Tetrahydrofuran–Maleic Anhydride Complexes as Photosensitisers for Vinyl Polymerisation

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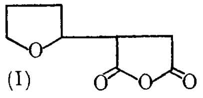
PREVIOUSLY it was found[1] that tetrahydrofuran (T.H.F.) formed a donor–acceptor complex with maleic anhydride, the absorption spectrum of which had a significant "tail" extending beyond 3100 Å into the visible region. Other work[2] shows that donor–acceptor complex formation is a general property of ether–anhydride systems. Irradiation of the T.H.F.–maleic anhydride solutions with light (>3100 Å) induced yellow to violet colour formation and a quantitative yield of the 1:1 adduct (I) was isolated by vacuum sublimation.[1]

It is now reported that addition of vinyl monomers, susceptible to free-radical polymerisation, suppresses the photochemical synthesis of (I) and


(I)

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[1] A. Ledwith and M. Sambhi, submitted to *J. Chem. Soc.*

[2] H. D. Scharf and F. Korte, *Chem. Ber.*, 1965, **98**, 764; *Angew. Chem., Internat. Edn.*, 1965, **4**, 429.

TABLE 1

Photochemical polymerisation of methyl methacrylate in tetrahydrofuran at 50·0°C

Methyl methacrylate[a] ml.	Tetrahydro-furan ml.	Maleic anhydride[b] gm.	Yield of polymer[c] %	$[\eta]$[d] dl./g.	Molecular weight[d] $\bar{M}_v$
5·0	5·0	0·10	14·6	1·00	$4{\cdot}26 \times 10^{5}$
5·0	5·0	0·30	20·8	0·75	$2{\cdot}92 \times 10^{5}$
5·0	5·0	0·60	28·0	0·59	$2{\cdot}12 \times 10^{5}$
5·0	5·0	1·00	36·3	0·40	$1{\cdot}29 \times 10^{5}$
4·0	6·0	1·00	39·4	0·28	$9{\cdot}56 \times 10^{4}$
7·0	3·0	1·00	28·4	0·735	$2{\cdot}85 \times 10^{5}$
9·0	1·0	1·00	15·7	1·725	$8{\cdot}79 \times 10^{5}$
10·0	0·0	0·60	3·9	4·60	$3{\cdot}20 \times 10^{6}$
5·0	5·0	0·00	3·8	2·80	$1{\cdot}66 \times 10^{6}$

[a] Prepolymerised *in vacuo* immediately before distilling into reaction vessel.

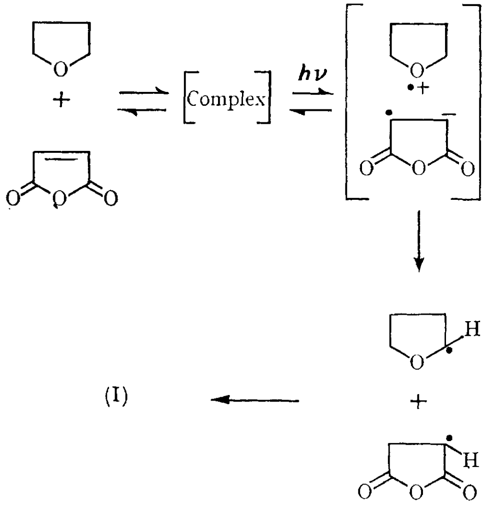
[b] Freshly sublimed.

[c] Polymerisation was carried out in glass vessels by irradiation for four hours with a Mazda ML/D, 250-watt mercury-vapour lamp, at a distance of twelve inches.

[d] Measured in benzene at 30·0°C. $\bar{M}_v$ was calculated using the expression derived in reference 9.

results in polymerisation of the added vinyl monomer. Typical results, using methyl methacrylate are shown in Table 1, and although these results were obtained using highly purified materials and working under high vacuum, similar results were obtained when working in air. The results show that increasing the concentration of the maleic anhydride–T.H.F. complex caused an increase in rate of polymerisation and a decrease in polymer molecular weight, suggesting that the maleic anhydride–T.H.F. complex functions in a manner similar to more conventional free-radical initiators.[3] In support of this conclusion it was further observed that copolymerisation of maleic anhydride occurred according to the well known relative monomer reactivities in free-radical polymerisations.[3] Thus there was no incorporation of maleic anhydride when methyl acrylate was used as monomer, but with vinyl acetate and isobutyl vinyl ether rapid and quantitative (based on maleic anhydride) formation of the well known 1 : 1 alternating copolymers occurred. In the latter reactions polymerisation stopped as soon as all the initiator was copolymerised.

Ether–anhydride complexes have recently been used to facilitate photochemical formation of cyclobutane derivatives from alkyl olefins[2] and in special circumstances to induce by photolysis the cationic polymerisation of *N*-vinylcarbazole and cyclic ethers.[4—6] It seems reasonable to assume therefore that the initial donor–acceptor complex, when photoactivated, gives rise to radical-ion formation *e.g.*



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[3] C. H. Bamford, W. C. Barb, A. D. Jenkins ,and P. F. Onyon, "The kinetics of vinyl polymerisation by radical mechanisms", Butterworths, London, 1958.

[4] K. Takakura, K. Hayashi, and S. Okamura, *J. Polymer Sci., Part B, Polymer Letters*, 1964, **2**, 861.

[5] C. E. H. Bawn, A. Ledwith, and A. Parry, unpublished results.

[6] K. Takakura, K. Hayashi, and S. Okamura, *J. Polymer Sci., Part B, Polymer Letters*, 1965, **3**, 565.

[7] R. Ward, *J. Chem. Phys.*, 1963, **38**, 852.

[8] L. Ellinger, *Polymer*, 1964, **5**, 559; H. Scott, G. A. Miller and M. M. Labes, *Tetrahedron Letters*, 1963, 1073. A. Ledwith and M. Sambhi, *Chem. Comm.*, 1965, 64. C. E. H. Bawn, C. Fitzsimmons, and A. Ledwith, *Proc. Chem. Soc.*, 1964, 391.

[9] T. G. Fox, J. B. Kinsinger, H. F. Mason, and E. M. Schuele, *Polymer*, 1962, **2**, 71.

The alternative possibility that a low-lying triplet (biradical) state of maleic anhydride is readily formed in these systems cannot be completely eliminated, although an oxidation similar to that shown above was proposed[7] to account for the formation of strong e.s.r. signals when pyromellitic dianhydride was irradiated in T.H.F. solution.

Clearly the nature of donor–acceptor complexes offers especially wide scope for similar photochemical and thermal[8] initiation reactions and several systems are currently being investigated.

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