

Studies of the antenna effect in polymer molecules

29. Isomerization of provitamin D₃ photosensitized by polymers containing pendant naphthalene groups

Maria Nowakowska¹, James E. Guillet^{*}

Department of Chemistry, University of Toronto, Toronto, Ont., M5S 3H6, Canada

Received 24 September 1996; accepted 25 November 1996

Abstract

The photosensitized isomerization of provitamin D₃ was studied in THF solutions of styrene-2-vinylnaphthalene copolymers, poly(2-vinylnaphthalene), poly(2-isopropenylnaphthalene) and poly(acenaphthalene). The effect of efficiency of excimer formation and energy migration on the quantum efficiency of provitamin formation was demonstrated. © 1997 Elsevier Science S.A.

Keywords: Polymeric photosensitizers; Photocatalysts; Energy transfer; Excimers; Isomerization; Vitamin D₃

1. Introduction

In the previous papers in this series it was shown that several different antenna polyelectrolytes commonly referred to as ‘photozymes’ behave as efficient microheterogeneous photocatalysts [1–12]. Aromatic chromophores such as naphthalene, anthracene, phenanthrene, or carbazole incorporated in the copolymer chain act as molecular antennas in these polymers by absorbing light in the near-UV visible spectral region and transferring the excitation energy to the molecule of substrate (probe), thus inducing its photochemical reaction.

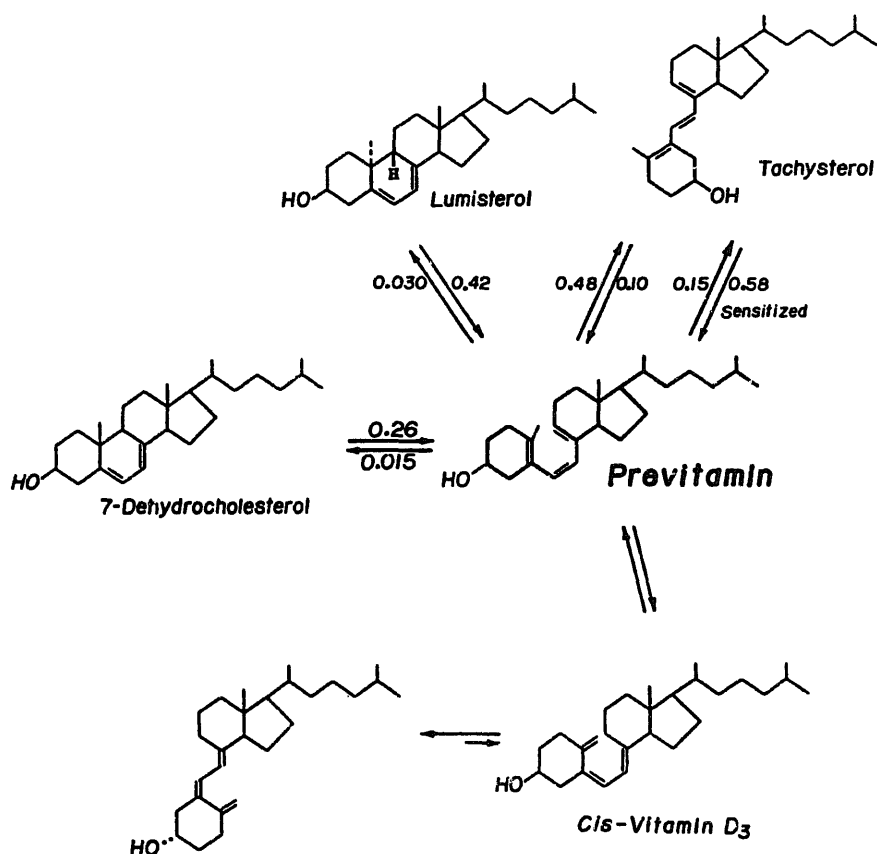
In a search for efficient polymeric photosensitizers one has to optimize the photophysical properties of the polymeric catalyst for each substrate used. Among the problems which should be addressed are the determination of the type of interactions between photosensitizer and probe, the importance of energy migration between the aromatic chromophores and the influence of excimer formation on photosensitization. It has been generally assumed that due to the high probability of excimer formation in polymeric photosensitizers containing aromatic chromophores their photosensitizing efficiency would be relatively low, but as shown in these studies, this is not necessarily true in all cases.

This paper reports the model studies carried out in well defined homogeneous solutions, in which polymers with naphthalene pendant groups are used as the photocatalysts. The photophysical properties of this class of polymers have been extensively investigated [13–35] and they are quite well established. The systems used include copolymers of styrene with 2-vinylnaphthalene (PSN), as well as the homopolymers poly(2-vinylnaphthalene) (PVN), poly(2-isopropenylnaphthalene) (PIP), and poly(acenaphthalene) (PACN). The polymers differ in both the extent of the energy migration and the efficiency of the excimer formation [17,32,35].

The photocatalytic properties of the polymers were tested in the sensitized photoisomerization of provitamin D₃ (7-dehydrocholesterol, DHC). The photochemistry of isomers belonging to the vitamin D family has been studied extensively for many years [36–45]. Irradiation of DHC in organic solvents results in its photoisomerization to previtamin D₃. Unfortunately, the previtamin is not photochemically stable. Once formed, it undergoes a back reaction leading to the regeneration of DHC, and photoisomerization resulting in formation of the side products tachysterol and lumisterol (Scheme 1). All these photoprocesses are reversible and all, except the reaction previtamin ↔ tachysterol, occur via singlet states of the respective molecules. The photoisomerization of previtamin to tachysterol can occur via both the singlet and triplet states. The reaction with participation of the triplet state can be of considerable importance only when induced

^{*} Corresponding author.

¹ Permanent address: Faculty of Chemistry, Jagiellonian University, 30-060 Krakow, Ingardena 3, Poland.



by a properly chosen photosensitizer since intersystem crossing in alkenes is very inefficient.

In a previous paper [10] we have shown that DHC photoisomerization to previtamin occurs in high yields in aqueous solutions of photozymes with naphthalene chromophores such as poly(sodium styrenesulfonate-co-2-vinylnaphthalene) (PSSS-VN) without the formation of undesirable side products.

Table 1
Parameters characterizing the polymers containing naphthalene chromophores

Polymer	Naphthalene content		\bar{M}_n^a	\bar{M}_w^a	$[\eta]^b$	\bar{M}_w/\bar{M}_n
	wt %	mol %				
PSN1	1.4	0.94	35200	54200	0.325	1.54
PSN2	6.2	4.3	42500	65100	0.317	1.53
PSN3	13.0	9.2	36800	56900	0.310	1.55
PSN4	24.0	17.0	41300	65800	0.280	1.59
PSN5	36.0	28.0	36213	56900	–	1.57
PSN6	58.0	48.0	34800	53100	–	1.53
PVN	100.0	100.0	42700	66500	0.245	1.56
PIP	100.0	100.0	4560	4925	–	1.08
PACN	100.0	100.0	32200	–	–	–

^a Determined by GPC.

^b Determined in toluene solution at 25 °C.

2. Experimental

2.1. Materials

The synthesis of the PSN, PVN and PIPN polymers has been described elsewhere [32,35]. PACN (Aldrich) was purified by precipitation from benzene with methanol. The composition of the polymers and their molecular weights are given in Table 1. 7-Dehydrocholesterol (Aldrich, 98%) and lumisterol (kindly provided by Dr. K. Pfoertner, Hoffman-La Roche, Basel) were recrystallized three times from ethyl acetate in an argon atmosphere. Vitamin D₃ (Aldrich, 99 + %) was used as received. Naphthalene (Aldrich, 99%) was purified by triple crystallization from methanol.

Polymer solutions were prepared in tetrahydrofuran.

Ethyl acetate (Aldrich, 99.5 + %), tetrahydrofuran (Caledon, distilled in glass), methanol, cyclohexane and chloroform (all Caledon, spectro grade) were used as received.

2.2. Procedures

2.2.1. Irradiation of samples

The samples were irradiated using two different irradiation systems. For the quantum efficiency determinations the high efficiency high uniformity illumination system (Sciencetech Inc.) equipped with 1000 W mercury/xenon lamp, IR filter, dichroic mirror (260–320 nm) and a 313 nm interference

filter was used. The incident light intensity was determined by using a ferrioxalate actinometer, $I_0 = 1.4 \times 10^{-9} \text{ E s}^{-1}$. For qualitative studies, irradiations were performed by using a Rayonet photochemical reactor (Southern New England Ultraviolet Company), equipped with 16 RPR 3000 Å lamps.

The solutions for irradiation were prepared as follows. The polymer solution in THF was placed in a quartz cell and the oxygen was removed by bubbling with argon for 20 min. The required amount of DHC was dissolved in oxygen-free THF, injected to the polymer solution and the mixture was bubbled with argon for 15 min prior to the irradiation. During this procedure the samples were protected against light and heat. The samples were stirred with a magnetic stirring bar and cooled by blowing air during irradiation.

2.2.2. Quantum efficiency determination

The quantum efficiencies of previtamin formation were determined in polymeric solutions containing the same total concentration of naphthalene chromophores, $c_N = 6.4 \times 10^{-3} \text{ M}$, and the same initial concentration of DHC, $c_{\text{DHC}}^0 = 6.2 \times 10^{-4} \text{ M}$. Under these experimental conditions 96% of the light at $\lambda = 313 \text{ nm}$ was absorbed by the naphthalene chromophores. In each experiment 10 ml of the solution was placed in the quartz cells. The quantum efficiencies were determined at a DHC conversion of about 1%.

2.2.3. Spectral measurements

The UV absorption spectra of the samples were measured using a Hewlett-Packard 8451 diode-array spectrophotometer, and the steady-state fluorescence spectra were recorded at room temperature on an SLM 4800S spectrofluorimeter.

2.2.4. Product analysis

Analysis of the products formed was carried out using a Waters HPLC system with a Whatman Partisil 5 silica gel analytical column (4.6 mm ID, 25 cm) equipped with a Hitachi Model 100-40 spectrophotometer UV detector. A Hewlett-Packard 8451A diode array UV spectrophotometer equipped with an HPLC flow-through quartz cell (1-cm path length, 8 μl volume) connected to the effluent stream of the HPLC was used to take on-line spectra of each component. By use of a simple BASIC program, the spectrophotometer was set to take 60 spectra in 60 s as the eluting component passed through the cell. The monitoring of the spectra of the products through its elution was important to ensure precise separation, and to determine the purity of the compound present in the eluting volume. This was especially important for determination of the content of previtamin because of its poor separation from lumisterol. A mixture of chloroform, cyclohexane, and tetrahydrofuran in the volume ratio 50:50:1 was used as the mobile phase. The products were detected by monitoring their absorption at 254 nm.

The samples for analysis were prepared as follows. The irradiated mixture was slowly added under a stream of argon to deaerated methanol and vigorously stirred with a magnetic stirring bar. This resulted in precipitation of the polymer. The

solvent was then partly removed under reduced pressure at room temperature and the polymer removed by centrifugation in an argon atmosphere. The clear solution which remained was analyzed by HPLC.

3. Results and discussion

3.1. Photophysical characteristics of the polymer

The steady state fluorescence spectra of PSNI and PVN is shown in Fig. 1A. For the PSN copolymers, the ratio of monomer to excimer fluorescence intensity (I_M/I_E) decreases with the concentration of the naphthalene units in the polymer, reaching the lowest value for the PVN homopolymer (see Fig. 1B). Calculation of the distribution function of the 2-vinylnaphthalene units into sequences of various length [46] shows that, although for the copolymers with low content of 2VN (up to 20 mol %) most of the 2VN occurs as isolated units (see Table 2), each of them also contains some longer sequences. The existence of the longer sequences should facilitate both excimer formation and energy migration.

Two other homopolymers used in this study, PIPN and PACN, behave quite differently. PIPN shows very little monomer emission ($I_M/I_E = 0.09$). The high efficiency of excimer formation in the PIPN polymer has been explained by its isotactic conformation which favors a concentration of excimer-forming sites in this sterically crowded polymer [31]. On the other hand, the probability of excimer formation in solutions of PACN is strongly limited by the rigid backbone and lack of flexibility of the naphthalene groups in this polymer ($I_M/I_E = 0.71$).

3.2. Photosensitized isomerization of provitamin DHC

It was observed that all of the polymers used in this study photosensitize the isomerization of DHC at 313 nm with

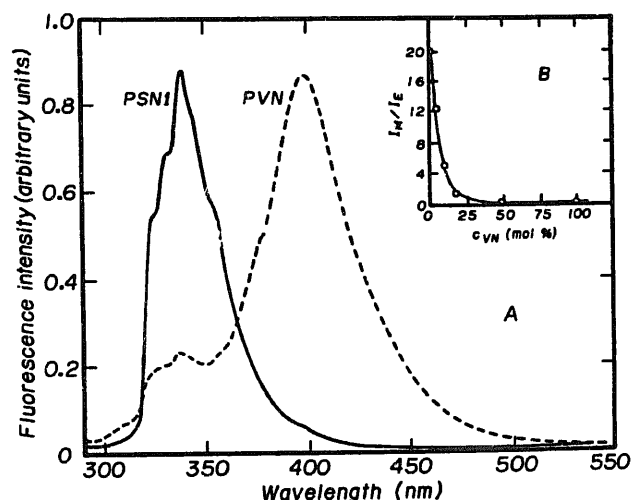


Fig. 1. (A) Steady-state fluorescence spectra of PSNI and PVN in THF solution (room temperature, $\lambda_{\text{ex}} = 254 \text{ nm}$). (B) Dependence of the ratio I_M/I_E on the content of 2-vinylnaphthalene in polymer.

Table 2
Distribution of 2VN units in sequences of various length in PSN copolymers

Polymer	2VN content (mol %)	Distribution of VN units (%)									
		n=1	n=2	n=3	n=4	n=5	n=6	n=7	n=8	n=9	n=10
PSN1	0.94	98.19	1.79	0.02	0.0003						
PSN2	4.30	91.06	8.32	0.57	0.03	0.002					
PSN3	9.20	82.46	15.16	2.09	0.26	0.006					
PSN4	17.0	66.44	24.57	6.81	2.66	0.39	0.09	0.02	0.04		
PSN5	28.0	51.85	29.03	12.19	4.55	1.59	0.53	0.17	0.06	0.02	0.005
PSN6	48.0	27.45	26.14	18.67	11.85	7.05	4.02	2.24	1.21	0.65	0.35

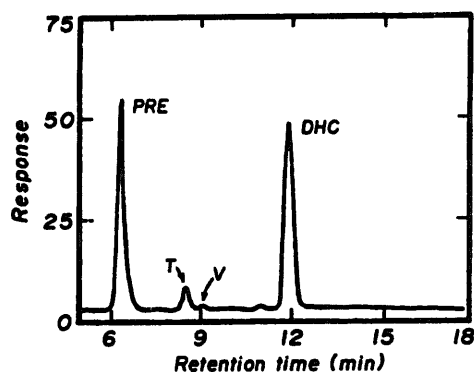


Fig. 2. HPLC traces for the reaction mixture obtained after irradiation of DHC + PVN in THF solution for 8 min with light at $\lambda = 300$ nm, $c_{\text{DHC}} = 5 \times 10^{-4}$ M, $c_{\text{PVN}} = 0.5$ g l $^{-1}$.

nearly the same efficiency. Fig. 2 shows HPLC traces obtained for the reaction mixture from irradiation of DHC + PVN in THF solution in the Rayonet photoreactor with light at $\lambda = 300$ nm for 8 min. It was found that 25.5% of the initial DHC was transformed to products under these conditions. The previtamin was the major product formed (about 96%). The reaction mixture also contained a small amount (about 3%) of tachysterol and vitamin D (about 0.5%). Longer irradiation leads to higher conversion of DHC; e.g., after 60 min of irradiation, 75% of the DHC is converted to products: 92% previtamin, ca. 1% vitamin, and 7% tachysterol.

3.3. Quantum efficiencies of previtamin formation

Fig. 3 shows the dependence of the relative quantum efficiencies of previtamin formation determined in polymer solutions containing the same total concentration of naphthalene chromophores and the same initial concentration of DHC on the content of 2VN in the polymer. The values obtained for PIPN and for PAcN are also presented.

When PSN copolymers were used the quantum efficiencies of previtamin formation decrease with increasing amounts of naphthalene chromophores in the polymer up to about 20 mol %, then increase, reaching the highest value for PVN. This can be explained considering that the photosensitization of DHC can occur due to the energy transfer from the naphthalene 'monomeric' unit. The copolymers with the low content of 2VN have the highest concentration of isolated naphtha-

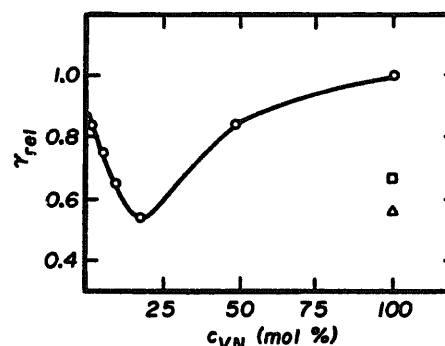


Fig. 3. Dependence of the relative efficiency of previtamin formation for the polymeric sensitizers as a function of the content of 2-vinylnaphthalene in the polymer: (O) PVN, (□) PAcN, (Δ) PIPN.

Table 3
Quantum efficiencies of previtamin D₃ formation

Polymer	Naphthalene content (mol %)	$\gamma \times 10^2$	γ_{rel}
PSN1	0.94	2.40	0.82
PSN2	4.30	2.20	0.75
PSN3	9.20	1.83	0.62
PSN4	17.0	1.70	0.57
PSN5	28.0	2.45	0.83
PSN6	48.0	2.48	0.84
PVN	100.0	2.95	1.00
PAcN	100.0	1.98	0.67
PIPn	100.0	1.65	0.56

lene chromophores (see Table 3). An increase in the amount of 2VN present in the copolymer is accompanied by a decrease in a concentration of isolated units and by a higher probability of excimer formation.

It should be pointed out, however, that the dependence of γ_{rel} on polymer composition is not very pronounced. The comparison of data obtained for the copolymers SN1 and SN20 shows that while the ratio of $I_{\text{M}}/I_{\text{E}}$ decreases about 15 times, the quantum efficiency is lowered by only about 50%. This can be explained assuming that the excitation energy is transferred from excited naphthalene chromophore to the DHC before the excimer is formed or that the energy migration enhances the efficiency of the energy transfer. The first possibility does not seem to be likely in this system, for kinetic reasons. The rate constant of quenching of naphthalene by DHC in THF solution was found to be $(3.0 \pm 0.5) \times 10^9$ M $^{-1}$

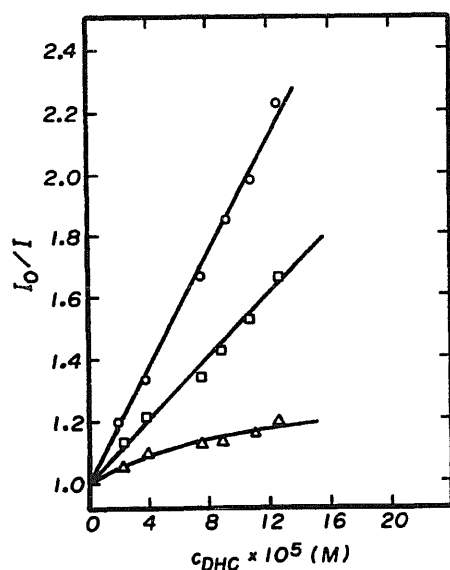


Fig. 4. Stern-Volmer plot for the quenching of polymer fluorescence by DHC: (○) PVN, (□) PACn, (△) PIPN.

s^{-1} [10]. The increase in values of γ_{rel} for the copolymers with longer sequences of naphthalene chromophores and the fact that it reaches its highest value for PVN, seems to indicate that energy migration along the chain minimizes the negative influence of excimer formation on photosensitizing ability of the polymers. This suggestion is supported by the results obtained when PIPN was used as a photosensitizer. This polymer with a very low amount of monomer emission can still photosensitize DHC isomerization, although somewhat less efficiently than PVN. Interestingly, although the PACn displays the lowest efficiency of excimer formation among the naphthalene family homopolymers, it also shows considerably lower efficiency of photosensitization. This may be due to the lower efficiency of the energy transfer from PACn to DHC because of the rigidity of the pendant groups of this polymer which makes the interaction with DHC difficult. The efficiency of energy transfer can also be decreased because the first excited singlet state of PACn is lower in energy than that for PVN ($S_1^{PACn} = 323$ nm and $S_1^{PVN} = 311$ nm).

DHC quenches the fluorescence of all the polymers used (Fig. 4). For PVN and PIPN the quenching can be described by the Stern-Volmer kinetic equation in the concentration range studied ($c_N = 1.5 \times 10^{-3}$ M, $0 < c_{DHC} \leq 2.5 \times 10^{-4}$ M). The dependence of I_0/I vs. DHC concentration determined for PACn deviates considerably from a linearity at DHC concentrations higher than 4×10^{-5} M. The experimentally determined values of the rate of quenching ($K_Q = k_q \tau$, where k_q is the rate constant of fluorescence quenching and τ is the lifetime of the excited singlet state quenched) for PVN and PIPN as well as the value for PACn calculated based on the slope of the initial part of the curve, are listed in Table 4.

The mechanism of the quenching of aromatic hydrocarbons by dienes has been thoroughly studied [47–49]. The results indicate that the process involves specific interactions between these two species, most likely exciplex formation [47]. It seems that the results obtained in this work indicate

Table 4

Rate constants for polymer fluorescence quenching by DHC in THF solution

Polymer	$K_Q \times 10^3$ M $^{-1}$
PVN	9.5
PIPn	5.4
PACn	2.5

that such a mechanism might explain the interaction between the polymeric naphthalene chromophores and DHC. Energy migration along the polymer chain increases the probability of excitation of the naphthalene chromophore located at the exciplex site, thus contributing to a higher quantum yield of photoisomerization of DHC.

4. Conclusions

Polymers containing pendant naphthalene chromophores sensitize photoisomerization of DHC in THF solution with preferential formation of previtamin D₃. The probability of excimer formation increases steadily with an increase in the content of the 2VN chromophores in SPV copolymer. The dependence of the quantum efficiency of formation of previtamin on the polymer composition is quite different; it first decreases with the concentration of 2VN (up to 20 mol %) and then increases, reaching the highest value for PVN. This, and the fact that PIPN (the polymer with exceptionally high efficiency of excimer formation) sensitizes previtamin formation tends to indicate that efficient energy migration in the polymers diminishes the negative effect of the energy dissipation via excimer formation. Energy migration along the polymer chain increases the probability that a naphthalene chromophore located at the naphthalene-DHC exciplex site can be excited and thus induce the photoisomerization of DHC.

Acknowledgements

The financial support of the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged. M.N. thanks the Polish State Committee for Scientific Research for support in the form of a research grant. We thank Dr Yasunori Takeuchi who synthesised the PSN polymers used in these studies.

References

- [1] M. Nowakowska, B. White, J.E. Guillet, *Macromolecules* 21 (1988) 3430.
- [2] M. Nowakowska, B. White, J.E. Guillet, *Macromolecules* 22 (1989) 2317.
- [3] M. Nowakowska, B. White, J.E. Guillet, *Macromolecules* 22 (1989) 3903.

- [4] E. Sustar, M. Nowakowska, J.E. Guillet, *Photochem. Photobiol. A. Chem.* 53 (1990) 233.
- [5] M. Nowakowska, E. Sustar, J.E. Guillet, *J. Am. Chem. Soc.* 113 (1991) 253.
- [6] M. Nowakowska, J.E. Guillet, *Macromolecules* 24 (1991) 474.
- [7] M. Nowakowska, L. White, S. Vogt, J.E. Guillet, *J. Polym. Sci. Polym. Chem. Ed.* 30 (1992) 271.
- [8] M. Nowakowska, H. Bakhtiyari, E. Osselton, M.R. Steele, J.E. Guillet, *J. Photochem. Photobiol. A. Chem.* 63 (1992) 357.
- [9] E. Sustar, M. Nowakowska, J.E. Guillet, *Photochem. Photobiol. A. Chem.* 63 (1992) 357.
- [10] M. Nowakowska, V.P. Foyle, J.E. Guillet, *J. Am. Chem. Soc.* 115 (1993) 5975.
- [11] M. Nowakowska, E. Sustar, J.E. Guillet, *J. Photochem. Photobiol. A. Chem.* 80 (1994) 369.
- [12] D.M. Gravett, J.E. Guillet, *Macromolecules* 28 (1995) 274.
- [13] M.T. Vala, J. Haebig, S.A. Rice, *J. Phys. Chem.* 43 (1965) 886.
- [14] R.F. Cozzens, R.B. Fox, *J. Chem. Phys.* 50 (1969) 1532.
- [15] R.B. Fox, T.R. Price, R.F. Cozzens, *J. Chem. Phys.* 54 (1971) 79.
- [16] C. David, W. Demartean, G. Geuskens, *Eur. Polym. J.* 6 (1970) 1397.
- [17] C. David, M. Lempereur, G. Geuskens, *Eur. Polym. J.* 8 (1972) 417.
- [18] R.B. Fox, T.R. Price, R.F. Cozzens, J.R. MacDonald, *J. Chem. Phys.* 57 (1972) 534.
- [19] Y. Nishijima, Y. Sasaki, M. Tsujisaki, M. Yamamoto, *Rep. Prog. Polym. Phys. Jpn.* 19 (1976) 421.
- [20] S. Ito, M. Yamamoto, Y. Nishijima, *Rep. Prog. Polym. Phys. Jpn.* 19 (1976) 421.
- [21] T. Ishii, S. Handa, S. Mori, Y. Utena, *Rep. Prog. Polym. Phys. Jpn.* 21 (1978) 361.
- [22] S. Ito, Y. Yamamoto, Y. Nishijima, *Rep. Prog. Polym. Phys. Jpn.* 21 (1978) 393.
- [23] C.W. Frank, M.A. Gashgari, *Macromolecules* 12 (1979) 163.
- [24] S.E. Webber, P.E. Avots-Avotins, *Macromolecules* 12 (1979) 708.
- [25] N. Kim, S.E. Webber, *Macromolecules* 13 (1980) 1233.
- [26] R.D. Burkhart, R.G. Avielés, K. Magrini, *Macromolecules* 14 (1981) 91.
- [27] P.D. Fitzgibbon, C.W. Frank, *Macromolecules* 14 (1981) 1650.
- [28] F.C. DeSchryver, K. Demeyer, M. Van der Auweraer, E. Quanten, *Ann. NY Acad. Sci.* 366 (1981) 93.
- [29] S. Ito, M. Yamamoto, Y. Nishijima, *Polym. J.* 13 (1981) 791.
- [30] S.E. Webber, P.E. Avots-Avotins, M. Deurnié, *Macromolecules* 14 (1981) 105.
- [31] J.S. Hargreaves, S.E. Webber, *Macromolecules* 15 (1982) 424.
- [32] D.A. Holden, J. Kovarova, J.E. Guillet, D. Engle, Th. Rhein, R.C. Schulz, *Eur. Polym. J.* 19 (1983) 1071.
- [33] D.A. Holden, X.X. Ren, J.E. Guillet, *Macromolecules* 17 (1984) 1500.
- [34] J.E. Guillet, *Polymer Photophysics and Photochemistry*, Cambridge University Press, Cambridge, UK, 1985.
- [35] J.E. Guillet, S.A.M. Hesp, Y. Takeuchi, in R.L. Clough, S.W. Shalaby, (eds.), *Radiation Effects on Polymers*, ACS Symp. Ser. 475 (1991) p.414.
- [36] See reviews and citations therein: (a) G.M. Senders, J. Pot, E. Havinga, *Fortschr. Chem. Org. Naturst.* 27 (1969) 131; (b) E. Havinga, *Experientia* 29 (1973) 1181; (c) H.J.C. Jacobs, E. Havinga, *Adv. Photochem.* 11 (1979) 305.
- [37] A. Windaus, A. Hess, O. Rosenheim, R. Pohl, T.A. Webster, *Chem. Ztg.* 51 (1927) 113.
- [38] E. Havinga, A.L. Koevoet, A. Verloop, *Recl. Trav. Chim. Pays-Bas* 74 (1955) 1230.
- [39] E. Havinga, R.J. De Kock, M.P. Rappoldt, *Tetrahedron* 11 (1960) 276.
- [40] A.E.C. Snoeren, M.R. Deha, J. Lugtenburg, E. Havinga, *Recl. Trav. Chim. Pays-Bas* 89 (1970) 261.
- [41] K. von Pfoertner, J.P. Weber, *Helv. Chim. Acta* 55 (1972) 921.
- [42] H.J.C. Jacobs, J.W.J. Gielen, E. Havinga, *Tetrahedron Lett.* 22 (1981) 4013.
- [43] V. Malatesta, C. Willies, P.A. Hackett, *J. Am. Chem. Soc.* 103 (1981) 6781.
- [44] S. Gliessing M. Reichenbacher, H.-D. Ilge, D. Fassler, *J. Prakt. Chem.* 2 (1987) 311.
- [45] A.A. Gorman, I. Hamblett, C. Lambert, A.L. Prescott, *Photochem. Photobiol.* 51 (1990) 29.
- [46] C. Tosi, *Adv. Polym. Sci.* 5 (1968) 451.
- [47] J. Puset, R. Beugelmans, *Tetrahedron* 32 (1976) 791.
- [48] S. Murov, G.S. Hammond, *J. Am. Chem. Soc.* 72 (1968) 11.
- [49] L.M. Stephenson, G.S. Hammond, *Pure Appl. Chem.* 16 (1968) 125.