Cationic and Free Radical Propagation of Copolymerization by the N-*Vinyl Carbazole Cation-radical*

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Copolymerization of N-*vinyl carbazole (NVC) and* p-*methoxy styrene in ethylene dichloride* ($EtCl_2$) *at 25°C gives copolymers of virtually identical composition whether the reaction is initiated by the cationic reagent* BF_3OEt_2 *or by the typical electron-acceptor tetracyanoethylene* (TCNE), provided the latter system is shielded from daylight. *The propagation mechanism is concluded to be cationic in both cases. The derived reactivity ratios are:*

$r_1(NVC) = 21{\cdot}4 \pm 0{\cdot}81;$
$r_2 = 0{\cdot}13 \pm 0{\cdot}005$ (BF_3OEt_2)
$r_1 = 20{\cdot}1 \pm 1{\cdot}5;$
$r_2 = 0{\cdot}09 \pm 0{\cdot}01$ (TCNE)

A photochemically induced copolymerization is found in daylight with TCNE–$EtCl_2$ *and with* $EtCl_2$ *alone giving copolymers slightly richer in* p-MeO *styrene. Evidence is offered that under these conditions, both cationic and a parallel free radical propagation mechanism can proceed. The reactivity ratios for the cationic copolymerization by* BF_3OEt_2 *show virtually no change over the temperature range 25° to 0°C.*

THE polymerization of *N*-vinyl carbazole by electron-accepting organic compounds is generally believed to be initiated by a cation-radical species, but the question whether the chains are propagated by the cationic or by the free radical 'function' has not yet been definitely settled. Though most general arguments and some specific evidence point to the former, the overall rates are generally low compared to those of most cationic polymerizations. It has therefore seemed worthwhile to apply the classic test of mechanism by measurement of the relative reactivity ratios in copolymerization.

These ratios in unequivocal free radical copolymerization are already known for the system NVC–styrene and indicate that an NVC radical has only a relatively low reactivity. A study of the NVC–styrene system initiated by cupric chloride ($CuCl_2$) in tetrahydrofuran (THF) as solvent has been made by Okamura and co-workers[1]. Their results, which show the copolymer to have predominantly NVC composition, definitely favour cationic propagation ($r_1 > 7$; $r_2 = 0{\cdot}01 \pm 0{\cdot}01$), but this very great difference in the reactivities of these two monomers makes for considerable quantitative uncertainties especially in r_1.

In this study NVC has been copolymerized with *p*-methoxystyrene whose reactivity in cationic polymerization is at least an order of magnitude greater than that of styrene. Even so, NVC is found to be heavily favoured in the copolymerization, whether the reaction be initiated by an authentic cationic catalyst (BF_3OEt_2) or by a typical electron-acceptor, tetracyanoethylene (TCNE).

A complicating factor is that NVC itself undergoes a slow photochemical polymerization in ethylene dichloride ($EtCl_2$). This does not affect rapid copolymerizations induced by active catalysts, but in the slow reactions induced by TCNE different copolymer compositions and apparent reactivity ratios are obtained from reactions carried out in the dark and in daylight.

Most copolymerization theory and procedures have been developed for free radical systems. In such systems molecular weights are normally high and both the reactivity ratios are of the same order of magnitude—conditions which are often absent in the ionic copolymerizations. It has been established here that the molecular weights of the copolymers are sufficiently high for the effects of initiation, termination and transfer reactions on the composition to be discounted.

The large difference in monomer reactivities causes a considerable 'drift' in monomer composition during the conversion, even when this is small. The differential form of the copolymerization equation is therefore unsuitable for calculation of the reactivity ratios (r_1, r_2). Using the integrated form of the equation, a computer calculation has been devised[2] which adapts the well-known 'method of intercepts', and gives appropriately weighted average values of r_1 and r_2 and their standard deviations.

Where, as in this case, the monomers differ greatly in reactivity, homopolymerization of the more reactive component may in principle be a complicating factor. This possibility is examined here (and excluded) by an experimental fractionation of the copolymer and theoretical arguments in the discussion.

EXPERIMENTAL METHODS

Materials

p-*Methoxy styrene*—Two samples were used, one commercial (Koch-Light) and one synthesized by the method of Mannich and Jacobsen[3] modified by the addition of a dehydration stage, on potassium hydrogen sulphate ($KHSO_4$), to complete the dehydration of the carbinol. After fractional distillation, storage over calcium hydride (CaH_2) *in vacuo,* and a final trap to remove distillates before use, both samples appeared identical showing less than one per cent impurity by analytical gas–liquid chromatography (GLC) (5 ft Carbowax column at 170°) and identical behaviour in copolymerization. Preparative GLC proved impracticable due to the formation of deposits on the detector elements.

N-*vinyl carbazole* (Schuhardt)—was recrystallized under nitrogen three times from methanol (m.pt 64·5°C) and stored *in vacuo.*

TCNE (Koch-Light and Eastman)—was repeatedly sublimed *in vacuo* through glass wool until pure white crystals were obtained (m.pt 199° to 200°C).

Boron trifluoride etherate (BF_3OEt_2)—and the solvent $EtCl_2$ were purified as described previously[4].

COPOLYMERIZATION PROCEDURE

The reactions were conducted in stoppered test tubes under nitrogen. The monomers were weighed in and the solvent added by pipette.

The reactions were stopped with methanol followed by precipitation from cold methanol and repeated washing of the precipitate with hot methanol (to remove the not very soluble NVC). Samples were then dried to constant weight *in vacuo*.

Analysis

The copolymer composition was conveniently determined (on milligramme samples) using the u.v. absorption in chloroform ($CHCl_3$) solution at 295·5 and 344 mμ. At these wavelengths the extinction coefficients of NVC are 47·5 and 16·5 respectively (C in g/l.), large in comparison with those of *p*-methoxy styrene (0·3 and ~0). At both wavelengths Beer's law is obeyed and the deduced values of the NVC percentage agree to within two per cent. The results are found to correlate well with compositions determined by nitrogen analysis (Dr Bernhardt).

% NVC by % N	26·5	54·5	56	67·5	78
% NVC from spectra	26·0	53·5	55	64	78

Molecular weights

Mechrolab instruments were used (VPO for $\overline{M}_n < 20\,000$ and a membrane osmometer for higher molecular weights), measurements being made at 25°C in benzene and toluene respectively.

EXPERIMENTAL RESULTS

Rates of copolymerization

These were not measured systematically, but are very different with the two initiators used. At total monomer concentration ~1M, convenient yields (say, ten per cent) were obtained in from two to ten minutes with 10^{-4}M BF_3OEt_2 but required five days with 2×10^{-2}M TCNE (both in $EtCl_2$ at 25°C). With no added initiator negligible copolymer was formed in five days in the dark but about ten per cent in daylight.

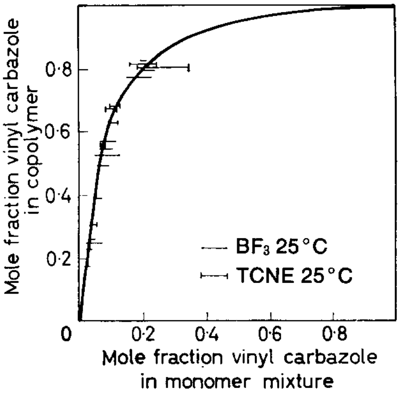

Figure 1—Curve calculated, for zero drift, from mean computed values of r_1, r_2. (Horizontal lines connect initial and final monomer mole fraction.)

Copolymer compositions

In a few trial experiments using styrene as comonomer with NVC and BF_3OEt_2 as initiator, the product was indistinguishable from pure poly-NVC.

With *p*-methoxy styrene, copolymers were obtained having compositions 20 to 90 per cent NVC according to initial monomer ratio, as indicated in *Figure 1*, which also shows the 'drift' in monomer composition during the conversions. This figure demonstrates clearly the predominant reactivity of the NVC and the qualitatively identical effect of the two different initiators BF_3OEt_2 and TCNE.

Quantitatively, the values of reactivity ratios (r_1, r_2) shown in *Table 1* confirm this conclusion. These values are derived from the copolymer compositions and conversions by the computer calculation explained in detail in ref. 2.

Table 1. Reactivity ratios

Initiator	*Conditions*	*No. of compositions*	r_1	r_2
BF_3OEt_2, 10^{-4}M	25° daylight	12	21·4 ± 0·81	0·13 ± 0·005
BF_3OEt_2, 10^{-4}M	0° daylight	10	23·2 ± 1·9	0·09 ± 0·01
TCNE, 5×10^{-2}M	25° dark	8	20·1 ± 1·48	0·095 ± 0·01
TCNE, 5×10^{-2}M	25° daylight	8	15·1 ± 1·2	0·13 ± 0·01
None	25° daylight	6*	14·9 ± 3·2	0·16 ± 0·08

*Only four compositions gave usable 'intersections'.

Molecular weights of copolymers

Copolymers prepared at 25°C under typical conditions (concentration and conversions) were found to have number average molecular weights, $\overline{M}_n$, of 18 000 (BF_3OEt_2) and 12 000 (TCNE-initiated).

Fractionation of copolymer

A high-conversion copolymer (initiated by BF_3OEt_2) containing 26 wt % NVC was fractionated from toluene solution by precipitation using *n*-amyl alcohol at 25°C. *Table 2* shows the conditions of fractionation and properties of the fractions.

Table 2. Fractionation of copolymer

Fract. No.	*Amyl alcohol vol. %*	*Cumulative wt %*	$\overline{M}_n$	*% NVC*
1	30·0	5·2	59 200	55·5
2	35·7	21·0	61 500	41·0
3	38·6	41·0	60 500	22·0
4	40·1	56·0	57 000	22·0
5	43·4	80·8	38 300	20·0
6	49·5	85·2	19 700	21·0
7	57·3	94·2	11 700	23·5
8	66·0	98·2	2 500	23·5

DISCUSSION

It is commonly assumed, without further consideration, that the product from simultaneous polymerization is a true copolymer. Usually, especially in free radical polymerization, this is a safe assumption, but where the apparent reactivity ratios differ very considerably, as here, some doubt must remain whether the product might be, wholly or in part, a mixture of homopolymers. The fractionation experiment is an attempt to test this question.

As *Table 2* shows, this BF_3OEt_2 initiated product has the lower three quarters of its material of constant composition, independent of molecular weight. The highest molecular weights are fractionated also by composition. The interpretation of this behaviour is therefore not entirely unambiguous. The considerably higher-than-average content of NVC in the first two fractions might be thought to imply that there was some pure poly-NVC here (and perhaps in all fractions) which might be separated by a more efficient fractionation. Such a conclusion, however, would go beyond the facts. In a high conversion copolymerization such as this, the more rapid consumption of the more reactive monomer changes the monomer ratio enough to produce very different copolymer compositions at the beginning and end of the conversion. The high NVC content of the first fraction is in fact close to the value calculated for the first five per cent conversion assuming the reactivity ratios calculated from all compositions. Another general argument against the presence of homopolymers in the product is that the cumulative weight distribution shows no sign of the two-stepped form found commonly with polyblends.

We conclude that the products formed by BF_3OEt_2 and by TCNE in the dark are true polymers and give valid reactivity ratios characteristic of the propagating species (since the molecular weights are high enough to eliminate errors associated with any anomalous initiation or termination processes). The products of the light-accelerated copolymerizations may contain mixtures (of different copolymers) as discussed later.

The virtual identity of the reactivity ratios implies then that the electron-transfer-initiated polymerization by TCNE in the dark is propagated by the same species as is produced by BF_3OEt_2. Chains initiated by TCNE grow as cations and not as radicals.

On the discrepancy between the reactivity ratios with TCNE in darkness and in light, the following comments may be made. First, the difference between r_1 values of 21 and 15 may seem large but in fact (because $r_1 \gg r_2$) it arises from a very small difference in the composition of the different products. In other words, the propagation mechanism in the 'light-accelerated' reaction is still essentially cationic. The discrepancy must arise from some complicating factor associated with the capacity of the chlorinated solvent itself to facilitate a light-sensitized polymerization. The following evidence from studies in the related solvent, carbon tetrachloride (CCl_4), suggests that in these solvents a parallel, free-radical reaction path becomes possible.

NVC in CCl_4 has been the subject of many conflicting reports. Thus, Chapiro and Hardy[5] and Breitenbach *et al.*[6,7] state that this monomer will polymerize in CCl_4 in the dark, whereas Ellinger[8] and Biswas and Ghosal[9] find no such dark reaction but a ready polymerization in sunlight.

Breitenbach and Srna found that NVC in CCl_4 showed no tendency to copolymerize with methyl methacrylate even when the cationic initiator sulphuric acid–amyl ether was added. On the other hand, Biswas and Ghosal claim that the product from the light-sensitized reaction contained a proportion of methyl methacrylate, and proposed a free-radical copolymerization initiated by $\cdot CCl_3$ radical from

$$NVC + CCl_4 \xrightarrow{h\nu} \text{Complex} \longrightarrow [NVC\cdot]^+Cl^- + \cdot CCl_3$$

Our (qualitative) evidence is that uncatalysed NVC does not polymerize in toluene solution in light or in dark, nor in $EtCl_2$ *in the dark.* In this latter solvent in daylight a slow polymerization takes place, and also copolymerization with *p*-methoxy styrene. The product of this photochemical copolymerization is on the whole closely similar to that from TCNE–$EtCl_2$ in daylight (see *Table 1*) but also shows some evidence that the copolymer equation is not being fully obeyed. Thus of the six compositions examined under these conditions, two (the richest in *p*-methoxy styrene) gave products *abnormally* rich in this monomer, so much so that their compositions could not be used in the reactivity ratio calculations. This behaviour is what would be expected if, as well as the 'normal' copolymerization, there was in addition some propagation by free radical, incorporating chiefly the *p*-methoxy styrene monomer.

The likely conclusion is therefore that in the absence of TCNE, i.e. in the purely photochemical polymerization and copolymerization, *both* the species postulated by Biswas and Ghosal, the NVC radical cation and a solvent free-radical species, are present and initiate cationic and free radical chains respectively.

In the 'light-accelerated' copolymerization by TCNE the same is most probably true, but with the free radical mechanism partially suppressed by the excess TCNE (which is a known free radical inhibitor).

For the copolymerization initiated by BF_3OEt_2 the difference in reactivity ratios at 25° and 0°C is within the experimental error for r_1 and only just outside it for r_2. Such a small temperature coefficient is quite normal and indicates that this system shows none of the anomalous behaviour, with relatively high temperature dependence, found in the cationic copolymerizations of α-methyl styrene[10].

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