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Photochemistry of Nonconjugated Bichromophoric Systems. Photopolymerization of Substituted *N,N′*-Alkylenebis(maleimides)

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ABSTRACT: The term photopolymerization, defined as a polymerization process in which every chain propagating step involves the absorption of a photon, is exemplified by the solution photopolymerization of some substituted *N,N′*-alkylenebis(maleimides). Quantum yield determinations and kinetic analysis clearly indicate that this photopolymerization is a multistep reaction. Quenching experiments and quantum yield measurements show that propagation proceeds only *via* the triplet excited state of the chromophore. The overall kinetics for this photopolymerization are sensitive to the ratio of competitive rate constants for the triplet excited state and to the initial chromophore concentration.

In foregoing papers[1-6] the term photopolymerization was defined as a polymerization process in which every chain propagating step involves the absorption of a photon. The general kinetic reaction scheme for the photopolymerization of a bichromophoric system A-A where the two chromophores react independently is given in Scheme I. The photochemical reaction can occur either from the first excited state (A^1) or from the triplet excited state (A^3) of the chromophore A. The probability of exciting simultaneously the two chromophores of the bichromophoric system under conditions of continuous irradiation is negligible. In this scheme A^0 represents the chromophore in the ground state.

Scheme I

$A^0 \xrightarrow{h\nu} A^1$	light absorption
$A^1 \xrightarrow{k_d^S} A^0$	unimolecular deactivation of the singlet excited state (radiative and nonradiative)
$A^1 \xrightarrow{k_{ST}} A^3$	intersystem crossing
$A^1 + Q \xrightarrow{k_Q^S} A^0$	singlet quenching
$A^1 + A^0 \xrightarrow{k_r^S} P$	bond formation from singlet excited state: propagation step
$A^3 \xrightarrow{k_d^T} A^0$	unimolecular deactivation of the triplet excited state (radiative and nonradiative)
$A^3 + Q \xrightarrow{k_Q^T} A^0$	triplet quenching
$A^3 + A^0 \xrightarrow{k_r^T} P'$	bond formation from triplet excited state: propagation step[7]

If the photopolymerization occurs only from the triplet excited state, and if all the incident light energy is absorbed by the bichromophoric system, the degree of conversion p[8] as a function of irradiation time in absence of quencher is given by[6]

$$2.303 \frac{k_d^T}{k_r^T[A^0]_0} \log\left(\frac{1}{1-p}\right) + p = \frac{2I_0\Phi_{ISC}}{[A^0]_0}(t - t_0) \quad (1)$$

$[A^0]_0$ represents the initial chromophore concentration in the ground state at time t_0 in moles per liter. I_0 is the incident light intensity in einstein l.$^{-1}$ sec^{-1}. $\Phi_{ISC} = k_{ST}/(k_{ST} + k_d^S)$ is the quantum yield of intersystem crossing. The relation between the degree of conversion p and the degree of polymerization $\bar{x}_n$ is given by

$$\bar{x}_n = 1/(1 - p) \quad (2)$$

Substituting eq 2 in eq 1, yields

$$2.303 \frac{k_d^T}{k_r^T[A^0]_0} \log \bar{x}_n + \frac{\bar{x}_n - 1}{\bar{x}_n} = \frac{2I_0\Phi_{ISC}(t - t_0)}{[A^0]_0} \quad (3)$$

The absolute values for k_d^T and k_r^T are determined from quenching experiments. In Scheme I the bimolecular reaction can occur from both the excited singlet state (A^1) and the excited triplet state (A^3). It is assumed that the added quencher Q quenches both excited singlet and triplet states of A, and that the intersystem crossing from the excited singlet to triplet is irreversible.

If reaction and quenching occurs only *via* the triplet excited state, the Stern–Volmer expression is given by

$$\Phi_r^0/\Phi_r = 1 + k_Q^T[Q]/(k_d^T + k_r^T[A^0]) \quad (4)$$

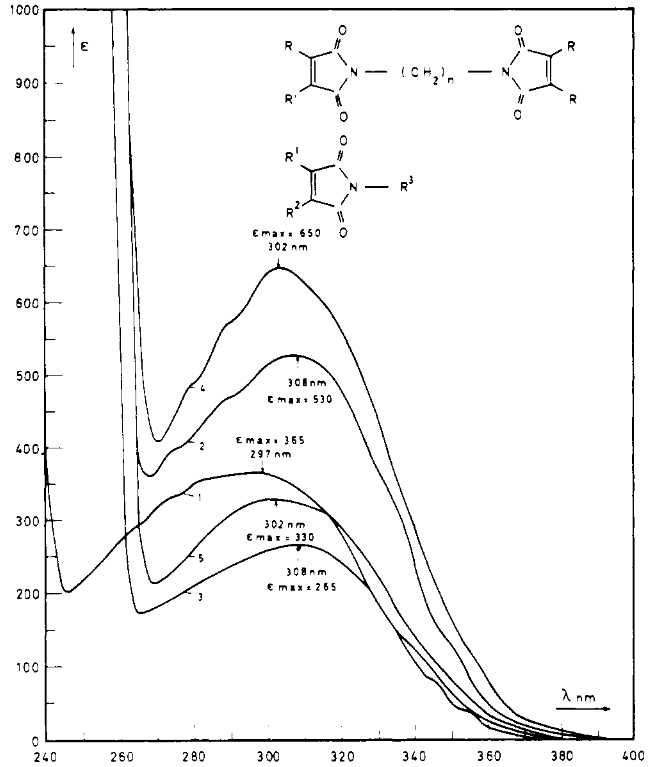

Figure 1. Ultraviolet spectra in CH_2Cl_2 of substituted bis(maleimides) **1**, **2**, and **4** and of model compounds **3** and **5**: **1**, $R = R^1 = (CH_2)_2$, $n = 9$; **2**, $R = R^1 = Cl$, $n = 9$; **4**, $R = Br$, $R^1 = H$, $n = 11$; **3**, $R^1 = R^2 = Cl$, $R^3 = n$-Bu; **5**, $R^1 = Br$, $R^2 = H$; $R^3 = n$-Prop.

The ratio k_d^T/k_r^T can also be calculated from quantum yield determination as a function of the chromophore concentration. If the triplet excited state is the only reactive one, the quantum yield for disappearance of the chromophore in the absence of quencher is expressed by

$$1/\Phi_r^0 = 1/2\Phi_{ISC} + k_d^T/2k_r^T\Phi_{ISC}[A^0] \qquad (5)$$

Photopolymerization of Substituted *N,N'*-Polymethylenebis(maleimides) in Solution

1. Photopolymerization of *N,N'*-Nonamethylenebis-3,4,5,6-tetrahydrophtalimide (1) in Dichloromethane. A. Uv and Florescence Spectra. In Figure 1 the uv spectrum of **1** in dichloromethane in the 250-400-nm region is shown. The maximum of the absorption band lies at the same wavelength (λ_{max} 297 nm) in CH_2Cl_2 (ϵ^{297nm} 365) and in CH_3CN (ϵ^{297nm} 340). Compound **1** is extremely weakly emissive in acetonitrile and methylcyclohexane solution at room temperature.

The quantum yield of fluorescence is very low ($<10^{-4}$) and fluorescence is a minor deactivation process of the singlet excited state.

B. Quenching of the Photopolymerization. Compound **1** is polymerized upon ultraviolet irradiation in solution giving polymers with cyclobutane rings in the main chain.[5] This type of photopolymerization involves the absorption of a photon in each propagation step. The reaction can be sensitized by high-energy triplet sensitizers (acetophenone) and is quenched by oxygen, ferrocene, and 3,3,4,4-tetramethyl-1,2-diazetine 1,2-dioxide (**6**). The nature of the excited state(s) involved in this photopolymerization and the rates of deactivation and reaction of the excited state(s) can be determined in quenching experiments. Degassed acetonitrile or dichloromethane solutions with a certain tetrahydrophtalimide chromophore concentration and containing various concentrations of a quencher were irradiated in parallel at 350 nm. Relative quantum yields of disappearance of the tetrahydrophtalimide chromophore were determined by uv analysis. Stern-Volmer plots are linear for all tetrahydrophtalimide chromophore concentrations and are dependent on the chromophore concentration. The lifetimes found from the Stern-Volmer analysis are too long to be singlet lifetimes. Since the reaction can be sensitized, the reactive state is the triplet excited state, which is quenched. The quenching equation is then given by eq 4. An example of a Stern-Volmer plot is shown in the Figure 2a. The slopes of the Stern-Volmer plots obtained for different quenchers and varying chromophore concentrations are tabulated in Tables I-III and τ_T^0 values are calculated on the assumption that $k_Q^T = 1.1 \times 10^{10}\ M^{-1}\ sec^{-1}$ in acetonitrile[9,10] and $k_Q^T = 1.66 \times 10^{10}\ M^{-1}\ sec^{-1}$ in dichloromethane.[11]

Table I
Quenching of the Photopolymerization of 1 in CH_3CN with Ferrocene

$[A^0]_0$, $10^{-3}\ M$	$k_Q^T\tau_T^0$, M^{-1}	τ_T^0, 10^{-6} sec	$10^{-5}/\tau_T^0$, sec^{-1}
4	47,250	4.30	2.33
22	44,500	4.05	2.47
44	38,500	3.50	2.86

$k_d^T = 2.23 \times 10^5\ sec^{-1}$; $k_r^T = 1.35 \times 10^6\ M^{-1}\ sec^{-1}$

Table II
Quenching of the Photopolymerization of 1 with 6 in CH_3CN

$[A^0]_0$, $10^{-3}\ M$	$k_Q^T\tau_T^0$, M^{-1}	τ_T^0, 10^{-6} sec	$10^{-5}/\tau_T^0$, sec^{-1}
4	14,810	1.35	7.43
22	13,500	1.23	8.15
50	10,750	0.98	10.23

$k_d^T = 7 \times 10^5\ sec^{-1}$; $k_r^T = 6.1 \times 10^6\ M^{-1}\ sec^{-1}$

Table III
Quenching of the Photopolymerization of 1 with 6 in CH_2Cl_2

$[A^0]_0$, $10^{-3}\ M$	$k_Q^T\tau_T^0$, M^{-1}	τ_T^0, 10^{-6} sec	$10^{-5}/\tau_T^0$, sec^{-1}
4	41,000	2.47	4.05
20	36,000	2.17	4.61
40	29,000	1.75	5.72

$k_d^T = 3.8 \times 10^5\ sec^{-1}$; $k_r^T = 4.5 \times 10^6\ M^{-1}\ sec^{-1}$

Table IV
Quantum Yields for the Disappearance of the Tetrahydrophtalimide Chromophore in the Photopolymerization of 1

Solvent	$[A^0]_0$, M	λ_{irr}, nm	Φ_r^0 [a]
CH_2Cl_2	4×10^{-2}	313	0.03
CH_3CN	4×10^{-2}	313	0.08
CH_3CN	4×10^{-2}	334	0.074

[a] The small values for Φ_r^0 clearly indicate that this type of photopolymerization is not a chain process.

An example of a plot of the value of $1/\tau_T^0$ as a function of the chromophore concentration is presented in Figure 2b; values of k_r^T and k_d^T obtained in this way are reported in Tables I-III.

The values for k_d^T, k_r^T, and the ratio k_d^T/k_r^T suggest that quenching of **1** by **6** (Table II; $k_d^T/k_r^T = 0.165$) is not diffusion controlled and that ferrocene enhances the deactivation of the triplet excited state (Table II; $k_d^T/k_r^T = 0.115$).

C. Quantum Yields. The quantum yields for disappearance of the tetrahydrophtalimide chromophore were

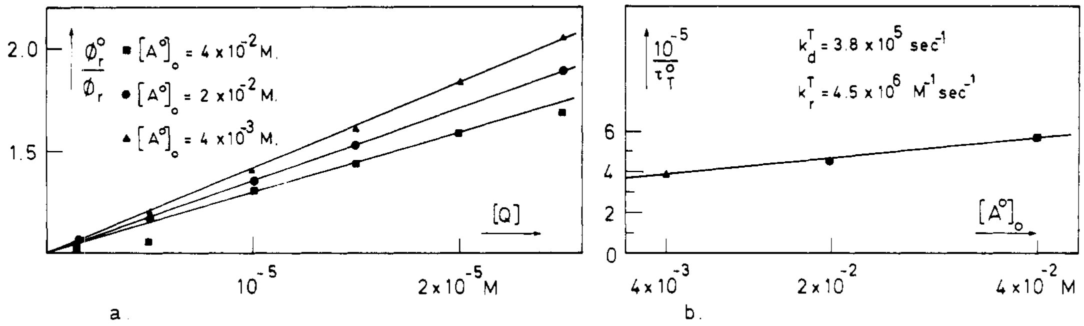

Figure 2. (a) Quenching of the photopolymerization of 1 in CH_2Cl_2 with 3,3,4,4-tetramethyl-1,2-diazetine 1,2-dioxide. (b) Determination of $k_d{}^T$ and $k_r{}^T$ for the photopolymerization of 1 in CH_2Cl_2, quencher 3,3,4,4-tetramethyl-1,2-diazetine 1,2-dioxide.

Table V
Kinetic Results for the Photopolymerization of 1 in CH_2Cl_2; $[A^0]_0 = 2 \times 10^{-1}$ *M*; Irradiation at 310 nm

Irrad. Time, *t* (hr)	A_{325nm} Dilution, 25×	Deg of Conversion, p^a	$\frac{1^a}{1-p}$	log $\frac{1^a}{1-p}$	p + log $\frac{1^a}{1-p}$	p + 3 log $\frac{1^a}{1-p}$	p + 0.97 log $\frac{1}{1-p}$	$\bar{x}_n{}^b$	0.97 log $\bar{x}_n + \frac{\bar{x}_n - 1^b}{\bar{x}_n}$
0	0.948	0.000	1.000	0.000	0.000	0.000	0.000	1.00	0.000
2.5	0.908	0.042	1.044	0.019	0.061	0.098	0.060	1.18	0.23
6.5	0.867	0.085	1.093	0.039	0.124	0.201	0.121	1.22	0.26
14	0.762	0.196	1.243	0.095	0.290	0.479	0.288	1.36	0.39
26	0.620	0.345	1.528	0.184	0.530	0.898	0.524	1.66	0.61
42	0.450	0.525	2.106	0.323	0.849	1.495	0.839	2.38	0.94
51.5	0.372	0.607	2.547	0.406	1.013	1.825	1.001	2.88	1.10
72	0.227	0.761	4.183	0.622	1.383	2.626	1.364	4.41	1.40
93	0.132	0.860	7.168	0.855	1.716	3.427	1.690	–	–

[a] Obtained from optical density measurements. [b] Obtained from molecular weight determinations.

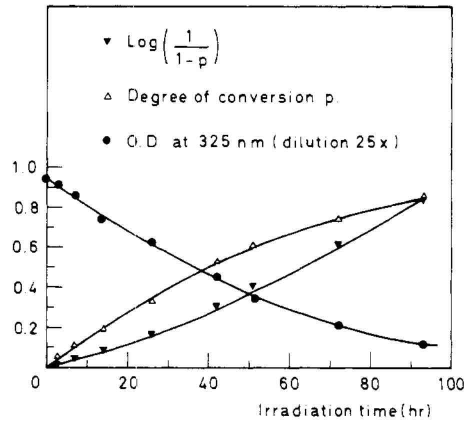

Figure 3. Photopolymerization of 1 in CH_2Cl_2; $[A^0]_0 = 2 \times 10^{-1}$ *M*; irradiation RPR-3000-A lamps, $T = 25°$.

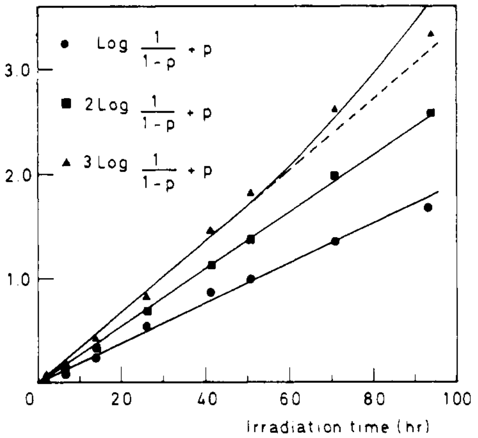

Figure 4. Photopolymerization of 1 in CH_2Cl_2; $[A^0]_0 = 2 \times 10^{-1}$ *M*; irradiation RPR-3000-A lamps, $T = 25°$. α log $[1/(1-p)] + p$ as a function of irradiation time.

measured by irradiation of a degassed solution of 1 in CH_2Cl_2 or CH_3CN with monochromatic light. The intensity of the incident light was measured by actinometry with *N*,*N'*-hexamethylenebis(maleimide) in CH_2Cl_2.[11] Yields of disappearance of the tetrahydrophtalimide chromophore concentration were measured as usual by uv analysis. The results are compiled in Table IV.

D. Kinetics. Degassed dichloromethane solutions 10^{-1} *M* in 1 were irradiated in parallel at 310 nm. The temperature was controlled at 25°. All the incident light was absorbed by the system during the whole irradiation time. The solution remained colorless during irradiation and no precipitate was formed. The reaction kinetics were followed by uv analysis at 325 nm. The long-wavelength absorption disappeared completely in the polymer. The molecular weight of the formed polymer was measured as a function of the irradiation time. The results are compiled in Table V. The degree of conversion p is calculated from the change in absorbance as a function of the irradiation time. The change in optical density (which is directly proportional to the chromophore concentration), the degree of conversion p and log $[1/(1-p)]$ are given as a function of the irradiation time in Figure 3. The change in chromophore concentration as a function of the irradiation time does not follow first-order nor zero-order kinetics; the plot of p as a function of the irradiation time curves downward, while that of log $[1/1-p)]$ as a function of the irradiation time curves upward. These results suggest that the kinetic behavior of the photopolymerization of 1 can be expressed by eq 6, which is identical with eq 1.

$$\alpha \log [1/(1-p)] + p = \beta(t - t_0) \qquad (6)$$

α and β are constants. The prelogaritmic factor α can be determined by giving various values to α and plot-

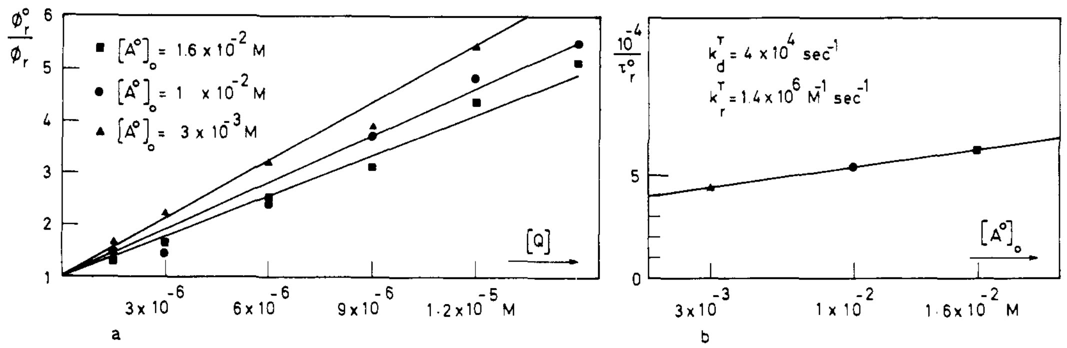

Figure 5. Quenching of the photopolymerization of 2 in CH_2Cl_2 with 3,3,4,4-tetramethyl-1,2-diazetine 1,2-dioxide. Determination of k_d^T and k_r^T for the photopolymerization of 2 in CH_2Cl_2.

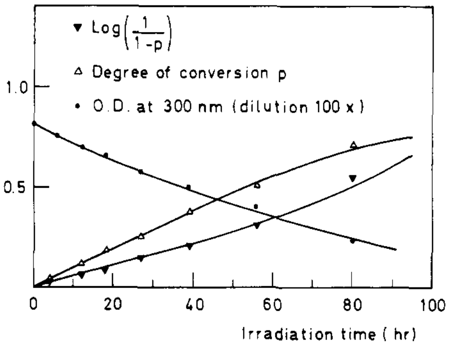

Figure 6. Photopolymerization of 2 in CH_2Cl_2; $[A^0]_0 = 3 \times 10^{-1}$ *M*; irradiation RUL-3500-A lamps, *T* 25°.

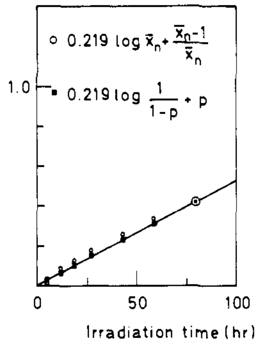

Figure 7. Photopolymerization of 2 in CH_2Cl_2; $[A^0]_0 = 3 \times 10^{-1}$ *M*; irradiation RUL-3500-A lamps; $T = 25°$. $0.219 \log [1/(1-p)] + p$ and $0.219 \log \bar{x}_n + (\bar{x}_n - 1)/\bar{x}_n$ as a function of time.

ting eq 6 (Figure 4). For $1 < \alpha < 2$, eq 6 is linear; for $\alpha > 3$, the plot of eq 6 curves upward. The factor $\alpha = 2.303(k_d^T/k_r^T[A^0]_0)$ can also be calculated from quenching experiments. A value for $\alpha = 0.97$ is found from quenching experiments (Table III) when $[A^0]_0 = 2 \times 10^{-1}$ *M*. The kinetic behavior of the photopolymerization of 1 can also be expressed by eq 7, which is identical with eq 3. Using the value 0.97 for α, the variation of the rate of

$$\alpha \log \bar{x}_n + (\bar{x}_n - 1)/\bar{x}_n = \beta(t - t_0) \qquad (7)$$

polymerization measured independently by the change of the degree of polymerization as a function of time can be calculated and is found to be within experimental error, similar to that obtained by eq 6 (Table V).

2. Photopolymerization of *N,N'*-Nonamethylenebis(dichloromaleimide) (2) in Dichloromethane. A. Uv and Fluorescence Spectra. In Figure 1 the uv spectra of 2 and *N*-*n*-butyldichloromaleimide (3) in CH_2Cl_2 in the 250–400-nm region are shown. The maxima lie at the same wavelength for 2 and 3. A small hypochromism and a small blue shift is observed when going from CH_2Cl_2 to CH_3CN as a solvent. The molar extinction coefficient for 2 is twice that for 3, indicating that there is no evidence for a substantial ground state interaction between the chromophores. Compounds 2 and 3 are very weakly emissive in acetonitrile solution at room temperature. In ether–pentane–alcohol at 77°K a structureless band is observed (λ_{max} 445 nm).

Table VI
Absorption Characteristics for 2 and 3

Compound	CH_2Cl_2		CH_3CN	
	λ_{max}	ϵ_{max}	λ_{max}	ϵ_{max}
2	308	530	306	485
3	308	265	306	240

Table VII
Quenching of the Photopolymerization of 2 in CH_2Cl_2 with 6

$[A^0]_0$,[a] 10^{-3} *M*	$k_Q^T\tau_T^0$, M^{-1}	τ_T^0, 10^{-5} sec	$10^{-4}/\tau_T^0$, sec^{-1}
3	374,000	2.25	4.44
10	300,000	1.81	5.53
16	260,000	1.57	6.38

$k_d^T = 4 \times 10^4$ sec^{-1}; $k_r^T = 1.4 \times 10^6$ M^{-1} sec^{-1}

[a] Initial dichloromaleimide chromophore concentration is given.

B. Quenching of the Photopolymerization. Compound 2 is polymerized upon ultraviolet irradiation in solution giving polymer with cyclobutane rings in the main chain, in the same way as 1. The reaction can be sensitized by benzophenone and is quenched by oxygen and 6. Degassed dichloromethane solutions with a given dichloromaleimide chromophore concentration and containing various concentrations of 6 were irradiated in parallel at 350 nm. Stern–Volmer plots were linear for all dichloromaleimide chromophore concentrations and were dependent on the chromophore concentration. The found lifetimes from this Stern–Volmer analysis are too long to be singlet lifetimes. Since the reaction can be sensitized, the reactive state is the triplet excited state which is quenched. The quenching equation is then given by eq 4 and quenching curves are plotted in Figure 5a. The slopes are tabulated in Table VII and τ_T^0 values are calculated on the assumption that k_Q^T equals 1.66×10^{10} M^{-1} sec^{-1} in CH_2Cl_2. The $1/\tau_T^0$ values are plotted in Figure 5b. The values for k_r^T and k_d^T are collected in Table VII. The quantum yield for disappearance of the dichloromaleimide chromophore is 0.04 at $[A^0]_0 = 10^{-2}$ *M* (λ_{irr} 334 nm) in dichloromethane solution. This small value supports the proposed photopolymerization scheme.

C. Kinetics. Degassed dichloromethane solutions 1.5 ×

Table VIII
Kinetic Results for the Photopolymerization of 2 in CH_2Cl_2; $[A^0]_0 = 3 \times 10^{-1}$ *M*; Irradiation at 350 nm

Irrad. Time, t (hr)	A_{300nm} Dilution, 100×	Deg of Conversion, p^a	$\frac{1^a}{1-p}$	$\log \frac{1^a}{1-p}$	$p + 0.219 \log \frac{1^a}{1-p}$	Mol Wt	$\bar{x}_n{}^b$	$\frac{\bar{x}_n - 1^b}{\bar{x}_n}$	$\log \bar{x}_n{}^b$	$0.219 \log \bar{x}_n{}^b + \frac{\bar{x}_n - 1}{\bar{x}_n}$
0	0.820	0.000	1.000	0.000	0.000	456	1	0	0	0
6	0.767	0.065	1.069	0.029	0.071	470	1.03	0.03	0.02	0.04
12	0.710	0.134	1.155	0.063	0.148	550	1.21	0.17	0.08	0.19
18	0.671	0.182	1.222	0.087	0.201	570	1.25	0.20	0.10	0.22
27	0.592	0.278	1.385	0.141	0.309	640	1.40	0.28	0.14	0.32
39	0.505	0.384	1.624	0.211	0.426	790	1.73	0.42	0.24	0.47
56	0.393	0.521	2.086	0.319	0.588	1020	2.24	0.56	0.36	0.64
80	0.236	0.712	3.475	0.541	0.830	1510	3.31	0.70	0.52	0.81

[a] Obtained from absorbance measurements. [b] Obtained from molecular weight determinations.

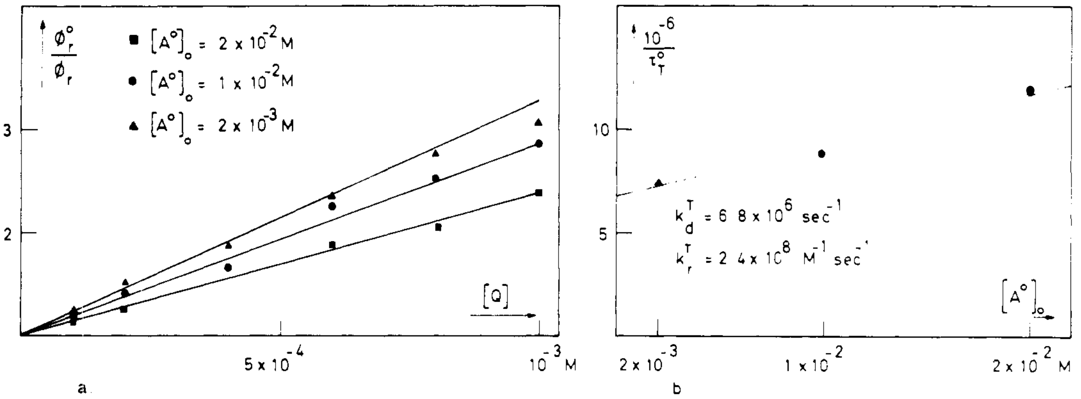

Figure 8. (a) Quenching of the photopolymerization of 4 in CH_2Cl_2 with 3,3,4,4-tetramethyl-1,2-diazetine 1,2-dioxide. (b) Determination of $k_d{}^T$ and $k_r{}^T$ for the photopolymerization of 4 in CH_2Cl_2.

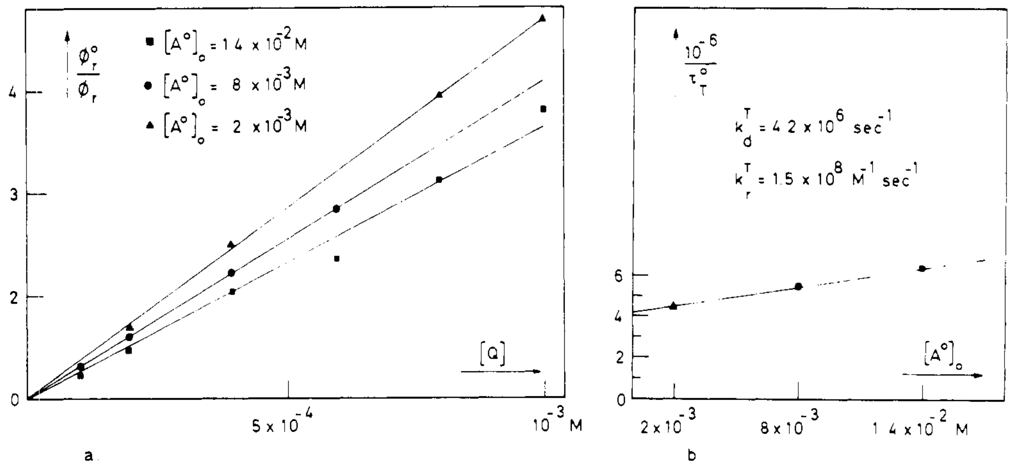

Figure 9. (a) Quenching of the photodimerization of 5 in CH_2Cl_2 with 3,3,4,4-tetramethyl-1,2-diazetine 1,2-dioxide. (b) Determination of $k_d{}^T$ and $k_r{}^T$ in the photodimerization of 5 in CH_2Cl_2.

10^{-1} *M* in 2 were irradiated in parallel at 350 nm. The temperature was controlled at 25°. All the incident light was absorbed by the system up to about 75% conversion. The solution became pale yellow after a long period of irradiation, no precipitate was formed. The reaction kinetics were followed by uv analysis at 300 nm. The long-wavelength absorption disappeared completely in the polymer. The molecular weight of the formed polymers was measured as a function of the irradiation time. The results for the photopolymerization of 2 are given in Table VIII. The change in optical density (or the chromophore concentration), the degree of conversion p and $\log [1/(1 - p)]$ are given as a function of the irradiation time in Figures 6 and 7.

3. Photopolymerization of *N*,*N*′-Undecamethylenebis(bromomaleimide) (4) in Dichloromethane. A. Uv and Fluorescence Spectra. The uv spectra of 4 and *N*-*n*-propylbromomaleimide (5) in CH_2Cl_2 in the 250–400-nm region are given in Figure 1. The maxima lie at the same wavelength for 4 and 5. A small hypochromism is observed when going from CH_2Cl_2 to CH_3CN as the solvent (Table IX). There is no evidence for ground-state interaction between the two chromophores. The bis(bromomaleimides) are weakly emissive in acetonitrile solution at room temperature. In ether-pentane-alcohol at 77°K a structureless band is obtained (λ_{max} 440 nm).

B. Quenching of the Photopolymerization (Photodimerization). Compound 4 is polymerized upon ultraviolet

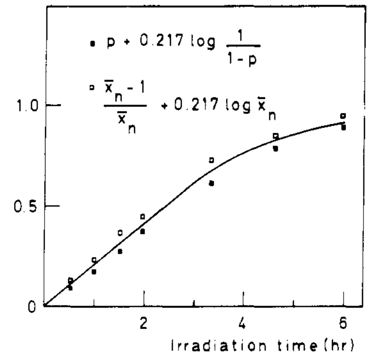

Figure 10. Photopolymerization of 4 in CH_2Cl_2; $[A^0]_0 = 3 \times 10^{-1}$ M. Irradiation RUL-3500-A lamps, $T = 25°$. $p + 0.217 \log [1/(1 - p)]$ and $(\bar{x}_n - 1)/\bar{x}_n + 0.217 \log \bar{x}_n$ as a function of time.

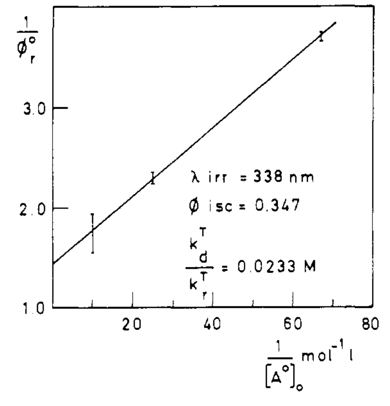

Figure 11. $1/\Phi_r^0$ as a function of $1/[A^0]_0$ of the photopolymerization of 4 in CH_2Cl_2. $\lambda_{irr} = 338$ nm ± 5; $\Phi_{ISC} = 0.347$; $k_d^T/k_r^T = 0.0233\,M$.

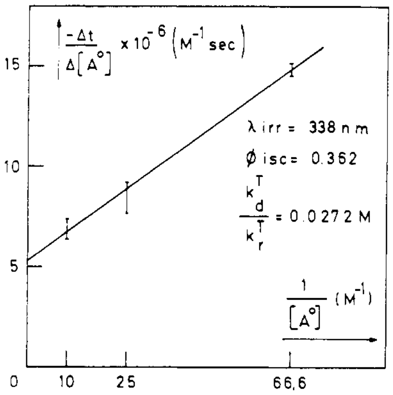

Figure 12. Initial kinetic analysis of the photopolymerization of 4 in CH_2Cl_2; $\lambda_{irr} = 338$ nm, $\Phi_{ISC} = 0.36$, $k_d^T/k_r^T = 0.027\,M$.

Table IX
Absorption Characteristics for 4 and 5

Bis(bromomaleimide)	CH_2Cl_2		CH_3CN	
	λ_{max}	ϵ_{max}	λ_{max}	ϵ_{max}
4	302	650	302	630
5	301	330	300	320

Table X
Quenching of the Photopolymerization of 4 in CH_2Cl_2 with 6

$[A^0]_0$, $10^{-3}\,M$	$k_Q^T\tau_T^0$, M^{-1}	τ_T^0, 10^{-7} sec	$10^{-6}/\tau_T^0$, sec^{-1}
2	2260	1.36	7.35
10	1880	1.13	8.83
20	1410	0.849	11.8

$k_d^T = 6.8 \times 10^6\ \text{sec}^{-1}$; $k_r^T = 2.4 \times 10^8\ M^{-1}\ \text{sec}^{-1}$

Table XI
Quenching of the Photodimerization of 5 in CH_2Cl_2 with 6

$[A^0]_0$, $10^{-3}\,M$	$k_Q^T\tau_T^0$, M^{-1}	τ_T^0, 10^{-7} sec	$10^{-6}/\tau_T^0$, sec^{-1}
2	3660	2.20	4.54
8	3090	1.86	5.37
14	2620	1.58	6.34

$k_d^T = 4.2 \times 10^6\ \text{sec}^{-1}$; $k_r^T = 1.5 \times 10^8\ M^{-1}\ \text{sec}^{-1}$

irradiation in solution giving cyclobutane ring containing polymers in the same way as 1 and 2. The reaction can be sensitized by benzophenone and is quenched by oxygen and 6. Compound 5 undergoes a 2 + 2 dimerization upon irradiation in solution; the reaction can also be sensitized and be quenched as in the case of 4. Degassed dichloromethane solutions with a certain bromomaleimide chromophore concentration and various concentrations of 6 were irradiated in parallel at 350 nm. Stern–Volmer plots were linear for all bromomaleimide chromophore concentrations and were dependent on the chromophore concentration. The found lifetimes in this Stern–Volmer analysis are too long to be singlet lifetimes. Since the reaction can be sensitized, the reactive state is the triplet excited state which is quenched. The quenching expression is then given by eq 4 and the Stern–Volmer curves are plotted in Figures 8a and 9a. The slopes are tabulated in Tables X and XI, and τ_T^0 values are calculated on the assumption that $k_Q^T = 1.66 \times 10^{10}\ M^{-1}\ \text{sec}^{-1}$ in CH_2Cl_2. The $1/\tau_T^0$ values are plotted in Figures 8b and 9b. The values for k_r^T and k_d^T are collected in Tables X and XI.

C. Kinetics. Degassed dichloromethane solutions 1.5×10^{-1} M in 4 were irradiated in parallel at 350 nm. The temperature was controlled at 25°. All the incident light was absorbed by the system up to about 80% conversion. The solution became bright yellow during the irradiation, absorbing part of the incident light, no precipitate was formed. The reaction kinetics were followed by uv analysis at 310 nm. The uv absorption at 310 nm disappeared completely during the irradiation. The molecular weight of the formed polymers was measured as a function of the irradiation time. The results for the photopolymerization of 4 are given in Table XII.

From quenching experiments (Table X) a value for $\alpha = 0.217$ is found for an initial concentration equal to $[A^0]_0 = 3 \times 10^{-1}$ M. The graph of eq 6 and 7 with $\alpha = 0.217$ curves downward (Figure 10). This would mean that the factor α is in fact greater in the overall reaction kinetics, probably due to the coloration of solution.

D. Quantum Yields and Initial Kinetic Analysis. The quantum yields for disappearance of the bromomaleimide chromophore and the initial kinetic analysis were measured by irradiation of degassed solutions of 4 in CH_2Cl_2 with monochromatic light. The intensity of the incident light was measured by actinometry with N,N'-hexamethylenebis(maleimide) in CH_2Cl_2.[11] Yields of disappearance of the bromomaleimide chromophore were measured as usual by uv analysis. The maximum conversion was 8%. The results are compiled in Table XIII. The quantum yield for disappearance of the bromomaleimide chromophore is given by eq 8 (Figure 11).

$$1/\Phi_r^0 = 1.44 + 0.0336/[A^0] \qquad (8)$$

When applying eq 5, the values for $\Phi_{ISC} = 0.347$[7] and $k_d^T/k_r^T = 0.0233\,M$ are found. From Table XIII it is clear that $-\Delta[A^0]/\Delta t = \Phi_r^0 \times I_{abs}$. The plot of $-\Delta t/\Delta[A^0]$ as a

Table XII
Kinetic Results for the Photopolymerization of 4 in CH_2Cl_2; $[A^0]_0 = 3 \times 10^{-1}$ *M*; Irradiation at 350 nm

Irrad. Time, t (hr)	A_{310nm} Dilution, 100×	Deg[a] of Conversion, p	$\frac{1^a}{1-p}$	$\log \frac{1^a}{1-p}$	$p + 0.217 \log \frac{1^a}{1-p}$	Mol Wt	$\bar{x}_n{}^b$	$\frac{\bar{x}_n - 1^b}{\bar{x}_n}$	$\log \bar{x}_n{}^b$	$0.217 \log \bar{x}_n{}^b + \frac{\bar{x}_n - 1}{\bar{x}_n}$
0	1.003	0.000	1.000	0.000	0.000	504[c]	1	0	0	0
0.5	0.904	0.099	1.110	0.045	0.109	580	1.15	0.13	0.06	0.14
1	0.820	0.183	1.223	0.087	0.202	650	1.29	0.22	0.11	0.24
1.5	0.728	0.274	1.378	0.139	0.304	760	1.51	0.34	0.18	0.38
2	0.646	0.356	1.553	0.191	0.397	850	1.69	0.41	0.23	0.46
3.33	0.448	0.553	2.239	0.350	0.629	1440	2.86	0.65	0.46	0.75
4.5	0.330	0.671	3.040	0.483	0.776	1770	3.52	0.71	0.55	0.83
6	0.238	0.763	4.214	0.625	0.898	2570	5.11	0.80	0.71	0.95

[a] Obtained from absorbance measurements. [b] Obtained from molecular weight determinations. [c] Obtained from mass spectroscopic determination.

Table XIII
Quantum Yields and Initial Kinetic Analysis for the Disappearance of the Bromomaleimide Chromophore in the Photopolymerization of 4 in CH_2Cl_2 (λ_{irr} = 338 nm)

$[A^0]_0$,[a] *M*	I_{abs},[b] 10^{-7} *M* sec^{-1}	$-\frac{\Delta[A^0]}{\Delta t}$ 10^{-8} *M* sec^{-1}	$\Phi_r{}^0$	$\frac{1}{[A^0]_0}$, M^{-1}	$1/\Phi_r{}^0$	$\frac{-\Delta t}{\Delta[A^0]}$ 10^6 *M*$^{-1}$ sec	$\Phi_r{}^0 \times I_{abs}$, 10^{-8} *M* sec^{-1}
1.5×10^{-2}	2.44	6.572	0.269	66.6	3.71	15.2	6.573
1.5×10^{-2}	2.46	6.854	0.278	66.6	3.59	14.6	6.844
4×10^{-2}	2.58	10.96	0.424	25	2.36	9.12	10.95
4×10^{-2}	2.91	12.96	0.446	25	2.24	7.72	12.96
10^{-1}	2.76	13.76	0.498	10	2.01	7.27	13.76
10^{-1}	2.50	15.72	0.623	10	1.59	6.37	15.71

[a] Initial bromomaleimide chromophore concentration is given. [b] Measured for a constant irradiated area; mean I_{abs} = 2.61×10^{-7} einstein/sec per l.

function of $1/[A^0]$ gives a straight line (Figure 12) with an intercept = 5.30×10^6 M^{-1} sec, and a slope = 1.44×10^5 *M*. Application of eq 5, with $I_{abs} = 2.61 \times 10^{-7}$ *M* sec^{-1}, gives the values for Φ_{ISC} = 0.362[7] and $k_d{}^T/k_r{}^T = 0.0272$ *M*. A value for $k_d{}^T/k_r{}^T = 0.0283$ *M* is found from quenching experiments (Table X).

Conclusion

The kinetic results prove the proposed reaction scheme and illustrate the importance of the ratio $k_d{}^T/k_r{}^T$ on the order of the polymerization reaction. The values of $k_d{}^T$ and k_r are obtained by quenching experiments which further indicate that reaction in these systems occurs from the triplet state only.

Experimental Section

Chemicals. Dichloromethane (Fluka puriss., Abfülldatum 30-11-72) and acetonitrile (Fluka, for ultraviolet spectroscopy) were used without further purification. Ferrocene (Baker photosensitizer and quencher kit) was sublimed twice prior to use.

Instrumentation. Ultraviolet spectra were recorded on a Perkin-Elmer double-beam spectrophotometer, Model 124. The uv analysis, to determine the conversions, was done on a Hitachi-Perkin-Elmer spectrophotometer, type 139. The molecular weights were determined in chloroform solution with a Mechrolab 301A vapor pressure osmometer. The kinetic experiments of **1** were done in a Rayonet Srinivasan-Griffin photochemical reactor, Model RPR 100, equipped with 16-RPR-3000-A lamps and a merry-go-round, Model MGR-100, for the quenching experiments of **1** 16-RPR-3500-A lamps were used; for the kinetic and quenching experiments of **2**, **4**, and **5** a Rayonet RS preparative photochemical reactor was used, equipped with 8-RUL-3500-A lamps, a NaBr-Pb(OAc)$_2$ cutoff filter and a merry-go-round apparatus. For the determination of the quantum yields a Bausch & Lomb monochromator with a super high pressure mercury light source (Osram 200 HB) was used. All measurements were thermostated at 20°.

Preparation of Substituted Maleimides and Bis(maleimides). The substituted bis(maleimides) were synthesized according to previously described methods.[5,12]

Preparation of 3,3,4,4-Tetramethyl-1,2-diazetine 1,2-Dioxide. The synthesis of **6** was achieved by the method of E. F. Ullman and P. Singh.[13]

Kinetics of the Photopolymerization. Calibrated Pyrex tubes, each containing an equal amount of 0.10 *M* solution of **1**, or a 0.15 *M* solution of **2** or **4** in CH_2Cl_2, were degassed in four successive freeze–thaw cycles and irradiated in parallel (*vide supra*). The absorbance of the solution (after dilution) and the molecular weight of the formed polymers were measured as a function of the irradiation time.

Quenching of the Photopolymerization (Photodimerization). Different samples (5 ml) with a given concentration of **1**, **2**, **4**, or **5**, but with various concentrations of quencher, in dichloromethane or acetonitrile, were degassed in four freeze–thaw cycles and irradiated in parallel (*vide supra*). The conversion in each sample was determined by uv analysis. The change in optical density in each sample was compared with that in the reference samples containing no quencher. Such a quenching was carried out for different chromophore concentrations. The maximum conversion in the reference sample was about 10%. No light was absorbed by the quencher.

Quantum Yields. Initial Kinetic Analysis. A solution (3 ml) with a given chromophore concetration in dichloromethane or acetonitrile was degassed in four freeze–thaw cycles. The solution was then poured into a quartz cell which was connected to the degassing flask. The cell was placed in a thermostated block at 20° in front of the monochromator, in a fixed position, and a constant area was irradiated. All the incident light was absorbed. During irradiation the solution was stirred with a magnetic stirrer. The degree of conversion was determined by monitoring the absorbance of the undiluted solution for **1** and **2** and after dilution for **4**. The maximum conversion was about 8%. The amount of light absorbed was calculated from optical density measurements. The incident light intensity was measured by actinometry with *N,N'*-hexamethylenebismaleimide in dichloromethane.

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(7) One referee suggested that the propagation step *via* the triplet excited state could proceed *via* an intermediate

$$A^3 + A^0 \xrightarrow{k_r{}^T} {}^*A - A^* \quad \text{formation of an intermediate}$$

$${}^*A - A^* \xrightarrow{k_{-r}{}^T} 2A^0 \quad \text{dissociation of the intermediate}$$

$${}^*A - A^* \xrightarrow{k_c{}^T} P' \quad \text{product formation}$$

In this case the right-hand side of eq 1 and 3 should be multiplied by $\Phi_P = k_c{}^T/(k_c{}^T + k_{-r}{}^T)$. Equation 5 rearranges to

$$1/\Phi_r{}^0 = (1/2\Phi_{ISC}\Phi_p) + (k_d{}^T/2k_r{}^T\Phi_{ISC}\Phi_p[A^0])$$

This would mean that the determined quantum yields for intersystem crossing (Figures 11 and 12) are in fact a product of $\Phi_P\Phi_{ISC}$. Since the value of Φ_{ISC} could not be determined by an independent route no distinction can be made between the two mechanisms. However, in the photodimerization of *N*-butylmaleimide it has been shown that Φ_P is close to unity.[11]

(8) The degree of conversion *p* is calculated from the change in absorbance as a function of the irradiation time and equals $1 - (OD)_t/(OD)_0$, where $(OD)_0$ is the absorbance at time t_0 and $(OD)_t$ is the absorbance at time *t*.

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Polymerization of γ-Benzyl L-Glutamate *N*-Carboxyanhydride with Metal Acetate–Tri-*n*-butylphosphine Catalyst System

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ABSTRACT: A novel type of catalyst, tri-*n*-butylphosphine–metal carboxylate (metal: Ni, Co, Cr, Cd, or Mg) catalyst system, was found for the polymerization of γ-benzyl L-glutamate *N*-carboxyanhydride. Molecular weights of polymers obtained with this type of catalyst depend on the nature of metal component of the catalysts and follow the order of Ni > Co > Cd > Mg > Cr. The polymers obtained with the nickel acetate–tri-*n*-butylphosphine catalyst system in higher than 90% yield have molecular weights larger than 2×10^5 and relatively sharp molecular weight distributions: *i.e.*, $\bar{M}_w/\bar{M}_n = 1.4$–2.1.

Although a large number of papers had been published on the polymerizations of α-amino acid *N*-carboxyanhydrides (NCA) using various kinds of catalyst such as water,[2] alcohols,[3] amines,[4] and alkali metal compounds,[5-9] only a few works had been published on the intended stereospecific and/or stereoelective polymerization.[10-13]

To realize the stereospecific and/or stereoelective polymerization of NCAs, it is necessary to search for the catalyst which is able to control effectively, in each step of the propagation reaction, the stereochemistry of addition of the monomer to the growing polymer end. During our explorative experiments, we found a novel type of catalyst, metal carboxylate–trialkylphosphine catalyst system. In these works, γ-benzyl glutamate NCA (BG-NCA) was selected as a monomer for testing most suitably the stereoregulating capacity of the catalyst, because poly(γ-benzyl glutamate) (P-BG) is known to dissolve easily in many kinds of solvents and is characterized by various types of physical methods.

Experimental Section

Materials. γ-Benzyl L-glutamate *N*-carboxyanhydride (L-BG-NCA)[14] was prepared from γ-benzyl L-glutamate[15] (mp 170.5°). Since the NCA is unstable at high temperatures and to a contaminating moisture, both preparation and recrystallization (three times from chloroform–*n*-hexane and then four times from ethyl acetate–*n*-hexane) were carried out in a specially designed apparatus (Figure 1). In these operations, the supernatant liquid was transferred through a connecting glass tube equipped with a glass filter F with compressed nitrogen or argon from a cooled recrystallization vessel A (from −78 to −20°) to a vessel B. A suitable amount of solvent was poured into vessel A containing the crystalline NCA under a nitrogen or an argon atmosphere at room temperature to dissolve the NCA, while the glass filter in vessel A was set in the state of (b). The solution of the NCA in vessel A was cooled at −78° to crystallize the NCA. By repeating the recrystallization process, the NCA was purified until the Beilstein test became negative. In the case of L-BG-NCA, the yield was 80.0%, mp 92–93°, $[\alpha]^{20}\text{D}$ −17.1° (*c* 3.32, ethyl acetate). *Anal.* Calcd for $C_{13}H_{13}NO_5$: C, 59.31; H, 5.05; N, 5.44. Found: C, 59.49; H, 5.05; N, 5.28.

Tri-*n*-butylphosphine (*n*-Bu_3P) was prepared by the method of Davies and Jones:[16] bp 144° (47 mm), n_D 1.4549. *Anal.* Calcd for $C_{12}H_{27}P$: C, 71.21; H, 13.26. Found: C, 69.78; H, 13.26.

Triphenylphosphine (Ph_3P) was recrystallized from benzene–diethyl ether (mp 80–81°).

Commercial reagent of $Ni(OAc)_2 \cdot 4H_2O$, $Co(OAc)_2 \cdot 2H_2O$, $Cd(OAc)_2 \cdot H_2O$, $Cr(OAc)_2 \cdot H_2O$, or $Mg(OAc)_2 \cdot 4H_2O$ was used without further purification because of the recrystallization from usual solvents being difficult. *Anal.* Calcd for $C_4H_{14}NiO_8$: C, 19.67; H, 5.62. Found: C, 19.64; H, 5.72. Calcd for $C_4H_{10}CoO_6$: C, 22.55; H, 4.73. Found: C, 22.30; H, 4.73. Calcd for $C_4H_8CdO_5$: C, 19.36; H, 3.22. Found: C, 19.76; H, 3.35. Calcd for $C_4H_{14}MgO_8$: C, 22.40; H, 6.58. Found: C, 22.43; H, 6.59.

The complex, $NiCl_2 \cdot 2(n\text{-}Bu_3P)$,[17] was recrystallized four times from ethanol: scarlet crystalline pellets, mp 46–47°. *Anal.* Calcd for $C_{24}H_{54}Cl_2NiP_2$: C, 59.3; H, 10.1. Found: C, 58.2; H, 10.3.

Purification of Solvents. All solvents were purified under a dry nitrogen or an argon atmosphere. Tetrahydrofuran was refluxed with metallic sodium for 48 hr and distilled, bp 66°.

Dioxane was refluxed with 10 vol % of 1 *N* HCl for 24 hr, allowed to stand over pellets of NaOH for 48 hr, and separated from aqueous layer. The acetate-free dioxane was refluxed with