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Effect of Impurities on the Polymerization of Vinylcarbazole by Azobisisobutyronitrile

L. P. ELLINGER*, *The British Oxygen Company Limited, Scientific Centre, London, England*

Synopsis

Polymerization of vinylcarbazole by free-radical initiators, especially azobisisobutyronitrile, yields polymer of higher molecular weight and better appearance than can be made by thermal polymerization. The polymerization is retarded and the molecular weight of the polymer lowered by amounts of anthracene comparable to or somewhat larger than the initiator concentration, but these effects soon show saturation at higher anthracene concentrations. Phenanthrene has a slight inhibiting effect which increases with concentration, the polymerization being almost completely inhibited at very high phenanthrene concentrations. The results are discussed in terms of the formation of an intermediate complex between the aromatic hydrocarbon and the growing polymer chain.

INTRODUCTION

Polymerization of vinylcarbazole can proceed by various mechanisms, including thermal and free-radical initiation. Thermal initiation even of pure monomer results in rather highly and unevenly colored polymer of moderate molecular weight. Better products are obtained by free-radical initiation with peroxides; in bulk polymerization di-*tert*-butyl peroxide in absence of oxygen has been claimed to give polymer of improved appearance and molecular weight.[1,28] The di-*tert*-butyl peroxide may be the sole initiator or an azo compound such as azobisisobutyronitrile may be added as accelerator. The di-*tert*-butyl peroxide–azobisisobutyronitrile system has also been used to initiate the polymerization in aqueous dispersion.[2,27]

Consideration of this initiator system suggests that improved products should be obtainable by use of the azo compound as sole initiator, since peroxides are liable to induced decomposition whereas azobisisobutyronitrile is not subject to this.[3] This has indeed been found to apply in bulk polymerization,[4] the products obtained with azobisisobutyronitrile alone being transparent, clear, and almost colorless (instead of yellow) and of higher molecular weight. In the aqueous dispersion polymerization the azo compound appears to be the only effective initiator, the di-*tert*-butyl peroxide having no marked effect upon the polymerization.

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* Present address: Research Department, The Distillers Company, Ltd., Great Burgh, Epsom, Surrey, England.

The concentration of azobisisobutyronitrile required for the best results in bulk polymerization is only 0.005–0.01%, and a very pure monomer is needed. Morpholine,[5] stearyl alcohol,[6] and amides and imides of formic and acetic acid[7] have been specified as stabilizers or retarders of the free-radical polymerization of vinylcarbazole. The effects of impurities which might be present in this monomer are of particular interest. Statements regarding anthracene are conflicting. 1% of anthracene and to a lesser extent phenanthrene are claimed to retard the polymerization initiated by 1% of di-*tert*-butyl peroxide,[8] but anthracene is stated to have no significant effect upon the thermal[2] or high energy electron[9]-initiated polymerization.

Anthracene has now been found to be present in commercial grade vinylcarbazole in concentrations (0.03–0.05%) in which it exerts a marked retarding effect upon the bulk polymerization by azobisisobutyronitrile.

The nature of the effect of both anthracene and phenanthrene upon the polymerization has revealed a quite complex pattern.

The mass spectrum of vinylcarbazole indicates the presence of 9-ethylcarbazole in the monomer, and several 9-alkylcarbazoles have been examined for their effect upon both the bulk and aqueous dispersion polymerizations. The latter include 9-(1′-methoxyethyl)carbazole,[10] which may be formed as impurity upon the recrystallization of the monomer from methanol.

EXPERIMENTAL

Materials

9-Vinylcarbazole (BASF Chemicals Ltd.) was the once- or twice-recrystallized grade. The once-recrystallized grade was recrystallized further from methanol[27] before use as stated, m.p. 67.4°C. 9-Methylcarbazole (Light & Co. Ltd.) was recrystallized twice from methanol, m.p. 88°C. 9-Ethylcarbazole, was prepared according to Levy[11] and recrystallized from methanol, m.p. 66–67°C. 9-*n*-Propylcarbazole[11] was recrystallized from methanol, m.p. 48–49.5°C. 9-Allylcarbazole was prepared according to Levy,[11] before an improved method became available,[12] yield 70.5%, recrystallized from methanol, m.p. 71.5°C. Tetrahydrocarbazole was prepared from cyclohexanone and phenylhydrazine and recrystallized from ethanol, m.p. 113–114°C.[13]

Anthracene (Hopkins & Williams Ltd.), purified grade, was sublimed twice and recrystallized from benzene, m.p. 217°C. Phenanthrene was recrystallized from benzene, m.p. 100°C.

Azobisisobutyronitrile was from Whiffen & Sons Ltd., low metal grade. Di-*tert*-butyl peroxide, *tert*-butyl hydroperoxide, and methyl ethyl ketone peroxide grades HA and SD (Laporte Chemicals Ltd.).

Nonex 64, poly(ethylene glycol) 1000 mono oleate was from Union Carbide Ltd.

Argon and nitrogen White Spot grade (B.O.C. Ltd.).

Bulk Polymerizations

Bulk polymerizations were carried out under an inert atmosphere (nitrogen or argon). The polymerizations listed in Table I were carried out in an autoclave under 30–40 atm. of nitrogen. The monomer was melted in a beaker, and the initiator was quickly mixed into the melt. The beaker and contents were heated in the autoclave to a maximum temperature of 120–160°C. during 3–6 hr. After a further 2–4 hr. near this temperature, the autoclave was allowed to cool in 6–10 hr. For the other bulk polymerizations the monomer was heated just above its melting point, and any additive, followed by the azobisisobutyronitrile (0.01%, unless stated otherwise), was mixed in quickly. The mixture was outgassed with inert gas at atmospheric pressure, and the temperature was raised to and maintained at 80°C. The product was dissolved as rapidly as possible in a hot 0.1% solution of hydroquinone in benzene (5 ml./g. original monomer). The polymer was precipitated by methanol addition (6 ml./g. of original monomer), and the polymer was extracted with boiling methanol (4 × 6 ml./g.). This purification proved adequate, except in experiments in presence of a high proportion of anthracene, which required repeated precipitation of the polymer.

TABLE I
Bulk Polymerization of Vinylcarbazole by Heat, or by Di-*tert*-butyl Peroxide or by Azobisisobutyronitrile, Alone or Together
(Vinylcarbazole: twice-recrystallized grade)

Polymerization on monomer, %			Polyvinylcarbazole	
Azobisiso-butyronitrile	Di-tert-butyl peroxide	Conversion %	Relative viscosity	Appearance
0	0		1.74	Fractured, yellow and dark brown
0	0.02		2.30	Yellow, clear
0.01	0.02		4.08	Yellow, some fractures
0.01	0.02		3.16	Yellow, clear
0.01	0.02		4.24	Yellow, clear
0.01	0	92.8	5.81	Almost colorless, clear
0.01	0		4.69	Almost colorless, clear
0.005	0	87.0	4.97	Almost colorless, clear

Polymerizations in Aqueous Dispersion

Vinylcarbazole (200 g.) and the additive (if any) were dispersed in an aqueous solution of Nonex 64 (0.225 g.) in distilled water (710 ml.), the temperature being raised with stirring (wing stirrer, 700 rpm). Peroxide

(0.4 g., if any) was introduced at 65°C., and at 70°C. a concentrated acetone solution of azobisisobutyronitrile (4 g.) was added. The polymerization soon became exothermic, and 5 min. after passing through a maximum temperature the reaction was discontinued. The polymer was washed with water, extracted with acetone, and dried.

Polarography

Polarographic determinations followed the procedure of Given and Peover[14] with the use of tetrabutylammonium iodide in dimethylformamide. Vinylcarbazole produced a weak, broad peak in the polarogram near the anthracene peak at −1.56 v. Allowance was easily made for this, and the method proved adequately quantitative for anthracene concentrations greater than 0.006% in vinylcarbazole and in polyvinylcarbazole.

Viscometry

Relative viscosities were determined in an Ostwald viscometer with the use of a 1% solution of the polymer in benzene at 20°C.

RESULTS

The polymerization of vinylcarbazole in bulk by thermal initiation, and by either di-*tert*-butyl peroxide or azobisisobutyronitrile alone, or both together have been compared (Table I). With slightly inferior monomer (once-recrystallized grade, recrystallized from methanol) and 0.01% azobisisobutyronitrile almost colorless polymer of relative viscosities 3.03, 3.12 was obtained in bulk polymerization.

In aqueous dispersion the polymerization appears to be controlled by azobisisobutyronitrile, di-*tert*-butyl peroxide having little effect upon its progress or upon the product.

Replacing this peroxide by other peroxides or hydroperoxides of lower decomposition temperatures had a deleterious effect (Table II).

TABLE II
Effect of Peroxides on Azobisisobutyronitrile-Initiated Polymerization of Vinylcarbazole in Aqueous Dispersion

	Polyvinylcarbazole		
Peroxide	Yield, %	Relative viscosity	Appearance
None	92	2.39	Foamed granules
Di-*tert*-butyl peroxide	93.6	2.39	Foamed granules
tert-Butyl hydroperoxide	82	1.75	Cohering granules
Methyl ethyl ketone HA	86	1.95	Lumps
Methyl ethyl ketone SD	71.5	2.39	Foamed granules

9-Allylcarbazole and tetrahydrocarbazole were the only carbazole derivatives to lower the molecular weight of the polymer upon polymerization (Tables III and IV).

The aqueous dispersion polymerization in presence of 9-allylcarbazole yielded a single polymer lump, but from all others foamed granules were obtained.

The addition of as little as 0.01% anthracene to monomer (once-recrystallized grade, recrystallized once from methanol to contain less than 0.006% of anthracene) significantly lowered the rate of the polymerization in bulk and the molecular weight of the polymer (Table V). Lower concentrations of anthracene may have some effect, but were insufficient to prevent a rise in temperature, which accompanies the rapid polymeriza-

TABLE III

Effect of the Addition of Carbazole Derivatives upon the Bulk Polymerization of Vinylcarbazole

Polymerization			Polymer	
Additive				
Carbazole	% on monomer	Time, min.	Yield, %	Relative viscosity
None	0	5	80	4.58
9-Ethylcarbazole	1.0	8.5	73	4.71
9-(1′-Methoxyethyl) carbazole	1.0	6	70	4.74
9-(1′-Methoxyethyl) carbazole	10.0	10	72	4.74
9-Allylcarbazole	1.0	9	70	2.92
tetrahydrocarbazole	2.0	9	72	2.59

TABLE IV

Effect of the Addition of 9-Alkylcarbazoles upon the Free-Radical-Initiated Polymerization of Vinylcarbazole in Aqueous Dispersion

Polymerization					Polymer	
Additive			Max. temp.			
Carbazole	% on monomer	Vinyl-carbazole, g.	°C.	At time after AZDN addn., min.	Yield, %	Relative viscosity
None	0	200	85	6	76.5	2.65
None	0	200	85	7	75	2.74
None	0	200	83	9	71	2.44
Methylcarbazole	4.7	193	85.5	8	77.3	2.31
Ethylcarbazole	5.3	190	86	10	78.2	2.24
Ethylcarbazole	5.3	190	85	11	82.5	2.02
n-Propylcarbazole	5.4	193	84.5	14	81.3	2.04
Allylcarbazole	5.3	193	81.0	14	78	1.49

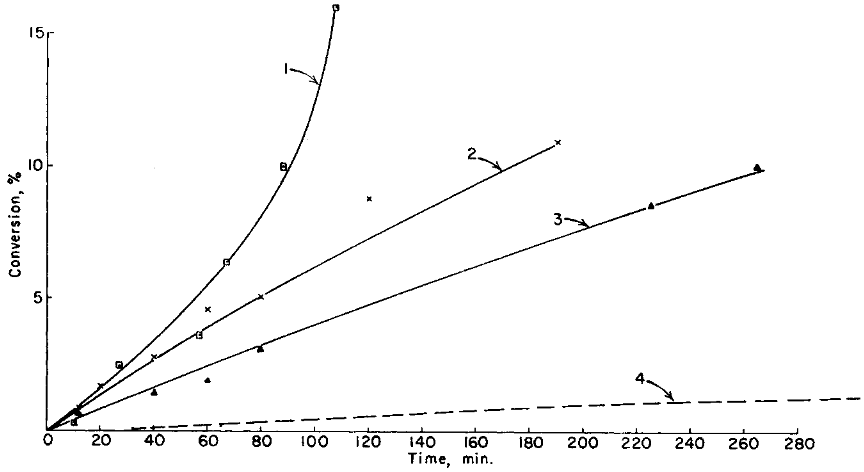

Fig. 1. Retarding effects of anthracene and phenanthrene on polymerization of vinylcarbazole by azobisisobutyronitrile: (*1*) anthracene, 0.02%; (*2*) anthracene, 0.04%; (*3*) anthracene, 0.08; (*4*) phenanthrene, 5%. Azobisisobutyronitrile, 0.01%; temperature, 80°C.

tion as it progresses under almost adiabatic conditions. The effect upon the kinetics is shown in Figure 1, where it can be noted that at the lowest anthracene concentration (0.02%), the effect of rising temperature results in some acceleration of the polymerization. The effect of very much higher concentrations of anthracene was also examined. The range of anthracene concentrations was limited by the solubility of anthracene in the monomer. Polymer essentially free of anthracene (0.02%) had the same ultraviolet and infrared adsorption spectra as polymer prepared in the absence of anthracene, there being no difference in the peak heights aromatic C=C/C=N. None of the reported bands due to dihydroan-

TABLE V
Effect of Anthracene Upon the Bulk Polymerization of Vinylcarbazole[a]

Anthracene, % on monomer	Time at 80°C. or above, min.	Max. temp., °C.	Polymer Yield, %	Polymer Relative viscosity
0	4	150	82	4.37
0	3	High	75	4.76
0.001	4	150	68	3.79
0.005	6	150	63	4.20
0.01	25	80	14	2.71
0.05	140	80	10	1.70
3.2	2760	80	55.0	1.21
10	1620	80	57.25	1.26
10	4170	80	55.0	1.27

[a] Anthracene content of monomer, <0.006%; phenanthrene content of monomer, undetectable.

thracene could be detected in the ultraviolet spectrum.[15] The nitrogen content is that calculated for the pure polymer.

Free-radical-initiated bulk polymerization of vinylcarbazole was retarded somewhat by phenanthrene, although under these conditions the temperature of the reaction mixture rose far above that of the oil bath, but without any change of the molecular weight of the polymer. A high concentration of phenanthrene (5%) effectively inhibited the polymerization (Fig. 1).

TABLE VI
Effect of Phenanthrene upon the Free-Radical-Initiated Bulk Polymerization of Vinylcarbazole[a]

			Polymer	
Phenanthrene, % on monomer	Time at 80°C., or above, min.	Max. temp., °C.	Yield, %	Relative viscosity
0	4	140	76	3.65
0.01	4	160	80	3.09
0.05	7	170	77	3.15
0.2	11	150	78	3.61
0.5	22	140	77	3.26
5.0	1440	80	2.8	1.43

[a] Anthracene content of monomer, <0.006%; phenanthrene, not detectable.

DISCUSSION

The thermal polymerization of vinylcarbazole clearly gives rather irreproducibly products of unsatisfactory appearance and molecular weight.[1,28] It seems to be readily inhibited and to proceed most readily with very pure monomer (see also Scott et al.[16]). Both control and reproducibility of the polymerization are greatly improved by a free-radical initiator. The results show that the azo compound alone at as low a concentration as 0.005% yields a product of higher molecular weight and of appreciably better appearance than the use of a peroxide alone, or in mixture with an azo compound, and this can be ascribed to induced decomposition of the peroxide.[3]

With azobisisobutyronitrile in low concentration as sole initiator, the quality of the bulk polymer and especially its molecular weight becomes very sensitive to the quality of the monomer. Of the 9-alkylcarbazoles and related compounds only 9-allylcarbazole showed an appreciable effect, lowering the molecular weight of the polymer. The effect can be ascribed to the stability to be expected in the free radical derived from the allyl derivative. A similar effect is caused also by tetrahydrocarbazole, the >NH hydrogen presumably facilitating chain transfer.

Anthracene was present in the vinylcarbazole in concentrations (0.03–0.05%) in which it affects bulk polymerization by azobisisobutyronitrile, but one or at most two recrystallizations[27] lowered the anthracene concentration below detection level. This monomer, although presumably not absolutely pure, gave reproducible results.

Anthracene is known to retard the free-radical-initiated polymerization of vinyl acetate,[17] of methyl methacrylate,[18] and of acrylonitrile,[19] lowering the molecular weight of polyacrylonitrile formed.[19] Thermally or photochemically initiated polymerization of styrene leads in presence of anthracene to a copolymer,[20–23] and a copolymer is also formed between 1,3-butadiene and anthracene upon free-radical-initiated dispersion polymerization.[15] Phenanthrene does not affect the free-radical-initiated polymerization of acrylonitrile,[19] and although copolymerization of styrene and phenanthrene by free-radical-initiation has been described,[24] this finding has been disputed.[15] The greater effect of anthracene than of phenanthracene has been explained in terms of their respective free valence numbers.[15]

Anthracene also retards the anionic polymerization of styrene with formation of a 1:1 complex.[25,26]

No dihydroanthracene–vinylcarbazole copolymer was detected in polyvinylcarbazole polymerized by azobisisobutyronitrile in the presence of even the highest anthracene concentration. The retardation of the polymerization and lowering of the molecular weight of the polyvinylcarbazole resemble those observed in the retardation of the azobisisobutyronitrile-initiated polymerization of acrylonitrile at 50°C.,[19] but the saturation of these effects in presence of the higher anthracene concentrations was not noted in the latter case.

The absence of any induction period, except possibly at the highest anthracene concentration, indicates that under these conditions anthracene does not react significantly with azobisisobutyronitrile or the free radicals formed upon its thermal decomposition. The results can be explained by the (reversible) formation of a complex between the free radical growing polymer chain and the anthracene. This complex must be sufficiently readily formed to account for the effect of even a very small concentration of anthracene and its stability such as to explain the retardation. It is concluded that the complex is a much less efficient initiator than the free radicals derived from azobisisobutyronitrile.

The possible role of polar factors in the formation of the postulated complex is uncertain. These were assumed to be involved in the retardation by anthracene of the azobisisobutyronitrile-initiated polymerization of acrylonitrile, but the observed effect in this case has been stated to be greater than would be expected.[19]

Reaction of the complex (radical–anthracene) with monomer would result in formation of dihydroanthracene–monomer copolymer, whereas its reaction with another free radical would provide a termination reaction, which should limit polymerization.

The particular reaction path is presumably determined by steric and polar factors.

The variety of possible reactions of the complex can account for some of the reported effects of anthracene upon free-radical-initiated vinyl polymerizations and should depend not only on the monomer, but upon all other conditions of the polymerization.

The rather inefficient inhibition by phenanthrene may be explained either by preferential reaction of the azobisisobutyronitrile or of the free radicals derived from it with phenanthrene or by reaction of an unstable intermediate corresponding to the one postulated for polyvinylcarbazole–anthracene with a further free radical. The latter can account for the slow formation of a little polymer of lower molecular weight with simultaneous inhibition of the polymerization in presence of a large excess of phenanthrene. It is also more consistent with the finding that phenanthrene does not retard the azobisisobutyronitrile-initiated polymerization of acrylonitrile,[19] though differences of temperature and of other conditions may explain this inconsistency.

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Résumé

La polymérisation du vinylcarbazole avec des initiateurs radicalaires, spécialement l'azobisisobutyronitrile, donne un polymère de poids moléculaire plus élevé et d'aspect meilleur que le polymère obtenu par polymérisation thermique. La polymérisation est retardée et le poids moléculaire abaissé en ajoutant de l'anthracène en quantités comparables ou quelque peu plus élevées que celles de l'initiateur. Mais ces effets présentent une saturation avec des concentrations plus élevées en anthracène. La phénanthrène a un léger effet inhibiteur qui augmente avec la concentration, la polymérisation étant presque complétement inhibée pour des concentrations élevées en phénanthrène. On a interprêté les résultats en faisant intervenir un complexe intermédiaire entre l'hydrocarbure aromatique et la chaîne polymérique en croissance.

Zusammenfassung

Die Polymerisation von Vinylcarbazol mit radikalischen Startern, besonders Azobisisobutyronitril, liefert ein Polymeres mit höherem Molekulargewicht und besserem Aussehen als es durch thermische Polymerisation erhalten wird. Die Polymerisation wird durch Anthrazenmengen, die vergleichbar mit oder etwas grösser als die Starterkonzentration sind, verzögert und das Molekulargewicht des Polymeren erniedrigt; diese Effekte zeigen aber bei höherer Anthrazenkonzentration bald Sättigung. Phenanthren besitzt einen schwachen Inhibitoreffekt, welcher mit der Konzentration zunimmt. Bei sehr hohen Phenanthrenkonzentrationen wird die Polymerisation fast vollständig verhindert. Die Ergebnisse werden auf Grundlage eines intermediären Komplexes zwischen dem aromatische Kohlenwasserstoff und der wachsenden Polymerkette diskutiert.

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