

The Polymerization of Vinylcarbazole by Electron Acceptors

III—Initiation by Lithium Chloride, Bromide and Iodide

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The polymerization of N-vinylcarbazole is initiated by lithium chloride, bromide and iodide, the activity of the halides increasing in that order. Conversions of over 85 per cent can be attained with lithium iodide at 70°C; chain transfer is substantial. No copolymer is formed with styrene and the proportion of isobutyl vinyl ether incorporated into the copolymer is much smaller than that obtained using cationic initiation. The polymerization is insensitive to oxygen, but is retarded or inhibited by electron donors stronger than the monomer. Polymerization is therefore neither free-radical nor cationic and the initiation is ascribed to increased mesomeric polarization due to association of the N-vinyl lone pair electrons with the lithium cation, the anion exerting a reinforcing effect depending on its nucleophilic power.

LITHIUM salts especially lithium chloride promote a variety of chemical reactions. In donor solvents lithium chloride behaves as a base, dehydrohalogenating 4-halo-3-ketosteroids¹ and polyvinyl chloride^{2, 3} and initiating the polymerizations of *N*-carboxy- α -amino acid anhydrides⁴ and of acrylonitrile⁵. The donor solvent is also an essential feature in the acceleration of the free radical initiated polymerization of acrylonitrile by lithium chloride in dimethylformamide^{5, 6}. Transfer to both carbon tetrabromide or triethylamine is promoted by the lithium chloride-solvent combination, and association of the nitrile group at the propagating free radical site with either Li⁺ or Cl⁻ has been postulated to explain this⁵. The base catalytic effect of the lithium salts in the presence of the donor solvent is ascribed to the tendency of the small Li⁺ to become solvated by electron donors much more than the chloride ion³. The radius of the solvated cation is much greater than that of the unsolvated anion, and the charge density on the surface of the anion is correspondingly greater. Thus the anion tends to remove cations from neighbouring molecules most commonly as protons.

The electron distribution in donor molecules should be affected when these solvate the lithium cation⁷. The effect of lithium chloride on a donor monomer such as *N*-vinylcarbazole should therefore resemble that of other electron acceptors⁸.

EXPERIMENTAL

(A) *Materials*

N-Vinylcarbazole (B.A.S.F.) was recrystallized from methanol¹⁸ and cyclohexane; m.pt 64.7°C.

Isobutyl vinyl ether (I.C.I. Ltd) was fractionated through a two foot column packed with Fenske glass helices the middle cut being used; b.pt 82.9-83.1°C/760 mm Hg.

Styrene (Forth Chemicals Ltd) was fractionated and the centre cut used; b.pt 39.4–39.6°C/12 mm Hg.

Pyromellitic dianhydride (B.D.H. Ltd) was sublimed *in vacuo*, m.pt 286°C.

Lithium chloride monohydrate (B.D.H. Ltd) was dried by heating *in vacuo*⁵, or more satisfactorily was purified and dried according to Lynch⁹.

Lithium bromide (B.D.H. Ltd) was dried by heating at <0.1 mm Hg/200°C for 24 hours.

Anhydrous lithium iodide was conveniently prepared in a high state of purity from lithium hydride and iodine in ether solution¹⁰; the preparation was improved by the use of a large excess (>100 per cent) of lithium hydride.

Boron trifluoride etherate (B.D.H. Ltd) was redistilled. Azobisisobutyronitrile (Laporte Ltd 'Genitron' L.M. grade) was used without further purification.

(B) Polymerizations

These were carried out in bulk at 70°C with stirring in the dark, generally under nitrogen. No colour developed during the polymerizations. The products were dissolved in benzene (8 ml per g monomer) and precipitated by the addition of methanol (40 ml per g monomer). After filtration the polymer was washed thoroughly with water, then with methanol and finally dried at 75°C/1 mm Hg for at least 24 hours.

(C) Evaluation

Copolymer compositions were determined by elementary analysis, and the results were supported by i.r. spectra. The i.r. spectra of the isobutyl vinyl ether copolymers prepared by lithium chloride, iodide or azobisisobutyronitrile initiation showed that a much smaller proportion of vinyl ether units were present than in the copolymer prepared by boron trifluoride etherate initiation.

Intrinsic viscosities were determined in 0.15% w/vol. benzene solution at 25°C in an Ostwald viscometer.

Molecular weights were determined in benzene solution in a Mechrolab 301A vapour pressure osmometer, extrapolating to infinite dilutions.

The molecular weight distribution of a *N*-vinylcarbazole-isobutyl vinyl ether copolymer prepared by lithium iodide initiation was determined by gel permeation chromatography (GPC) on a Waters column using tetrahydrofuran as a solvent at 25°C.

RESULTS AND DISCUSSION

Lithium chloride, bromide and iodide all initiate the polymerization of *N*-vinylcarbazole, the rate of polymerization increasing in that order (Table I). With lithium iodide conversions of over 85 per cent are attained more rapidly than with weak organic electron acceptors or molecular dipoles^{11, 12}, and it is probable that the high viscosity of the medium progressively slows polymerization and ultimately limits conversion.

The polymerization is much retarded by dimethylformamide and completely inhibited by dimethyl sulphoxide when these donors are added

Table 1. Polymerization of *N*-vinylcarbazole by lithium chloride, bromide and iodide; polymerization temperature, 70°C

Polymerization				Polymer						
<i>N</i> -Vinylcarbazole 10^{-2} mole	Initiator		Additive 10^{-4} mole	Atmosphere	Time, h	Yield		Intrinsic viscosity η_{sp}/C (C_0H_0)	Molecular weight M_n	
		10^{-4} mole				g	%		Found	Calc.
6.4	LiCl	11.6	nil	N ₂	1.83	0.073	0.59	1.978	—	10 615
5.96	LiCl	10.9	nil	N ₂	24	0.69	6.0	0.280	1 540	10 422
7.72	LiCl	13.9	nil	N ₂	49.75	10.8	72.5	0.157	2 592	10 808
7.6	LiBr	14	nil	N ₂	1.9	0.15	1.03	0.206	2 980	10 422
3.65	LiI	13.9	nil	N ₂	0.5	6.12	86.8	0.0734	2 607	5 076
3.94	LiI	15	nil	air	0.5	6.56	86.3	0.0967	2 724	5 076
2.65	LiI	5.3	nil	N ₂	3.0	4.3	84.15	0.144	2 693	9 650
3.37	LiI	6.7	hydroquinone	N ₂	3.0	5.75	89.1	0.125	3 136	9 650
3.5	LiI	7.0	dimethylformamide	N ₂	3.0	1.8	26.7	0.066	3 169	9 650
3.03	LiI	6.11	dimethyl sulphoxide	N ₂	3.0	negligible	—	—	—	9 650

NOTE: The mole ratio dimethylformamide/LiI and dimethyl sulphoxide/LiI are 1.48 and 1.86.

Table 2. Attempted copolymerizations of *N*-vinylcarbazole and isobutyl vinyl ether or styrene in presence of various initiators

N-Vinyl carbazole 10^{-2} mole		Polymerization			Polymer						Vinylcarbazole-comonomer. Molar ratio		
4.0	Isobutyl vinyl ether	10^{-3} mole	Initiator	Polymn time, h	Yield on total monomers		Mol wt M_n	N %	O %	M_w/M_n	Intrinsic viscosity η_{sp}/c (C_2H_5)	In monomer mixture	In copolymer
					g	%							
4.0	Isobutyl vinyl ether	2.0	LiCl	68	1.3	13.4	1 380	6.71	0.93	185-195	0.038	2.0	8.39
3.63	Isobutyl vinyl ether	3.62	LiI	3	4.3	38.1	1 690	6.36	1.66	150-160	0.026	1.0	4.48
2.0	Isobutyl vinyl ether	2.0	$BF_3 \cdot Et_2O$	rapid	5.3	90.5	5 950	4.99	5.28	—	0.105	1.0	1.05
2.0	Isobutyl vinyl ether	2.0	Azobisisobutyronitrile	4	3.75	64.0	very high	6.94	1.02	—	1.050	1.0	7.62
1.0	Isobutyl vinyl ether	1.0	Pyromellitic dianhydride	24 (at 80°C)	0.75	25.6	2 230	7.03	1.16	—	0.1003	1.0	6.64
2.3	Styrene	4.6	LiI	3	1.8	19.5	—	7.17	—	205-215	0.038	0.5	Pure poly-N-vinylcarbazole
2.0	Styrene	2.0	$BF_3 \cdot Et_2O$	rapid	3.6	60.6	9 568	7.17	—	—	0.229	1.0	Pure poly-N-vinylcarbazole
2.19	Styrene	2.11	Azobisisobutyronitrile	4	0.65	10.0	Very high	1.38	—	—	0.545	1.04	0.122

in molar quantities only little greater than that of the lithium iodide. This supports the view that the lithium cation is preferentially solvated by the strongest donor present in the reaction medium



(VC, vinylcarbazole; the broken arrow represents a solvating bond). The initiation is therefore related to the accepting power of the lithium cation.

The effect of other donor molecules is ascribed to their displacing the vinylcarbazole from solvating the lithium cation. Donor molecules (dimethylformamide, dimethylsulphoxide, amines, ethers etc.) should similarly retard or inhibit the polymerization of vinylcarbazole by electron acceptors, if the analogy between the effect of the latter and of these lithium salts is well founded.

Copolymerization experiments with isobutyl vinyl ether and with styrene show a pattern for lithium iodide initiation which resembles that following initiation by pyromellitic dianhydride but which differs from that following initiation by boron trifluoride etherate or by azobisisobutyronitrile (*Table 2*).

That the polymerization by lithium iodide has no free radical character is indicated by the absence of any effect of oxygen or of hydroquinone, and by the formation of poly-*N*-vinylcarbazole free from polystyrene when polymerization of a mixture of the corresponding monomers is attempted. Following free radical initiation a *N*-vinylcarbazole-styrene copolymer is formed¹⁶, but there is no copolymerization following cationic initiation.

The copolymerization experiments also indicate a mechanism which is not cationic; whereas isobutyl vinyl ether is incorporated into a copolymer following lithium iodide initiation, the proportion of the vinyl ether is much smaller than that found upon cationic polymerization under otherwise similar conditions. The copolymer also resembles the product prepared when using pyromellitic dianhydride as initiator.

The homogeneity of the vinyl ether copolymer prepared by lithium iodide initiation was tested by fractional precipitation. A sample of isobutyl vinyl ether copolymer (2 g N, 6.36; O, 1.66%) prepared by lithium iodide initiation was fractionally precipitated from benzene (200 ml) solution by methanol addition. Following the first (0.57 g) fraction (N, 6.56; O, 1.21%) and several small fractions (total 0.41 g), the final fraction (0.59 g) was found to contain N, 6.28; O, 1.69%. The differences in composition between fractions are thus small and it is unlikely that a mixture of products formed by different polymerization mechanisms has been obtained. This result was confirmed by GPC, a single, smooth, symmetrical and rather narrow peak pointing to the homogeneity of this copolymer.

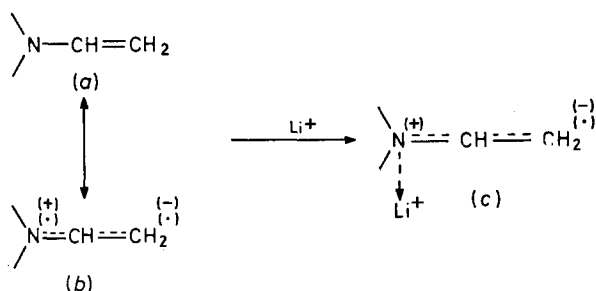
The results of the copolymerization experiments using lithium iodide as the initiator differ from those in which boron trifluoride etherate is the initiator and in which the mechanism must be regarded as cationic. The view that lithium iodide initiates cationically by a mechanism involving complete charge transfer is hardly tenable, involving as it does the conversion of a lithium cation to a lithium atom.

The differences in the catalytic activities of the lithium halides are

probably in part due to wide differences in solubility. No data are available for *N*-vinylcarbazole, but in acetonitrile at 25°C the solubilities of lithium chloride and iodide are 0.14 g and 154 g per 100 ml respectively¹⁷.

The results indicate that on solvating the lithium cation the electron distribution in vinylcarbazole is so altered as to lead to polymerization. It is suggested that this electron shift is similar to that caused by electron acceptors^{8, 11}. This is reasonable since both solvation and electron donation are centred on the lone pair electrons of the nitrogen. As noted above the solvation of the lithium cation cannot involve complete electron transfer and corresponds therefore to interaction with an electron acceptor too weak to cause complete electron transfer^{8, 11}.

The effect on the mesomeric *N*-vinyl structures of the monomer (a) and (b) of solvation is represented by (c):



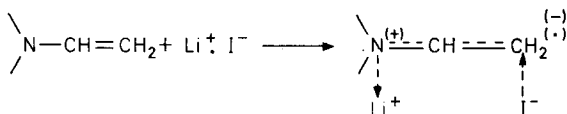
where (+) and (-) represent partial charge, (·) a partial unshared electron and the broken arrows solvating bonds. The mesomeric uncomplexed monomer structure (b) is preferred to that involving complete charge

separation: $\text{N}^+ = \text{CH} - \text{CH}_2^-$ as this is subject to severe steric hindrance.

If the lithium cation is solvated by the monomer, the anion should show basicity. This is unlikely to promote the polymerization; indeed lithium chloride, which following cation solvation should show greater base activity than lithium iodide¹, is the less effective polymerization initiator. Moreover *N*-vinylcarbazole is not polymerized by anionic initiators, but is converted to carbazole¹³.

Some contribution may, however, be ascribable to the donor activities of the halide anions. Thus lithium chloride, bromide, iodide and thiocyanate form complexes with organic acceptors such as *s*-trinitrobenzene and chloranil^{14, 15}. The larger the anion the greater should be its nucleophilic power. In the present instance this would reinforce the polarizing effect of the solvated lithium cation. With the iodide the effect should be greater than with the chloride ion. It is suggested that it is mainly this effect which accounts for the superior catalytic activity of the iodide over the chloride. The interaction of vinylcarbazole with lithium iodide which leads to initiation

therefore resembles that of molecular dipoles¹²:



It is concluded therefore that the role of these lithium salts under the present conditions is very similar to that of weak electron acceptors and of molecular dipoles, and that these lithium salts show nucleophilic reactivity in the presence and electrophilic reactivity in the absence of an added donor.

It is considered that as with weak electron acceptors and molecular dipoles initiation and propagation proceed by a mechanism involving the addition of monomer activated by solvation to similarly activated monomer or polymer molecules^{8, 11}. The initial polymerization rate should therefore be proportional to $[(\text{Li}^+)^2]$ rather than $[\text{Li}^+]$. No kinetic data have been obtained but it is notable that in presence of only a minor proportion of styrene which in this context may be regarded as diluent the polymerization is very much slower than in bulk.

The molecular weights of the polyvinylcarbazole prepared by lithium halide initiation are lower than calculated from the monomer/salt ratios. A similar effect is typical for the polymerizations initiated by weak electron acceptors and is ascribed to transfer to monomer^{8, 11}. This will be controlled by the relative solvating power of monomer and of polymer units and end

groups; it is thought that only the terminal $\begin{array}{c} \diagup \\ \diagdown \end{array} \text{N}-\text{C}=\text{CH}_2$ (R polymer

R

chain) group of the polymer contributes appreciably to solvation of the lithium cation.

The polymerizations proceed to high conversions and are probably limited by the viscosity of the medium. There is no evidence of oxidative and other termination reactions which are characteristic of polymerizations carried out under conditions (strong electron acceptor, possibly also ionizing solvent) favouring the formation of charged (cation radical⁸ or cation²¹) propagating species.

Polyvinylcarbazole is the major product when vinylcarbazole is heated with a minor proportion of acceptor monomer (methyl methacrylate, acrylonitrile); a smaller quantity of copolymer is formed also^{8, 11, 12}, but no homopolymer of the electrophilic monomer has been isolated¹². Similar findings have been reported recently using a large excess of acrylonitrile¹⁹. If formation of the polyvinylcarbazole involves electron transfer as is suggested¹⁹, formation of polyacrylonitrile (or polymethyl methacrylate) would be expected. The formation of the copolymer appears to involve a free radical mechanism^{13, 19}; the effect of a donor upon these polymerizations may further elucidate their mechanism which is thought to involve partial charge transfer.

The polymerization of vinylcarbazole by hydrated lithium perchlorate and by other metal salts²⁰ appears to have very different features from the polymerization reported here.

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