PHOTOPOLYMERIZATION

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Photopolymerization is defined as a process in which from a low molecular weight material a macromolecule is obtained by a stepwise condensation reaction, and in which for each of these chain-extending steps the absorption of a quantum of light is necessary. Three types of photopolymerization have been exemplified: the singlet, the triplet and the 'reactive intermediate' photopolymerization. The kinetics of triplet photopolymerization are worked out and verified for *N*,*N'*-alkylene-bis (dimethyl maleimide), for *N*,*N'*-alkylene-bis-(bromomaleimide) and for *N*,*N'*-alkylene-bis(dichloromaleimide). The importance of rate constants for thermal deactivation of the triplet and of the rate constant for reaction are stressed.

One of the main problems around which our research is centred, is the study of non-conjugated bichromophoric systems. Let us consider the processes which can occur on excitation of one of the chromophores.

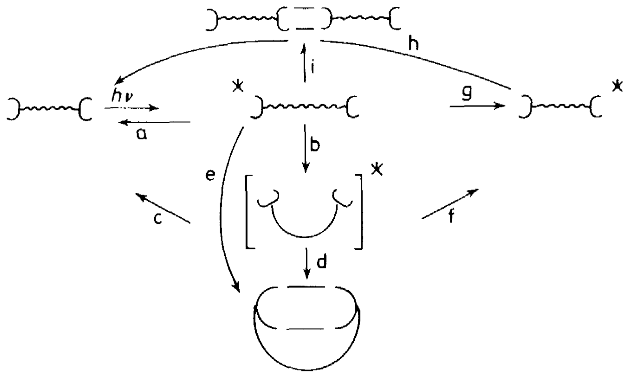


Figure 1. Possible reaction pathways in non-conjugated bichromophores.

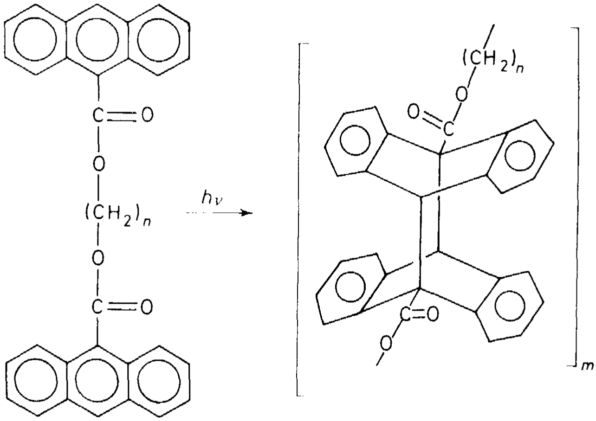
Deactivation of the excited state (*path a*) leads to the ground state starting material. The localized excited state can form an excited state in which excitation is delocalized over the two chromophores (*path b*). This complex can deactivate either by emitting luminescence or radiationlessly to the ground state starting material (*path c*). If, however, the chromophores are chosen suitably the complex can collapse into a ground state cyclomer (*path d*). The same process can also be conceived in a concerted fashion by path e. If the two chromophores are non-identical, the delocalized complex could play a role in intramolecular energy transfer (*path f*). The same process of energy transfer can occur by path g, and the so-formed localized excited state can deactivate by path h. All these processes are intramolecular in nature. If, however, the bichromophoric system is chosen suitably one could conceive that *intermolecular* reaction could occur, leading to the formation of polymeric material (*path i*).

This leads us to a new concept of photopolymerization. Indeed, contrary to photoinitiation in which light intervenes in the initiation step only, in this concept each propagation step requires the interaction of the reacting species with light. We can define the photopolymerization as *a process in which from a low molecular weight material a macromolecule is obtained by a stepwise condensation reaction, and in which for each of these chain-extending steps the absorption of a quantum of light is necessary*[1].

On this basis three types of polymerization can be considered: singlet photopolymerization in which the excited state involved in the propagation step is a singlet, triplet photopolymerization in which the triplet excited state is the reacting entity and reactive intermediate photopolymerization in which a reactive species, formed in a prior photochemical reaction, does intervene in each propagation step.

Let us now consider if these proposed types of photopolymerization can be realized.

As a model reaction for singlet polymerization, the dimerization of anthracene was chosen. The dimerization of anthracene[2] and of 9-anthrylcarboxylic acid[3] was shown to occur from the singlet excited state. Upon irradiation of a bisanthracene (**1**) intermolecular bond formation between respectively the 9 and 10 positions should lead to a polymer with structure (**2**).



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It could be shown in model compound studies that addition occurred only in the head-to-tail fashion in this anthracene derivative[4]. As can be seen from the data reported in *Table 1*, high molecular weight materials are formed on irradiation of the respective bisanthracene monomers using light of wavelength above 330 nm. The structure of the polymer could be confirmed by comparison of the n.m.r. spectra of dimer derived from 9-methylanthracene with those of the polymer and by the thermal and photochemical reversibility of the polymer, which is analogous to the behaviour of the photodimer under identical reaction conditions.

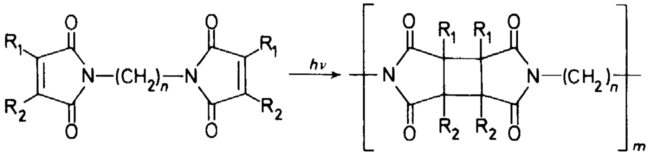
Table 1. Photopolymerization of bisanthracene

n	$[\eta]^{25°C}_{CHCl_3}$*	$\bar{M}_n$†
9	0.88	—
10	0.61	—
11	1.3	52 000
12	0.68	28 000

* Intrinsic viscosity; † Number average molecular weight measured by osmometry in chloroform.

Let us now illustrate the possibility of triplet photopolymerization by two examples.

A first example is the photopolymerization of *N*,*N*′-polymethylene-bismaleimides (**3**). We reported[5] some time ago on the sensitized photopolymerization of *N*,*N*′-polymethylene-bis(dichloromaleimides) **9**. $R_1 = R_2 = Cl$. It could be shown that on sensitization with benzophenone polymers (**4**) with molecular weights of the order 30 000 and higher could be obtained.



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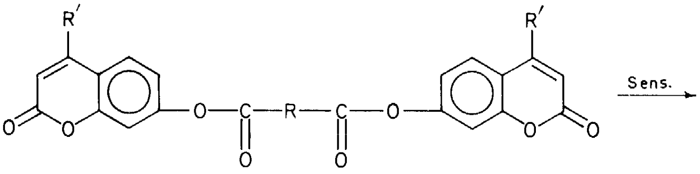
More recently we demonstrated[6] that *N*,*N*′-polymethylene-bis(dimethylmaleimides) and *N*,*N*′-polymethylene-bisbromomaleimide did on direct irradiation form polycycloaddition products (*Table 2*).

Table 2. Triplet photopolymerization of undecamethylene-bismaleimides

R_1, R_2	$[\eta]$	$\bar{M}_n$‡
$R_1 = R_2 = Cl$	0.74*	—
$R_1 = H, R_2 = Br$	0.4†	14 300
$R_1 = R_2 = CH_3$	0.9†	20 800

* Intrinsic viscosity in DMF at 25°C;
† Intrinsic viscosity in $CHCl_3$ at 25°C;
‡ Number average molecular weight in $CHCl_3$.

A second example of triplet photopolymerization is the benzophenone-sensitized photopolymerization of biscoumarines (**5**). Studies on the model compound[7], 7-acetoxycoumarine, showed that for more than 95 per cent a head-to-head exo dimer was formed on sensitization. The same type of addition is presumed to be the main sort of link present in the polymers (**6**) reported in *Table 3*. As can be seen from this table polymers with intrinsic viscosities up to 0.5 are formed in this reaction.



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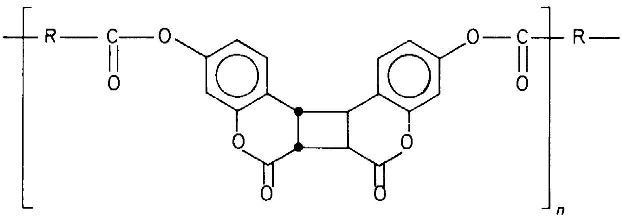

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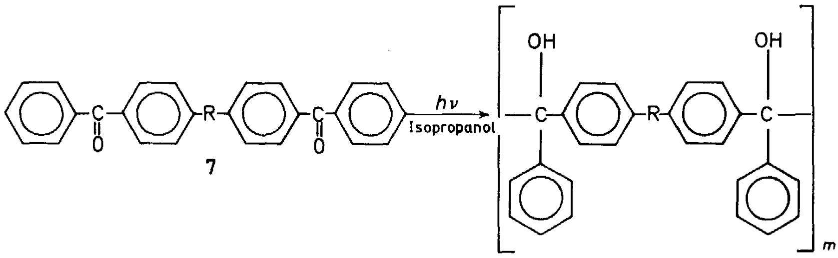
Table 3. Photopolymerization of biscoumarines (R = Me).

η	$[\eta]$*	M_n†
7	0.3	—
8	0.4	—
10	0.3	—
11	0.4	—
12	0.5	22000

* Intrinsic viscosity in chloroform.
† Number average molecular weight as measured by osmometry in chloroform.

As third and last class, the photopolymerization through a reactive ground state formed in a previous photochemical reaction can be exemplified by the photopolyreduction of bisbenzophenones (**7**). Irradiation of bisbenzophenone **7** in isopropanol leads to the formation of polybenzpinacols **8**. This reaction has been reported by Higgins and co-workers[8] and by ourselves[9]. As can be seen from *Table 4* polymeric materials are formed. This process, occurring through the intermediacy of a radical species, is, however, prone to further side reactions.

All the above-mentioned examples of photopolymerization are solution phase polymerizations. A true photopolymerization is, however, also possible



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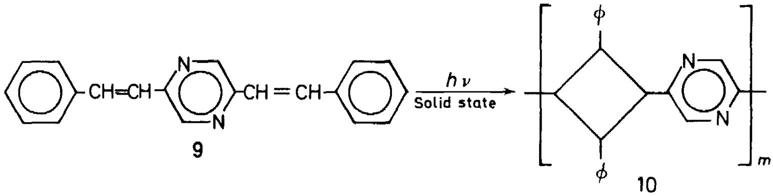

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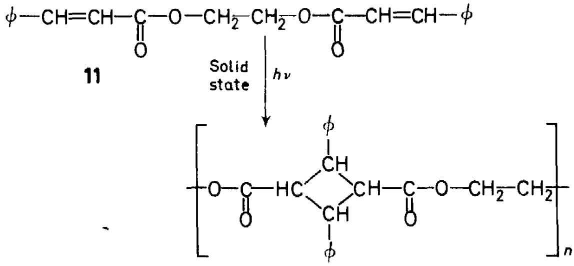
in the solid state. Hasegawa and co-workers reported[10] some time ago the solid state—they named this reaction the four-centre polymerization—photopolymerization of 2,5-distyrylpyrazine **9**. This type of photopolymerization was recently extended[11] by the same group to other systems such as biscinnamates **12** and phenylene diacrylic acid derivatives **13**[12] and was found to be strongly related to solid state photodimerization as developed by the late Schmidt[18] and co-workers.

Table 4. Photoreduction of bis-benzophenones.

R	[η]	$\bar{M}_n$‡
$-CH_2-$	0.25*§	—
—	—	26000
$-(CH_2)_2-$	0.45*§	—
$-(CH_2)_6-$	0.26†	—
$-(CH_2)_8-$	—	11000
$-(CH_2)_{10}-$	0.32†	—
—S—	0.1*§	—
—O—	0.3*§	—

* In dioxane; † In DMF at 25°C; ‡ Vapour pressure osmometry in DMF; § Data by Higgings and co-workers.



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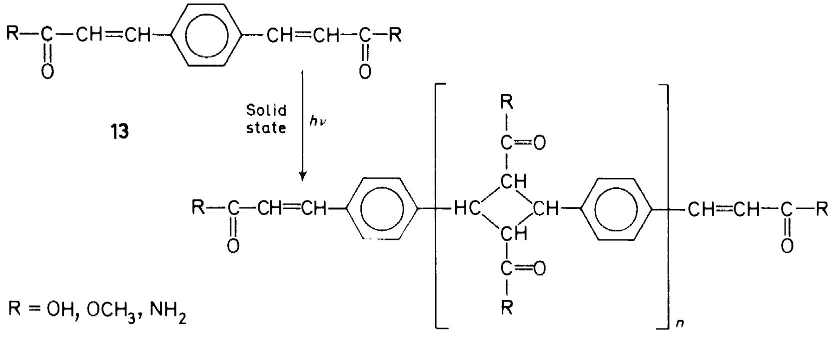

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Another type of solid state photopolymerization in which a 'shearing reaction' is needed to bring about the polymerization reaction was reported by Wegner[14].

We could show[15] that *N*,*N*′-alkylene-bis(dichloromaleimide) polymerizes in the solid state and that, as in the above-mentioned cases, this polymerization is lattice controlled. This could be shown by changing the length of the methylene chain linking the two maleimides (*Table* 5). This leads to a change in molecular packing resulting in the non-ability to polymerize for *N*,*N*′-polymethylene-bis(dichloromaleimides) with more than three methylenes in the link.

Table 5. Polymerization of *N*,*N*′-alkylenebismaleimides in the solid state.

n	Monomer	Polymerizable
3	$R_1 = R_2 = R_3 = R_4 = Cl$	+
3	$R_1 = R_2 = R_3 = R_4 = CH_3$	+
3	$R_1 = R_2 = R_3 = R_4 = H$	
3	3,4,5,6-tetrahydro- phthalimide	+ +
4	$R_1 = R_2 = R_3 = R_4 = Cl$	−
5	$R_1 = R_2 = R_3 = R_4 = Cl$	−
6	$R_1 = R_2 = R_3 = R_4 = Cl$	−

Accepting this concept of photopolymerization we can put forward the following general scheme for the singlet and triplet photopolycycloaddition polymerization.

$M^0 \rightarrow M^1$	excitation
$M^1 \xrightarrow{k_{ds}} M^0$	singlet deactivation
$M^1 \xrightarrow{k_{isc}} M^3$	intersystem crossing
$M^1 + M^0 \xrightarrow{k_{rs}}$ polymer P	addition from the singlet manifold
$M^3 \xrightarrow{k_{dt}} M^0$	deactivation of triplet
$M^3 + M^0 \xrightarrow{k_{rt}}$ polymer P′	addition from the triplet manifold

The disappearance of the chromophore concentration as a function of time or the rate of polymer formation can then be expressed respectively for singlet (equation 1) and for triplet (equation 2) polymerization, thus:

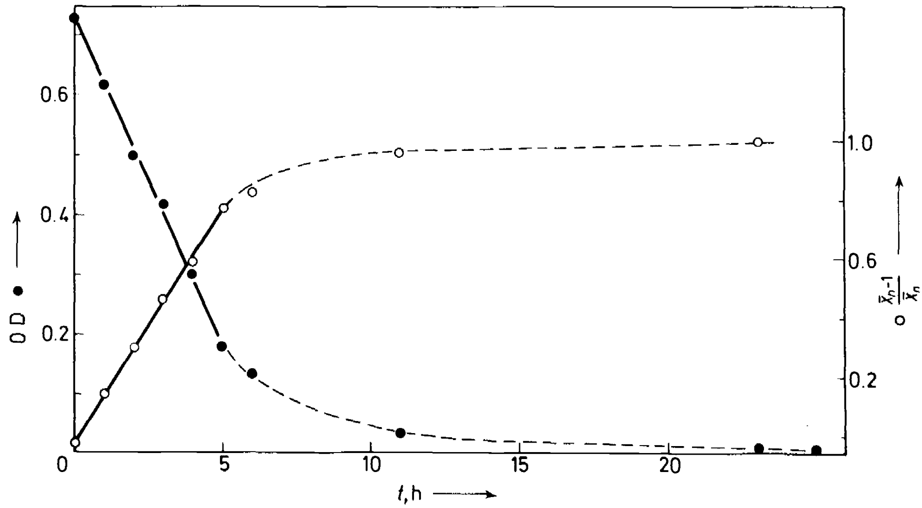
$$-\frac{\mathrm{d}[\overline{\mathrm{M}}]}{\mathrm{d}t} = \frac{\mathrm{d}P}{\mathrm{d}t} = \frac{k_{\mathrm{rs}}[\mathrm{M}^0] \, . \, I_{\mathrm{abs}}}{k_{\mathrm{ds}} + k_{\mathrm{isc}} + k_{\mathrm{rs}}[\mathrm{M}^0]} \tag{1}$$

$$-\frac{\mathrm{d}[\overline{\mathrm{M}}]}{\mathrm{d}t} = \frac{\mathrm{d}P'}{\mathrm{d}t} = \frac{k_{\mathrm{rt}}[\mathrm{M}^0] \, . \, \Phi_{\mathrm{isc}} \, . \, I_{\mathrm{abs}}}{k_{\mathrm{dt}} + k_{\mathrm{rt}}[\mathrm{M}^0]} \tag{2}$$

Let us now consider a system in which polymerization occurs by attack of a triplet excited state on a ground state molecule ($k_{\mathrm{rs}} = 0$) and in which light absorption is complete ($I_{\mathrm{abs}} = I_0$). On integration of equation 2 between the initial concentration, C_0, and the concentration at a certain reaction time, $C_0(1 - P)$, the following equation is obtained:

$$\frac{k_{\mathrm{dt}}}{k_{\mathrm{rt}}} \, . \ln \frac{1}{1 - P} + P[\mathrm{M}]_{\mathrm{init.}} = I_0 \Phi_{\mathrm{isc}} (t - t_0) \tag{3}$$

indicating that the disappearance of chromophore as a function of time is expressed by the sum of a first order and a zero order reaction. Since in a polycondensation reaction $X_n = 1/(1 - P)$ equation 3 can be rearranged to express the change in degree of polymerization as a function of time (equation 4).



Photopolymerization of *N,N'*-undecamethylene-bis (dimethylmaleimide) in CH_2Cl_2

$[M]_0 = 10^{-1}$ mol. l^{-1}

$\lambda_{irr} = 350$ nm

Optical density as a function of irradiation time

● Optical density is measured at 300 nm

Dilution: 50 x

○ $\frac{\bar{X}_n - 1}{\bar{X}_n}$ as a function of irradiation time

Figure 2.

$$\frac{k_{\mathrm{dt}}}{k_{\mathrm{rt}}} \cdot \ln \bar{x}_n + \frac{\bar{x}_n - 1}{\bar{x}_n} \cdot [\mathrm{M}^0]_{\mathrm{init.}} = I_0 \cdot \Phi_{\mathrm{isc}} (t - t_0) \tag{4}$$

This permits us to check the validity of the proposed equation by two independent methods: by monitoring the change in optical density, and thus of chromophore concentration, as a function of time and by checking the variation of the degree of polymerization as a function of time. If now $k_{\mathrm{rt}} \gg k_{\mathrm{dt}}$ the first term of equation 3 and equation 4 can be neglected and the photopolymerization process obeys zero order kinetics. This condition is fulfilled in the case of the *N*,*N*′-polymethylene-bis(dimethylmaleimide).

If $k_{\mathrm{rt}} \ll k_{\mathrm{dt}}$ the second term can be neglected and then photopolymerization will be first order in chromophore concentration as a function of time. This case is exemplified by the *N*,*N*′-polymethylene-bis(bromomaleimides).

If $k_{\mathrm{rt}} \sim k_{\mathrm{dt}}$, the reaction is neither first nor zero order in chromophore concentration. This is the case for the *N*,*N*′-polymethylene-bis(dichloromaleimides).

The disappearance of the chromophore concentration for *N*,*N*′-undecamethylene-bis(dimethylmaleimide) as a function of time is given in *Figure 2* and is shown to be zero order as long as light absorption is complete. Independently, the degree of polymerization was determined by measuring the change in the number average molecular weight as a function of time. A plot of the ratio $(\bar{x}_n - 1)/\bar{x}_n$ as a function of time gives a straight line in agreement with the above derived equation. These results indicate that $k_{\mathrm{rt}} \gg k_{\mathrm{dt}}$. The values of these rate constants were determined by quenching the photopolymerization by ferrocene and by comparing the quantum yield of the quenched reaction with the quantum yield of the reaction in the absence of quencher.

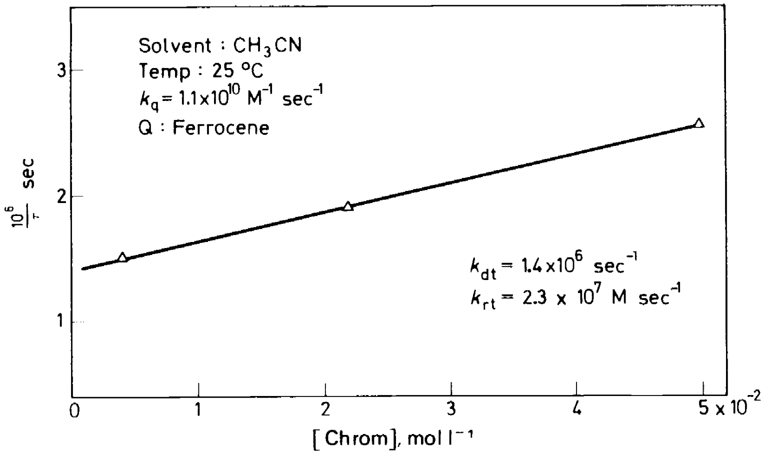


Figure 3. $1/\tau$ versus concentration of *N*,*N*′-undecamethylene-bis(dimethylmaleimide).

$$\frac{\Phi_0}{\Phi} = 1 + \frac{k_{\mathrm{Q}}[\mathrm{Q}]}{k_{\mathrm{rt}}[\mathrm{M}_0] + k_{\mathrm{dt}}} = 1 + k_{\mathrm{Q}}[\mathrm{Q}]\tau \tag{5}$$

Assuming diffusion controlled quenching the lifetime τ can be calculated from the slope of the Stern–Volmer curves.

If measured for different initial chromophore concentrations the values of k_{rt} and k_{dt} can be determined by plotting the value $1/\tau$ as a function of the chromophore concentration. A plot of $1/\tau$ as a function of the chromophore concentration for *N*,*N*′-undecamethylene-bis(dimethylmaleimides) (*Figure 3*) shows that k_{rt} is twenty times larger than k_{dt}. It should be pointed out that in the solvent used for photopolymerization k_{rt} can be estimated[17] to be one hundred times larger than k_{dt}.

Let us now consider the bisbromo derivative in which case $k_{rt} \ll k_{dt}$.

On plotting the logarithm of the ratio $1/(1 - P)$ or the logarithm of the optical density as a function of time a straight line is obtained indicating a first order reaction in chromophore concentration (*Figure 4*). Again the validity of the result was checked by plotting the logarithm of the independently determined degree of polymerization as a function of time. As can be seen in *Figure 5* a straight line is obtained. Thus in the bisbromo derivative $k_{dt} \gg k_{rt}$ can be understood by the influence of the bromine atoms on the ease of the deactivation of the triplet excited state to singlet ground state.

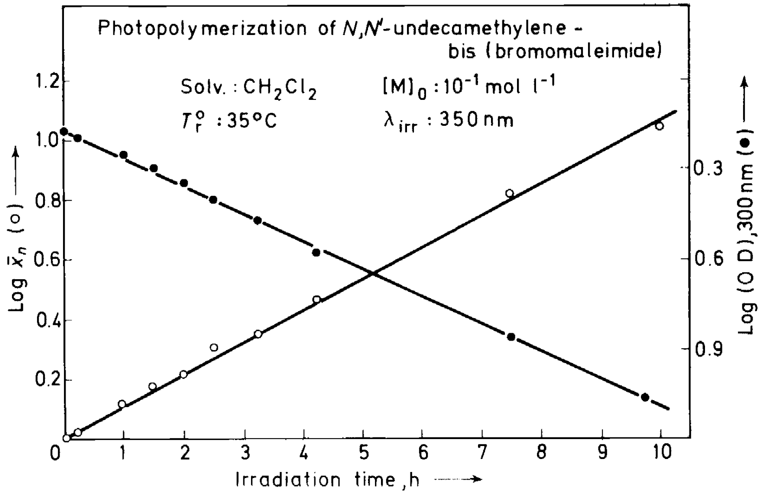


Figure 4.

The photopolymerization of *N*,*N*′-undecamethylene-bis(dichloromaleimides) is an intermediate case. A plot of the change in optical density as a function of time fits neither zero order nor first order kinetics as can be seen from *Figure 6*. The concept of photopolymerization presented here is in fact a stepwise polymerization. In a stepwise polymerization the degree of polymerization, $\bar{x}_n$, equals the ratio $1/(1 - P)$. Plotting x_n or $\overline{M}_n$ as a function of the extent of conversion, P, should give a hyperbola. In *Figure 6* the value of the number average molecular weight is plotted as a function of the degree of conversion for the photopolymerization of *N*,*N*′-undecamethylene-bis-

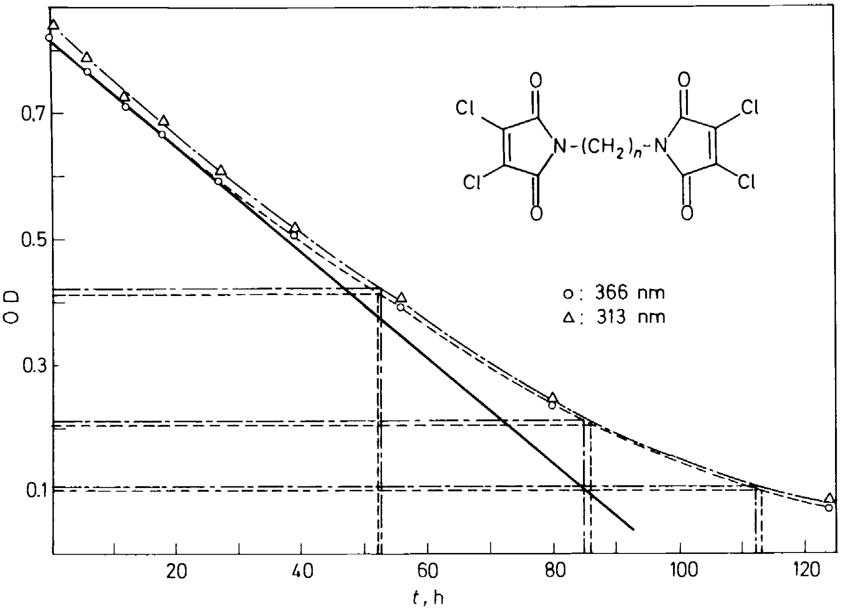
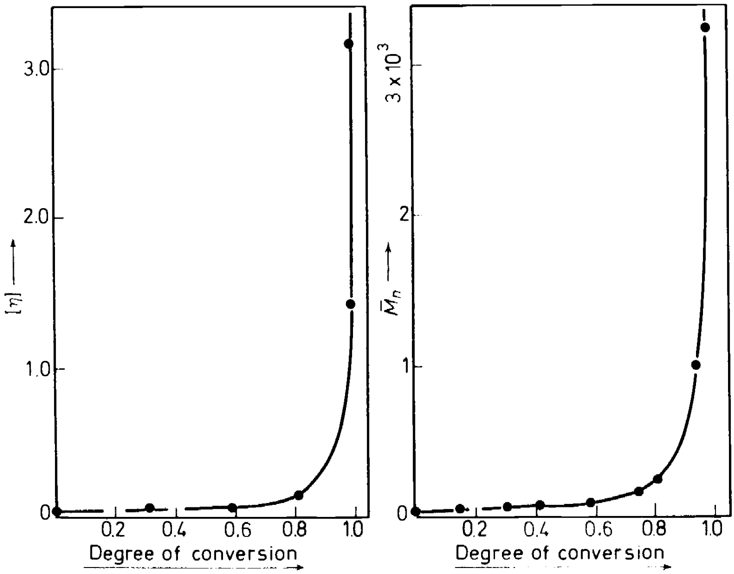


Figure 5. Photopolymerization of *N*,*N'*-undecamethylene-bis(dichloromaleimide) in CH_2Cl_2. λ_m = 350 nm; O.D. is measured at 313 nm (Δ) after dilution and at 366 nm (o).



Intrinsic viscosity as a function of *P* Molecular weight as a function of *P*

Figure 6. Photopolymerization of *N*,*N'*-undecamethylene-bis(dimethylmaleimide).

(dimethylmaleimide). A hyperbola is obtained as expected. On plotting the intrinsic viscosity as a function of the degree of conversion (*Figure 6*) an identical hyperbola is obtained. This leads to the intriguing conclusion that in this polymer system the value of the coefficient α in the equation

$$[\eta] = KM^{\alpha} \tag{6}$$

should be close to unity.

What might this type of photopolymerization bring, besides a new concept, to the field of polymer chemistry? Besides new and difficult-to-obtain polymers, a very good possibility exists for forming, by making the right choice of comonomers, alternating copolymers.

These types of polymers could contribute to a better understanding of the structure/property relation in polymer solutions since many of the polymer-forming reactions are stereo- and regio-selective and by changing the reaction conditions the selectivity can be altered. In this ecology-minded age it should be mentioned that many of the polymeric materials formed by stepwise polyaddition can be reversed back to monomers, by light or by heat, a property which could eventually be useful in photodegradable or thermodegradable systems.

ACKNOWLEDGEMENT

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REFERENCES

[1] F. C. De Schryver, 'Fotopolymerisatiekinetika', *Verhandelingen* Koninklijke Academie voor Wetenschappen, Letteren en Schone Kunsten van België **33**, 120 (1971).

[2] J. B. Birks, *Photophysics of Aromatic Molecules*, pp 320 and 629. Wiley: New York (1970).

[3] D. O. Cowan and W. W. Schmiegel, *Angew. Chem.* **83**, 545 (1971).

[4] F. C. De Schryver, L. Anand, G. Smets and J. Switten, *J. Polymer Sci.* **9**, 777 (1971).

[5] F. C. De Schryver, W. J. Feast and G. Smets, *J. Polymer Sci. A-1*, **8**, 1939 (1970).

[6] F. C. De Schryver, N. Boens and G. Smets, *J. Polymer Sci. A-1*, **10**. 1687 (1972).

[7] L. Leenders, E. Schouteden and F. C. De Schryver, in press.

[8] J. Higgings. A. H. Joannes, J. E. Jones, R. Schutz, D. McCombs and C. S. Menon, *J. Polymer Sci. A-1*, **8**, 1987 (1970).

[9] F. C. De Schryver, T. Van Tran and G. Smets, *J. Polymer Sci. B-1*, **9**, 425 (1971).

[10] F. Suzuki, Y. Suzuki, H. Nakanishi and M. Hasegawa, *J. Polymer Sci. A-1*. 7, 743 and 2319 (1969).

[11] F. Nakanishi and M. Hasegawa, *J. Polymer Sci. B-1*, **5**, 813 (1968).

[12] F. Nakanishi and M. Hasegawa, *J. Polymer Sci. A-1*, **8**, 2151 (1970), and references cited therein.

[13] G. M. J. Schmidt in *Reactivity of the Photoexcited Organic Molecule*, p 227. Wiley: New York (1967).

[14] G. Wegner, *Z. Naturforsch.* **24b**, 824 (1969); *Polymer Preprints*, **13** (1), 470 (1972) and references cited therein.

[15] F. C. De Schryver, N. Boens and G. Smets, unpublished results.

[16] J. Put, F. C. De Schryver, unpublished results.

[17] F. C. De Schryver, N. Boens, unpublished results.