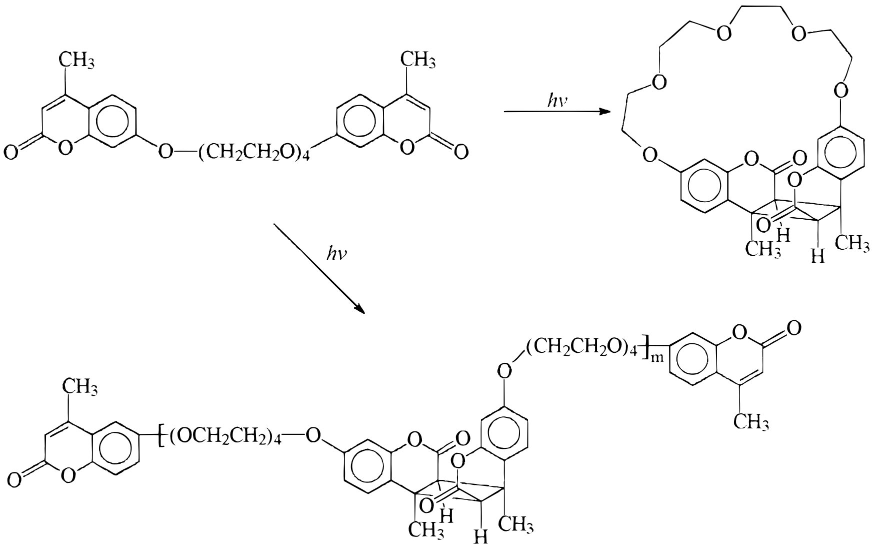


Figure 3. 400 M Hz ^{1}H NMR spectrum of the cyclomer from C-P$_4$-C.

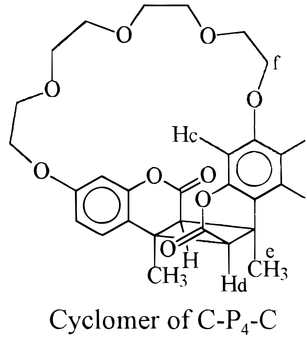
Scheme 2



molecules in this study from entering them.[17] However, their mode of inclusion, swelling of the amorphous parts of the polymer matrix, opens spaces inside the films large enough for the guests to enter. When the swelling solvent is removed selectively (by its more rapid diffusion to the air), the guest molecules are trapped. Coincidentally, the "walls" of the reaction cavities collapse around the guest molecules in orientations that maximize van der Waals contacts.

We have suggested that in the LDPE inclusion sample the groups tethered to the ends of chains experience a more mobile environment than in the bulk of the native LDPE due to the disordering effect caused by guest molecule; large guest molecules can plasticize the chains of polyethylene that constitute the walls of the reaction cages (making them "softer"[6]).[9] In this way, slow conformational changes bring the two reactive groups at the chain ends into sufficient proximity for them to react within an excited-state lifetime. At any moment, the fraction of molecules in reactive conformations may be small, but eventually all can adopt the necessary shapes. The key is that the rates of these conformational changes

Table 3. ^{1}H NMR Data and Structural Assignments of the Cyclomer from C-P$_4$-C



δ (ppm)	peak multiplicity	integration	assignment
7.05	d	2H	H_a
6.63	d	2H	H_b
6.04	s	2H	H_c
3.70−3.95	m	16H	H_f
3.40	s	2H	H_d
1.66	s	6H	H_e

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are significantly faster than the rates at which two molecules meet in one reaction cavity. We suspect that polyethylene films will be useful to synthesize a large variety of macrocycles under concentration conditions that would lead to significant intermolecular (i.e., polymerization) reactions. Since each kind of polyethylene differs from the others in some morphological details, exact reproducibility from laboratory to laboratory should not be expected. However, the gross observation—that bichromophoric molecules can be (reactively) isolated from each other at relatively high bulk concentrations—should be common to all polyethylenes!

Thus, LDPE complements zeolites, which we demonstrated earlier to serve a similar role in isolating molecules for intramolecular cyclizations.[11d] By contrast, the reaction cavities of zeolites have fixed volumes and shapes and very "hard" walls.[6] Each medium has its relative merits; now, it is possible to select the one that is more compatible with a particular reactant and cyclization reaction.

Experimental Section

Materials and Instruments. Spectral-grade chloroform, hexane, and benzene were used without further purification as the swelling solvent for LDPE and the solvent for photochemical reactions, respectively. Low-density polyethylene films (42% crystallinity, mp 116 °C, 0.918 g/cm^3, 70 μm thick[12]) were a gift from DuPont of Canada. Before use, films were immersed overnight in chloroform to remove antioxidants and plasticizers, washed with methanol, and dried in a stream of nitrogen. Naphthalene end-labeled poly(ethylene glycol) (N-P_n-N) was prepared as reported previously.[11b]

7-Coumarinyl end-labeled tetra(ethylene glycol) (C-P_4-C) was synthesized by the following procedure. To a mixture of 7 mL (0.04 mol) of tetraethylene glycol and 11.7 mL (0.08 mol) of triethylamine in 100 mL of 1,2-dichloroethane was slowly added 15.6 g (0.08 mol) of *p*-toluenesulfonyl chloride over 1 h. After being stirred for 12 h at room temperature, the reaction mixture was filtered to remove the resulting salt. The solvent was evaporated, and the products were separated by column chromatography on silica (ethyl acetate/petroleum ether (2:1, v/v)); 12 g (60%) of α,ω-di(*p*-toluenesulfonyl)tetraethylene glycol was obtained. ^{1}H NMR ($CDCl_3$) (ppm): δ7.82 (d, 4H), 7.38 (d, 2H), 4.2 (m, 4H), 3.75 (m, 4H), 3.6 (s, 8H), 2.5 (s, 6H). Anhydrous potassium carbonate (2.8 g (0.02 mol)) and 3.5 g (0.02 mol) of 7-hydroxy-4-methylcoumarin were added to a solution of 5 g (0.01 mol) of the di(*p*-toluenesulfonyl) tetraethylene glycol in 80 mL of acetonitrile. The mixture was stirred under reflux for 12 h. After being cooled, the solvent was removed under vacuum to yield a solid residue. The product (3 g, 60%) was isolated by column chromatography on silica (ethyl acetate/petroleum ether (4:1, v/v)). ^{1}H NMR ($CDCl_3$) (ppm): δ7.5 (d, 2H), 6.9 (d, 2H), 6.8 (s, 2H), 6.15 (s, 2H), 4.2 (t, 4H), 3.9 (t, 4H), 3.75 (t, 8H), 2.4 (s, 6H).

^{1}H NMR spectra were recorded at 400 MHz with a Varian XL-400 spectrometer. MS spectra were run on a VG ZAB spectrometer. UV absorption spectra were measured with a Shimadzu UV 1601PC spectrophotometer. Photocycloaddition products were separated and analyzed using a Shimadzu LC-10AS liquid chromatograph with a 25 cm Hyper ODS2 C_{18} column (eluted with methanol/water (85/15); UV detection at 254 nm).

Inclusion of Substrates within LDPE and Photoirradiation. A LDPE film was immersed in a 0.2 M substrate solution in chloroform. After equilibration was reached, the solvent was removed, and the film surface was washed rapidly with methanol and dried with a nitrogen stream. The substrate content was calculated from UV absorption spectra of the doped films, assuming Beers law behavior and molar extinction coefficients of the guest molecules in nonpolar solvents. The sample was placed in a Pyrex glass cell, which was purged with nitrogen and irradiated with a 450-W Hanovia medium-pressure mercury lamp. After the irradiation period, the products were extracted with chloroform and analyzed by HPLC. Structures of all products were identified by MS and ^{1}H NMR spectra.

Intramolecular cyclomer of N-P_4-N: ^{1}H NMR ($CDCl_3$) (ppm): δ 6.95−6.97 (8H, m, ArH), 4.55 (2H, d, H_a), 4.42 (2H, dd, H_c), 4.35 (4H, m, H_d), 3.92 (2H, d, H_b), 3.65−3.85 (12H, m, H_e). MS: *m/e* 502 (M^+), 199 ($NpCOOC_2H_4^+$), 172 ($NpCO_2H^+$), 155 ($NpCO^+$), 127 (Np^+). Intramolecular cyclomer of C-P_4-C: ^{1}H NMR ($CDCl_3$) (ppm): δ 7.05 (d, 2H), 6.63 (d, 2H), 6.04 (s, 2H), 3.70−3.95 (m, 16H), 3.4 (s, 2H), 1.66 (s, 6H).

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