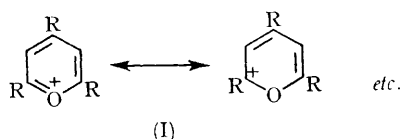


## Pyrylium Salts as Initiators for Vinyl Polymerisation

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THE use of donor-acceptor complexes as initiators for vinyl polymerisations is now well established, especially for monomers such as *N*-vinylcarbazole and alkyl vinyl ethers.<sup>1-3</sup> Tropylium cation is a particularly good electron acceptor<sup>4,5</sup> and has been shown to initiate cationic polymerisations.<sup>2</sup> In principle, other planar cationic systems, known to be electron acceptors,<sup>6</sup> should also function as initiators for cationic polymerisation and this has now been substantiated.



2,4,6-Trimethylpyrylium hexachloroantimonate<sup>7</sup> (I, R = Me) is a white crystalline material very stable in air and initiates vinyl ether polymerisation at a rate which is somewhat slower than the propagation reaction.<sup>2</sup> The systems remain colourless throughout and water-white poly(alkyl vinyl ether) can be precipitated at the end of each reaction. Viscosity average molecular weights are also slightly higher than can be obtained under similar conditions with other homogeneous catalysts making pyrylium salts particularly advantageous for vinyl ether polymerisation. With *N*-vinylcarbazole as monomer there is clear evidence of coloured complex formation between catalyst and monomer, especially at temperatures below 0°C.

In the investigation of these monomer-catalyst

TABLE: Vinyl polymerisations initiated by 2,4,6-trimethylpyrylium hexachloroantimonate in CH<sub>2</sub>Cl<sub>2</sub>

Monomer	[Monomer] mole/l.	10 <sup>4</sup> [Catalyst] mole/l.	Temp. °C	Yield <sup>a</sup> %	[η] <sup>b</sup> dl./gram.
Isobutyl vinyl ether .. ..	0.66	9.9	25	93	0.10
	2.12	9.9	25	99	0.16
	3.06	9.9	25	98	0.20
	2.12	3.3	25	100	0.16
	2.12	0.66	25	70	0.17
	2.12	9.9	0	100	0.18
	2.12	9.9	-25	100	0.23
<i>N</i> -Vinylcarbazole .. ..	0.09	6.0	25	90	0.31
	0.20	6.0	25	91	0.34
	0.38	6.0	25	99	0.38
	0.52	6.0	25	100	0.39
	0.90	6.0	25	98	0.43
	1.25	6.0	25	96	0.44

<sup>a</sup> Polymerisations were carried out in air for 30 min. and the polymer was recovered by precipitation into methanol. Actual reaction times were probably less than ten minutes in most cases.

<sup>b</sup> Measured in benzene at 25.0°C.

Pyrylium salts (I) have resonance forms which are very similar to the propagating carboxonium ion in vinyl ether polymerisation and in fact are very useful initiators. Typical data for polymerisation of isobutyl vinyl ether and *N*-vinylcarbazole are shown in the Table.

complexes it is expedient to use the highly coloured 2,4,6-triphenylpyrylium tetrafluoroborate (I, R = Ph) as initiator. This compound gives overall polymerisation results similar to those shown in Table 1 but initiates at a much slower rate and consequently the initiation reaction can be studied

<sup>1</sup> L. P. Ellinger, *Chem. and Ind.*, 1963, 1982; *Polymer*, 1964, 5, 559. H. Scott, G. A. Miller, and M. M. Labes, *Tetrahedron Letters*, 1963, 1073.

<sup>2</sup> C. E. H. Bawn, C. Fitzsimmons, and A. Ledwith, *Proc. Chem. Soc.*, 1964, 391.

<sup>3</sup> C. E. H. Bawn, A. Ledwith, and A. Parry, *Chem. Comm.*, 1965, 490.

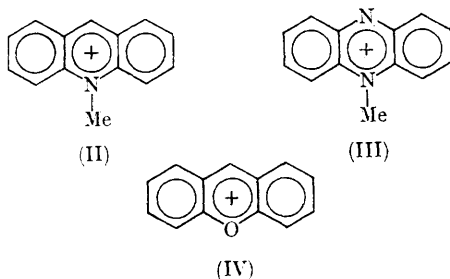
<sup>4</sup> M. Feldman and S. Winstein, *J. Amer. Chem. Soc.*, 1961, 83, 3338.

<sup>5</sup> A. Ledwith and M. Sambhi, *Chem. Comm.*, 1965, 64.

<sup>6</sup> M. Feldman and S. Winstein, *Tetrahedron Letters*, 1962, 853.

<sup>7</sup> For details concerning preparation of pyrylium salts see: A. T. Balaban and C. D. Nenitzescu, *Org. Syntheses*, 1965, 44, 98.

by observing the disappearance of the initiator colour.



*N*-Methylacridinium (II) and *N*-methylphenazonium salts (III) likewise initiate cationic polymerisation of vinyl ethers and *N*-vinylcarbazole,

the rates of initiation being slower in  $\text{CH}_2\text{Cl}_2$  than when using 2,4,6-trimethylpyrylium salts, but faster than those obtained using 2,4,6-triphenylpyrylium salts. However, xanthylum salts (IV) react violently with these monomers and the resulting polymerisations are not reproducible. For all the catalysts employed, rates of initiation are much faster in more polar solvents such as nitromethane.

With the planar cationic systems used, the nature of the gegen-ion is important only in controlling the solubility of the cation-salt. Detailed investigation of these initiation reactions is now in progress and preliminary results indicate that donor-acceptor complex formation is important in all cases.

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