

Polyvinylcarbazole Foams. I. Preparation

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Synopsis

The polymerization of vinylcarbazole in aqueous dispersion by azobisisobutyronitrile can yield—depending on the protective colloid used—polyvinylcarbazole beads or granules. These require impregnation by a polymer solvent and preferably also by azobisisobutyronitrile before they can be molded to panels or simple shapes.

INTRODUCTION

Polyvinylcarbazole has since its first discovery evoked interest, especially owing to its good dielectric properties at radar frequencies and a softening range above those of polystyrene, polyethylene, and even polyurethanes.^{1,2} The bulk polymer is very hard and rather brittle. It has been commercially available as a molding powder made by polymerization of vinylcarbazole in hot aqueous dispersion initiated by alkaline dichromate^{3,4} and marketed in Germany as Luvican M-150 and in U.S.A. as Pollectron.

Polymerization in aqueous dispersion⁵ with the use of a free-radical initiator system of di-*tert*-butyl peroxide and azobisisobutyronitrile^{6,7} has yielded porous polymer beads or granules, which could be molded under light pressure to simple shapes of densities down to 0.1–0.2 g./cc. At 20°C. the dielectric constant of polyvinylcarbazole in such moldings ranged between 2.92 and 3.15, both at 1 and 44 Mcycle/sec., while the power factors under the same conditions were in the range $8-16 \times 10^{-4}$.⁵

The preparation of foamed polyvinylcarbazole by molding a mixture of polyvinylcarbazole powder and trihydrazinotriazine has been claimed.⁸ Several patents describe the making of polystyrene and of styrene-vinylcarbazole copolymer foams, by dispersion of the polymer powder in a solvent-nonsolvent mixture, followed by heating of the impregnated polymer.⁹⁻¹¹ In another process,¹² which might appear more appropriate to polyvinylcarbazole, the polymer is dissolved in a low-boiling solvent (methylene dichloride), the solution is dispersed in water, and most of the solvent is removed by nitrogen spraying. The resultant granules are partly dried and molded hot with appreciable expansion, densities down to 0.03 g./cc. being claimed. A method for obtaining reticulated porous polymers from several vinyl polymers, including poly(vinyl chloride), involves the impregnation of the bulk polymer with a plasticizer followed by its removal.¹³

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The present work is limited to the polymerization of vinylcarbazole to foamed beads and granules and the molding of these in the density range 0.04–0.2 g./cc.

Vinylation of carbazole is at present the only important source of the monomer. Impurities in the latter are mainly introduced with the carbazole, and of these sulfur compounds⁵ and anthracene¹⁴ are known to have a deleterious effect upon its free radical-initiated polymerization. Fortunately monomer available from B.A.S.F. Chemicals Ltd. proved sufficiently free from sulfur-containing impurities, and the best quality material (twice-recrystallized grade, unfortunately no longer available) contained too little anthracene to affect the aqueous dispersion polymerization. However, the once-recrystallized grade monomer was found to contain enough anthracene to exert a harmful effect¹⁴ and to require purification of the monomer.

Bulk polyvinylcarbazole of improved appearance and of higher molecular weight is obtained with the use of azobisisobutyronitrile as sole initiator^{14,15} rather than together with di-*tert*-butyl peroxide.⁵⁻⁷ In aqueous dispersion di-*tert*-butyl peroxide has now been found not to affect the polymerization initiated by azobisisobutyronitrile.

The size of the expanded polymer granules depends on the conditions of polymerization. Very small granules do not expand on molding. Granules of 0.5–1.5 mm. in diameter, described hereafter as beads, and larger granules of 0.5–5 mm. diameter, described hereafter as granules, expand on molding.

The aqueous dispersion polymerization requires quite careful control of conditions if a reproducible and satisfactory product is to be obtained; conditions for the polymerization of up to 2 kg./batch were established.

The polymer granules and beads from which acetone-soluble impurities and most volatiles have been removed expand on heating above 170°C., but when molding to a density below 0.2 g./cc. was attempted, intergranular cohesion upon molding was found to be very poor. Impregnation of the granules with dioxane or benzene and with azobisisobutyronitrile¹⁶ resulted in much-improved molding properties and panels up to 6 × 6 × 2 in. or 12 × 12 × 1 in. were molded satisfactorily from polymer granules down to a density of 0.05 g./cc. It was hoped that moldings of a more uniform porous structure could be obtained from polymer beads, and conditions for molding these into panels (6 × 6 × 1 in.) at a density of 0.1 g./cc. were established.

The molding of a simple shaped structure from impregnated granules was attempted successfully.

MATERIALS

N-Vinylcarbazole (B.A.S.F. Chemicals Ltd.) was the once-recrystallized grade. A superior (twice-recrystallized) grade monomer suitable for the dispersion polymerization without further purification was available only during the earlier part of the work.

Azobisisobutyronitrile (AIBN) was Genitron (Whiffen & Sons Ltd.), L.M. grade. This was the only one of several grades satisfactory for the polymerization, and was used also for impregnation.

Di-*tert*-butyl peroxide was obtained from Laporte Chemicals Ltd.

Poly(vinyl alcohol) was Elvanol (Du Pont Ltd.), grades 52:22 and 51:05.

Polyvinylpyrrolidone was from B.O.C. Ltd.

Poly(ethylene glycol)-1000 monooleate, Nonex 64 (Union Carbide Ltd.), was used. The results from several samples showed this to be the best protective colloid for aqueous dispersion polymerization to polyvinylcarbazole granules, but with more recent samples persistently bad results were obtained. This reagent was apparently made by half esterification of poly(ethylene glycol) of average molecular weight 1000, but of undefined molecular weight distribution. For satisfactory results a narrow cut poly(ethylene glycol) seems necessary. Other poly(ethylene glycols) used were poly(ethylene glycol)-200 monolaurate, Nonex 31; poly(ethylene glycol)-200 monostearate, Nonex 54; poly(ethylene glycol)-400 mono laurate, refined, Nonex 139; poly(ethylene glycol)-600 monooleate, Nonex 52; poly(ethylene glycol)-1000 monolaurate, Nonex 94; and a mixed poly(ethylene glycol)monooleate, Nonex 33, consisting of equal parts of the monooleates of poly(ethylene glycol)-300 and poly(ethylene glycol)-1540. The numbers in each case refer to the aggregate molecular weights of the poly(ethylene glycols) (all Union Carbide Ltd.).

Porofor BSH (75% benzene sulfohydrazide, 25% paraffin oil), Porofor TR (substituted thiotriazole), Porofor D33 powder (diphenylsulfone disulfohydrazide), Porofor B13/CP 50 (50% benzene disulfohydrazide, 50% chlorinated paraffin), and Porofor S44 (a disulfohydrazide) were all Bayer A.G. products, obtained through K.M. Steel, Manchester.¹⁷

Dioxane was from Griffin & George Ltd., technical and analar grades.

Methylene dichloride, chloroform, carbon tetrachloride (B.D.H. Ltd. and Griffin & George Ltd.) were laboratory grade.

B.S. Plasticiser (*n*-butyl cyclohexyl phthalate) was from Howard's of Ilford.

Silicone stop-cock grease was from Edwards High Vacuum Ltd.

Oxygen and nitrogen were White Spot grade; argon was from British Oxygen Co. Ltd.

EQUIPMENT

Dispersion polymerizations up to a batch scale of 800 g. monomer were carried out in mold-blown, dome-shaped Pyrex vessels (A.D. Wood, Ltd.), (5 in. deep, 5 in. i.d., 750 ml. capacity; 7 in. deep, 6 in. i.d., 2 l. capacity; or 9½ in. deep, 7 in. i.d., 3.2 l. capacity). These were closed by a stainless steel top plate, fitted with a nylon-packed stirrer gland, a charging port, and openings for a thermometer and a condenser, and provided with suitable positioned holes for fixing to a stirrer frame. The top plate was fitted to the glass vessel by a rod frame of suitable size and was held in position by bolts. Agitation and heating were provided by stirrers sited in a bank

equipped to hold three vessels in a water bath fitted with an immersion heater. The bank was fitted with a constant speed motor ($\frac{1}{8}$ h.p., 1440 rpm) and a variable speed gear drive, allowing stirrer speeds of 200–1100 rpm.

For polymerization of 800–1800 g. monomer a 10-l. bolt head flask or a 20-l. polypropylene vessel was used; these were heated and stirred in a separate rig designed to hold only one of these.

The wing stirrer developed for the 200-g. scale was made from 17 gauge stainless steel plate, 6–7 mm. wide, of a diameter of 12.5 cm. and a height of 6.0 cm., and was found to be satisfactory up to a batch scale of 1.8 kg.

Molded foamed polymer panels were made in a simple press built round two brass ($\frac{1}{2}$ in. thick) platens of about 13×14 in. Each of these was fitted with an electric heater element rated at 6 kw. and controlled by a thermostat (Diamond H, Electricity Board), the temperature being sensed by chromel–alumel thermocouples inserted into the platens. Compensation for convection losses was provided by insulating material placed around the molding frame.

The molding frames for $6 \times 6 \times 1$ in. and $12 \times 12 \times 1$ in. moldings consisted of top and bottom plates of $\frac{1}{4}$ in. mild steel. For the $12 \times 12 \times 1$ in. frame these plates were 14×15 in. An outer frame ($13 \times 13 \times 1$ in. i.d.) was soldered on and an inner frame ($12 \times 12 \times 1$ in. i.d.) was screwed to the lower plate. The $\frac{3}{8}$ in. gap between the two frames provided air insulation or could be filled with asbestos, and it was fitted with two thermocouple pockets. The top plate was hinged to the bottom plate, and was locked on the opposite side to the outer frame by a bolt and hole fitment.

Shaped moldings in the shape of a flanged hemisphere of an outer diameter about 18 cm. and a thickness about $\frac{1}{2}$ in. (volume 813 ml.) were made in a two-piece steel mold, the molding surfaces being of polished stainless steel. The top of the mold was held to the body by simple quick-closing clamps. Sixteen $\frac{1}{16}$ in. vertical holes were drilled equidistantly through the upper outside edge of the top plate to allow venting of vapors during molding. This mold was heated in an air oven.

EXPERIMENTAL

Relative viscosities were determined on a 1% benzene solution of the polymer at 20°C. in an Ostwald viscometer, type A, for relative viscosities below 2.5 and in a type B instrument for relative viscosities above 2.5.

Anthracene determinations were by polarography following the procedure of Given and Peover¹⁸ with the use of tetrabutylammonium iodide in dimethylformamide.¹⁴

For aqueous dispersion polymerization to beads, monomer (500 g., once-recrystallized grade, recrystallized once from methanol), distilled water (1750 ml.), and Elvanol (5 ml. of 3% aqueous solution) were charged to the reactor bowl heated in a water bath (90°C.). Stirring (700 rpm) was started when the monomer had melted, and upon the reactor temperature rising to

90°C. a solution of AIBN (0.5 g.) in acetone (3 ml.) was added. The polymerization became exothermic 3–8 min. after catalyst addition. After a further 10 min. stirring was discontinued, and the beads were filtered, washed with distilled water, and dried at 80°C. The beads were extracted with methanol at ambient temperature and with boiling acetone, and were air dried.

For aqueous dispersion polymerization to granules, monomer (200 g., twice-recrystallized grade or once-recrystallized grade, recrystallized again from methanol), distilled water (700 ml.), and Nonex 64 (3% aqueous solution, 10 ml.) were charged to the reactor and were heated in the water bath with stirring at 700 rpm until the reactor temperature had reached 70°C., when AIBN (4 g.) dispersed in a little acetone was added. After 4–10 min. the temperature rose sharply, and 15 min. later stirring was discontinued, and the polymer granules were washed with distilled water and dried at 80°C.

Di-*tert*-butyl peroxide (0.4 g.), when used, was added before the addition of AIBN at a reactor temperature of 65°C. The granules were extracted with methanol at ambient temperature and with boiling acetone and were air dried.

For the impregnation of polymer granules these (1 kg.) were covered with a solution of AIBN (60 g.) in dioxane (500 ml.) and acetone (1500 ml.). After standing overnight at ambient temperature the granules were drained, spread on cardboard trays to a depth of less than 1 in., and dried at 60–80°C. During the first stage of drying, they were raked every 2–3 min. to avoid cohesion. Drying was continued until the weight of the granules corresponded to the correct weight increase. The granules were stored in well-stoppered bottles.

To mold a 12 × 12 × 1 in. panel of density 0.1 g./cc. granules (260 g.) were impregnated as above and dried to a weight increase of 6.7%. They were charged quickly and evenly to the preheated (250°C.) molding frame, whose inner surfaces had been greased very lightly (one application sufficing for several moldings) with silicone stopcock grease. The frame was closed quickly and heated in the molding press in the temperature range 230–250°C. for a period of 6 min., vapors being vented every 2 min. Finally the frame was immersed in distilled water for 1 min. and the molding was dried to constant weight at 80°C. The remaining volatiles could be removed by heating at 130°C. and at 160°C. for 24 hr. each.

RESULTS

Purification of Vinylcarbazole

The twice-recrystallized grade monomer was colorless and contained less sulfur (10–22 ppm sulfur by chemical analysis, 5–15 ppm sulfur by radioactivation analysis) than seemed likely to affect its polymerization by AIBN, and no detectable anthracene (<60 ppm).¹⁴ The once-recrystallized grade vinylcarbazole had a very light yellow hue and a characteristic

odor not noted with the better grade material. Its sulfur content was 23–25 ppm (by chemical analysis), but the concentration of anthracene (about 400 ppm) was sufficient to slow down the rate of bulk polymerization by AIBN and to lower the molecular weight of bulk polymer made from it.

The twice-recrystallized grade monomer could be polymerized satisfactorily in aqueous dispersion to either beads or granules, but these were obtained with difficulty from the once-recrystallized grade monomer, and when obtained were of lower molecular weight. It was therefore necessary to purify this monomer. Recrystallization from methanol was found to be satisfactory, anthracene being removed sufficiently by one recrystallization, provided conditions were such as to avoid the separation of molten monomer (vinylcarbazole, m.p. 64.75°C., solubility in methanol at boiling point 307 g./kg.; methanol, b.p. 64.65°C.; molar elevation of boiling point of methanol, 0.83°C./kg.). Upon separation of molten monomer from the solution the anthracene partitions between the two phases, and its separation from the monomer is much less effective. During the recrystallization, trace acid contamination and prolonged boiling had to be avoided, since vinylcarbazole adds methanol under these conditions to yield 9-(1'-methoxyethyl)carbazole,¹⁹ which is very soluble in methanol. While it did not affect the polymerization,¹⁴ its formation resulted in the loss of monomer.

The recrystallization did not require an inert atmosphere.

Use of one of a number of adsorbents during the recrystallization was not found advantageous.

Dispersion Polymerization to Beads

Foamed polyvinylcarbazole beads (0.5–1 mm. diameter) suitable for molding were made by aqueous dispersion polymerization with the use of poly(vinyl alcohol) as protective colloid and AIBN as initiator (Table I). The concentration of the protective colloid depended on the quality of the

TABLE I
Aqueous Dispersion Polymerization of Vinylcarbazole to Foamed Beads

Mono- mer (500 g.) ^a	Elvanol soln., ml.	Wt. AIBN, g.	Temp. AIBN addition, °C.	Conver- sion, %	Polyvinylcarbazole	
					Relative viscosity	Appearance
A	1.2	10	70	90	—	Fine beads
A	2.5	10	70	89	—	Fine beads
A	3	0.5	80	—	3.65	Small beads
A	3	0.5	85	—	4.03	Beads, 1.0–1.5 mm.
A	3	0.5	90	—	5.0	Lump
A	6	0.5	87	—	5.5	Beads, 0.5–1 mm.
B	3	0.5	80	—	2.22	Beads
B	5	1.0	85	—	2.99	Beads
B	5	0.5	90	—	2.95	Beads

^a Monomer code: A = once-recrystallized grade, recrystallized once from methanol; B = once-recrystallized grade, as received.

monomer, more being required with the once-recrystallized grade than with the twice-recrystallized grade. The twice-recrystallized grade monomer resulted in polymer of higher molecular weight than could be obtained from the once-recrystallized grade monomer.

Dispersion Polymerization to Granules

The reported polymerization to foamed granules (2–5 mm.)⁵ could not be reproduced with Elvanol as protective colloid; polyvinylpyrrolidone (relative viscosity 1.26–1.33) also proved unsatisfactory.

Certain of the half esters of poly(ethylene glycol) of the Nonex range gave better results, the best being obtained with Nonex 64 (Table II). Under optimum conditions Nonex 52 and Nonex 99 might also be suitable.

The conversions to granules in presence of Nonex 64 were notably higher than those quoted for Elvanol;⁵ the molecular weights were, however, somewhat lower than those obtained with Elvanol, both in the earlier⁵ and present work.

While seeking a satisfactory protective colloid, several stirrer types were examined and the optimum speed ranges of the best of these were shown to be in the range 500–900 rpm (Table III).

Nonex 64 with the best stirrer type at the optimum speed provided satisfactory dispersion up to a batch scale of 1.8 kg. monomer.

To assess the quality of the polymer produced, its expansion and cohesion on heating were tested, and, wherever possible, a small disk (2 in. diameter, 1 in. thickness) was molded.

Granules could not satisfactorily be obtained from the once-recrystallized grade monomer under the conditions suitable for the higher grade material. Under the microscope both grades of monomer appear similar, consisting of discrete crystals about 0.5 mm. long and weighing 1–2 mg. On dispersing the monomer in hot water containing Nonex 64 under polymerization conditions, but in absence of any initiator, and then cooling, the twice-recrystallized grade monomer was recovered in essentially spherical granules 1–2 mm. in diameter and weighing 10–20 mg., while the once-recrystallized grade monomer was isolated in small discrete crystals similar to those of the original monomer.

Polymer granules might thus be obtainable from once-recrystallized grade monomer by reducing the Nonex 64 concentration. This was found to be the case, but even under the best conditions the molecular weight of the polymer was found to be appreciably lower than that from the higher grade monomer.

The aqueous dispersion polymerizations were carried out under air. Alteration of the oxygen concentration affected the time interval between the addition of the initiator and the point at which the polymerization became exothermic (Table IV). Under nitrogen and argon the polymerization proceeded faster and yielded polyvinylcarbazole which was only partially soluble in benzene; the benzene-soluble fraction had a somewhat higher molecular weight than polymer prepared under air.

TABLE II
Aqueous Dispersion Polymerization of Vinylcarbazole in Presence of Nonex Range Protective Colloids^a

Nonex Type	Stirrer		Polymer						
	Vol., ml.	Type ^b	Speed, rpm	Conv., %	Rel. visc.	Appearance	Expansion ^c	Cohe-sion ^d	Disk ^e
64	0.5	A	600	94.7	2.07	Light, rocklike mass	+	++	+
64	1	A	600	96.5	2.07	Light, rocklike mass	+	++	+
64	5	A	600	98.5	1.77	Large, regular, rough granules	++	++	+++
64	10	A	600	88	3.17	Large, regular, rough granules	++	++	++
64	10	B	1380	82	2.65	Large, regular, rough granules	++	-	-
64	5	C	600	86	2.80	Large, uniform granules	++	+	-
64	5	D	600	87.3	2.66	Large, uniform granules	++	++	-
31	10	C	600	87.6	2.65	Large, expanded mass	+ / +++	+	+
31	10	C	600	83.7	2.65	Large, expanded mass	+ / +++	-	-
52	10	C	600	88.2	2.30	Small lumps	++	++	+
99	10	B	1380	80	2.95	Irregular large granules and fines	++	-	-
139	10	C	600	85.4	2.65	Large expanded mass, lighter than water	+	+	+

^a Materials: half the quantities given under Experimental for polymerization to granules were used (including di-*tert*-butyl peroxide).

^b Stirrers: (A) glass link, diameter 9 cm.; (B) six-bladed stainless steel impeller, diameter 5.6 cm.; (C) stainless steel wing stirrer, diameter 7.7 cm.; (D) stainless steel two-bladed stirrer, diameter 7.0 cm.

^c Code: + + + +, mold forced open; + + +, mold filled; ++, moderate, some cavities; +, slight expansion; -, no expansion.

^d Code: + + +, granules completely fused, boundaries merged; ++, moderate, granules fused, boundaries clearly visible; +, granules badly fused and easily broken; -, no fusion.

^e Code: + + +, smooth surfaces, well-formed edges; ++, fairly good surfaces, irregular edges; +, disk incompletely formed; -, no disk formed.

The elementary composition of the polymer was not affected markedly by the atmosphere under which it was polymerized.

The structure of the polymer granules was that of a labyrinth of spaces of various sizes and shapes surrounded by a hard outer shell of polymer. The microscopic structure of the outer shell could vary widely ranging from very irregular, rough and porous to very smooth.

In attempts to determine the nature of the gas in the granules, freshly made granules were washed with water, methanol, and acetone, and were

TABLE III
Aqueous Dispersion of Polymerization of Vinylcarbazole: Effect of Stirrer Type and Speed^a

Stirrer Type	Speed, rpm	Tip velocity, ft./min.	Polymerization rate %	Conv., %	Rel. visc.	Polymer		
						Appearance	Expansion	Cohesion
C	300	240	Very rapid	93.3	2.07	Expanded to fill reactor, friable porous sponge	+	++
D	300	220	Very rapid	97.3	2.12	Expanded to fill reactor	+	++
C	400	320	Rapid	90.7	3.07	Two large pieces and some elongated granules	+	+
D	400	290	Very rapid	91.6	3.32	Solid mass, $d < 1$ g./cc.	+	+
C	500	400	Fairly rapid	—	2.70	Granules of fairly uniform size, $d < 1$ g./cc.	++	—
D	500	370	Fairly rapid	—	3.32	Small and moderately sized irregular particles	+	+
C	600	480	Fairly rapid	86.0	2.80	Large, uniform granules	++	+
D	600	440	Fairly rapid	87.3	2.66	Large, uniform granules	++	++
C	700	560	Slow	86.8	2.86	Uniform granules	++	—
D	700	510	Slow	88.4	2.99	Uniform granules	++	+
C	800	640	Fast	80.3	2.66	Expanded mass, $d < 1$ g./cc.	+	+
D	800	590	Slow	82.7	2.86	Fairly small granules	—	—
C	900	720	Fast	85.4	2.48	Smooth granules, $d < 1$ g./cc.	+	—
D	900	600	Moderate	91.0	2.84	Smooth granules, $d < 1$ g./cc.	++	++

^a Materials: Nonex 64; otherwise materials, conditions, and codes as for Table II.

TABLE IV
Aqueous Dispersion and Polymerization of Vinylcarbazole Under Various Gas Atmospheres^a

Atmosphere	Time from AIBN addn. to start of temp. rise, min.	Polymer		
		Conversion, %	Rel. visc. ^b	Appearance
Argon	2	75.3	(3.16)	Lump
Nitrogen	2.5	72.5	(3.32)	Lump
Air	7-8	88	2.60	Granules
Air	7-8	92	2.60	Granules
Oxygen	30	70	1.52	Yellow, tacky lump
Oxygen	20	88.5	1.65	Slightly cohering granules

^a Materials and conditions as given under Experimental.

^b Relative viscosities in parentheses refer to the benzene-soluble fraction of particle-insoluble polymer.

then kept under water until ready for weighing. After weighing, the granules were immediately dissolved in hot benzene, and the separating gas was analyzed in an Atlas mass spectrometer. Analysis of the gas (4.65 ml. at NTP) from such granules (2.69 g.) showed it to consist of N_2 , 77.9%; O_2 , 20.8%; A, 0.7%; CO_2 , 0.6 vol.-%, indicating that very soon after their preparation the granules are filled with air. Attempts at further elucidation by polymerization under argon yielded foamed polymer lumps (Table IV), which proved unsuitable sources of gas samples.

The density of polymer granules as formed in the polymerization was usually, but not invariably, below 1.0. Until dried the granules always contained water. The ease with which they were dried points to the porosity of their surface.

Purification of Polymer Granules and Beads

The dried foamed polymer granules or beads were extracted with methanol at ambient temperature and with boiling acetone. Adequate extraction particularly of beads was essential for satisfactory molding properties. The extracted granules or beads were air dried.

The acetone extract (3-6% on unextracted polymer) consisted largely of monomer and of polymer of low molecular weight (relative viscosity 1.28) probably largely formed from the residual monomer during the extraction. A novel decomposition product of azobisisobutyronitrile, m.p. 104-106°C. (found, C, 62.1%; H, 9.2%; N, 18.2%; $C_8N_{14}N_2O$ requires C, 62.3%; H, 9.2%; N, 18.2%) was also isolated. Its infrared spectrum indicates the presence of a nitrile and of a noncyclic secondary (probably isopropyl) amide group, and is consistent with the structure $(CH_3)_2C(CN)NHCOCH-(CH_3)_2$.

The relative viscosities quoted for granules and beads were determined following the preceding extraction and drying. The size distribution (by sieving) of the granules ($>1/4$ in., 8-17%; $1/4$ - $3/16$ in., 39-49%; $3/16$ - $1/8$ in., 30-47%; $1/8$ - $1/32$ in., 4-6%) and their bulk density (0.36-0.48 g./cc.) were also determined at this stage.

Impregnation and Molding of Polymer Granules

While the foamed, methanol- and acetone-extracted polyvinylcarbazole granules generally expanded readily on heating above 150°C., cohesion between the expanding granules was insufficient to give the molding (especially at densities <0.1 g./cc.) appreciable mechanical strength. This was considered to be due either to protective colloid in the granule surface exerting a repellent effect, or to some intrinsic property of the polymer.

Very thorough hot extraction of polymer granules (relative viscosity 2.12) with acetone and/or methanol and/or water followed by drying resulted in deterioration of cohesion upon molding at 250°C.

Attempts to mold at 250°C. ground, water- and methanol-washed polymer granules (in which the original granule surfaces had been destroyed)

TABLE V
Effect of Solvent Impregnation Upon the Molding Properties of Polyvinylcarbazole Granules^a

Solvent	Impregnation				Molding conditions				Molding	
	Vol. solvent, ml.	Ace- tone, ml.	Drying		Poly- mer, g.	Temp., °C.	Time, min.	Expansion ^b	Cohesion ^b	Appearance
			Temp., °C.	Time, min.						
None	—	—	—	—	7.5	250	10	—	—	No disk; discolored
C ₆ H ₆	10	190	25	70	7.5	250	5	++	++	Very good, no cavities
					5.0	250	5	++	+	Incompletely filled mold
C ₆ H ₆	100	100	25	70	7.5	250	3	++	++	Very good, hard, fibrous
					5.0	250	3	++	++	Good, fibrous, cavities
C ₆ H ₅ CH ₃	10	190	25	100	7.5	250	5	++	—	Poor, slight cohesion
C ₆ H ₄ (CH ₃) ₂	10	190	25	128	7.5	250	5	+	—	No disk obtained
(CH ₂) ₂ CO	50	150	50	60	7.5	250	3	+	—	No disk obtained
O(C ₂ H ₅) ₂ O	50	150	50	80	2.1	218-224	6	—	—	Good disk
(CH ₂) ₂ O	10	190	25	70	7.5	250	5	+	—	No disk obtained
HCON(CH ₃) ₂	50	150	50	80	2.1	—	6	—	—	No disk obtained
CH ₂ Cl ₂	50	150	50	80	2.1	223-228	6	—	—	Poor disk, incompletely expanded
CHCl ₃	50	150	50	80	2.1	223-228	6	—	—	Poor disk, expansion and cohesion inadequate
C ₂ HCl ₃	10	190	25	70	7.5	250	—	++	++	Fibrous disk
C ₃ H ₅ N	50	150	50	85-95	2.1	220-226	6	++	++	Well-fused disk, somewhat collapsed in center
C ₃ H ₅ N + 3% AIBN	—	—	—	—	2.1	212-232	4	++	++	Well-fused disk, incompletely expanded

^a Polyvinylcarbazole granules, relative viscosity, 2.55. Acetone was used as diluent. Moldings were made in a 2 1/4-in. diameter, 1-in. thick, circular mold.

^b See Table II.

TABLE VI
Molding of Solution-Impregnated Polyvinylcarbazole Granules in Various Alternative Diluents^a

Diluent	Impregnation		Drying		Wt. increase after impregna- tion and drying, %	Molding temp., °C.	Disk		
	Solvent	Soln., ml.	Polymer, g.	Temp., °C.			Time, min.	Expansion ^b	Cohesion ^b
Acetone	Benzene	100	50	80	120	212-223	++	++	Fair
Acetone	Dioxane	100	50	80	120	218-222	+++	++	Good
Ether	Benzene	250	100	20	—	213-220	++	+	Poor
Ether	Benzene	250	100	80	180	220-222	++	+	Poor
Ether	Dioxane	250	100	20	—	220-222	++	+	Poor
Ether	Dioxane	250	100	80	180	216-222	++	+	Poor
Methanol	Benzene	100	50	80	120	210-230	++	+	Poor

^a Polyvinylcarbazole granules, relative viscosity, 2.55. The granules were evacuated for 2½ min. under the solvent mixture containing 25% solvent and 3% AIBN and were left to stand under the mixture at atmospheric pressure for 45 min. Molding times in 2¼ × 1½ in. circular frame were 6 min.

^b See Table II.

TABLE VII

Molding of Polyvinylcarbazole Granules Impregnated with Benzene-Acetone Solution^a

Impregnation		Molding		Disk				
Benzene, vol.-%	Drying time, min.	Polymer, g.	Time, min.	Expansion ^b	Cohesion ^b	Appearance		
5	60	7.5	5	+	-	-		
		7.5	5	++	-	-		
		7.5	3	++	++	Good, but some cavities		
	180	7.5	5	++	+++	Good		
		7.5	10	++	+	Shrunk, little cohesion		
		10	3	+++	+++	Hard, fibrous		
		10	5	++	+++	Hard, fibrous		
		20	180	5	2	+++	+++	Hard, fibrous
				7.5	2	+++	+++	Hard, fibrous
		25	180	5	1	++++	++	Some cavities, incompletely fused
5	2			+++	+++	Hard, fibrous		
5	3			++	+++	Some cavities		
7.5	3			+++	+++	Hard, fibrous		
30	180			3.75	1½	++	++	Some cavities
				3.75	2	+++	+++	Hard, fibrous
5	180			5	1½	++++	+++	Hard, fibrous
				5	2	+++	+++	Hard, fibrous
				5	4	++	+	Cavities, very poor cohesion
				6.6	1½	+	+	Cavities, very poor cohesion
		12	2	++	++	Incomplete fusion		
15	2	+++	++	Fair				

^a Approx. 8 ml./g. impregnation solution was used. For conditions see Experimental. The impregnated granules were dried at 70°C.; Molding temperature, 250°C. Moldings were made in a 2¼-in. circular, 1-in. thick mold.

^b See Table II.

revealed a lack of cohesion, and the grinding also affected expansion adversely.

The possibility of chemical change during molding affecting cohesion seemed unlikely, since neither the solubility nor the molecular weight of the granules was found to be affected by molding.

Thus the poor cohesion between granule surfaces on attempted molding appeared to be an intrinsic property of the granule surface. Fusion between the surfaces (upon molding) is due to a sufficient increase in chain mobility and a decrease in chain order near the softening range. Stretching of the polymer chains would occur during expansion of the hot granules and could enhance the orientation and chain order while decreasing the chain mobility. Interlocking between the polymer molecules is likely to be exceptionally hindered by the closely spaced, large carbazole substituents lining the

molecule. A polymer solvent should increase the mobility of the polymer molecules. To avoid undue softening or tackiness of the granules, the solvent was applied in a lower boiling diluent (with which it should not form an azeotropic mixture), which was chosen so as to dissolve the solvent, but not the polymer.

The effect of impregnation of polyvinylcarbazole granules (relative viscosity 2.5–2.7) with a number of solvents and related compounds in acetone solution upon their molding properties showed benzene, dioxane and pyridine to be most promising (Tables V and VI).

The granules impregnated with a 50/50 benzene–acetone solution were very tacky and had to be separated. Granules impregnated with cyclohexanone showed neither appreciable expansion nor cohesion on molding but acquired a remarkable gloss and transparency.

Rather surprisingly methanol and diethyl ether proved greatly inferior to acetone as diluents (Table VI).

Impregnation with benzene–acetone solutions allowed the molding of satisfactory disks down to a density of about 0.1 g./cc. (Table VII). Inadequate expansion rather than poor cohesion limited molding to this density.

The effect of impregnation with blowing agents upon the molding properties was therefore examined, and AIBN was selected for study, since a very pure product is commercially available which should be without deleterious effect upon the electrical properties of the product.

The effect of AIBN impregnation upon the molding properties resembled that produced by benzene or by dioxane (Table VIII). Impregnation with an acetone solution containing both benzene and AIBN gave still further improvement, so that 12 × 12 × 1 in. panels of satisfactory quality could be

TABLE VIII
Effect of Impregnation by Azobisisobutyronitrile upon the Molding Properties of Polyvinylcarbazole Granules^a

Impregnation			Molding		Disk		
Polyvinylcarbazole, g.	AIBN, tone, g.	Ace-ml.	Polymer, g.	Time, min.	Expansion ^b	Cohesion ^b	Appearance
Control (unimpregnated granules)			7.5	3	+++	—	—
			5	3	+	+++	Well formed, cavities
100	6	500	7.5	3	+++	+++	Well formed, some cavities
			7.5	4	+++	+++	Well formed, coherent

^a Polyvinylcarbazole, relative viscosity, 2.6. The granules were evacuated under the solution until there was essentially complete penetration.

^b See Table II.

obtained down to a density of 0.1 g./cc., and smaller moldings even below this limit (Table IX). Satisfactory results were obtained with a solution of 3% AIBN in 25% benzene-acetone and still further improvement was attained when the benzene in such mixtures was replaced by dioxane. 12 × 12 × 1 in. and 6 × 6 × 2 in. panels could be molded down to a density of 0.05 g./cc. following impregnation with the latter mixture (Table X). The molding of 6 × 6 × 2 in. panels was found to require a longer molding period than was required for the thinner moldings, especially when molding at the higher densities. If the molding period was too short, the interiors of the moldings were incompletely fused, despite their excellent outside appearance.

TABLE IX

Effect of Impregnation by AIBN-Benzene-Acetone Solution upon the Molding Properties of Polyvinylcarbazole Granules^a

Molding		Disk		
Polymer, g.	Time, min.	Expansion ^b	Cohesion ^b	Appearance
2	3	+++	+++	Fused, fibrous
2	3	+++	+++	Fused, fibrous
3	3	++++	+++	Good, fused, fibrous
3	3	++++	+++	Good, fused, fibrous
4	3	+++	+++	Good, fused, fibrous
5	3	++++	+++	Very good, fused, fibrous
5	3	++++	+++	Very good, fused, fibrous
7.5	4	+++	+++	Very good

^a Solutions contained 3% AIBN in 25% benzene-acetone. The impregnated granules were dried for 3 hr. at 65°C. Moldings were made in a 2¹/₄-in. circular, 1¹/₂-in. thick mold at a molding temperature of 250°C.

^b See Table II.

Quantitative control of the impregnation by AIBN-benzene-acetone depended upon infrared absorption spectrophotometry. The impregnated granules were extracted with boiling carbon tetrachloride (6 hr. in Soxhlet), and the absorptions at 1710 (acetone), 1930 (benzene), and at 2230 cm.⁻¹ (AIBN) were determined in 0.1 and 1 cm. cells, varying the path length against standards. The technique could not be adapted to control of the more important AIBN-dioxane-acetone impregnation, since there is too much overlap between the stronger absorption lines of dioxane and the other components.

Attempts to evaluate and control the impregnation by determining the weight increase following impregnation and drying of the impregnated granules proved complex, since some of the polymer dissolved in the impregnation solution rendering the data difficult to interpret. With the AIBN-dioxane-acetone solutions good results when molding to densities

TABLE X
 Effect of Impregnation by AIBN-Benzene-Acetone or by AIBN-Dioxane-Acetone
 Upon the Molding Properties of Polyvinylcarbazole Granules

Impregnation		Molding					Panel		
Solution ^a	Temp., °C.	Drying		Frame dimensions, in.	Polymer, g.	Temp., °C.		Time, min.	Density, g./cc.
		Temp., °C.	Time, min.						
A	80	120		6 × 6 × 1	35	220-233	5	0.054	Incompletely fused, many cav- ities
				6 × 6 × 1	35	209-220	6	0.059	Smooth, well fused
				6 × 6 × 1	35	207-219	10	0.059	Incompletely fused, many cav- ities
				6 × 6 × 1	72	215-220	8	0.11	Good, smooth, few cavities
				6 × 6 × 1	72	216-224	8	0.11	Good, smooth, few cavities
				6 × 6 × 1	118	205-220	11	0.18	Good, smooth, few small cav- ities
A	80	120		12 × 12 × 1	288	200-219	19	0.11	Fairly good, somewhat uneven

A	80	120	12 × 12 × 1	288	217-224	10	0.10	Fairly good
A	80	120	12 × 12 × 1	288	215-227	10	0.11	Very good
A	80	120	12 × 12 × 1	471	215-225	13	0.17	Very good, uniform
A	—	—	12 × 12 × 1	472	218-227	13	0.16	Very good
B	—	—	12 × 12 × 1	174	149-204	8	0.066	Good
B	80	—	12 × 12 × 1	174	245-238	6	0.067	Fairly good
B	—	—	12 × 12 × 1	260	245-238	6	0.103	Good
B	80	—	12 × 12 × 1	260	245-238	6	0.103	Very good
B	80	120	12 × 12 × 1	400	132-202	14	0.166	Good
B	80	—	12 × 12 × 1	438	245-235	6	0.177	Good
B	85	120	6 × 6 × 2	80	221-228	10	0.065	Good
B	—	—	6 × 6 × 2	80	149-210	14	0.060	Good
B	80	540	6 × 6 × 2	125	205-227	12	0.10	Very good
B	80	270	6 × 6 × 2	140	139-209	14	0.113	Good
B	80	270	6 × 6 × 2	250	188-218	14	0.192	Good surfaces, incompletely expanded core
B	80	540	6 × 6 × 2	220	185-225	40	0.176	Very good

* Solution A: 3% AIBN in 25% benzene-acetone; solution B: 3% AIBN in 25% dioxane-acetone.

below 0.1 g./cc. were obtained following such a weight increase of 6–10%; for molding at and above 0.1 g./cc. it should preferably be 5–7%.

Attempts to mold down to a density of 0.03 g./cc. with the use of polyvinylcarbazole granules impregnated with AIBN–dioxane–acetone to a weight increase of 8–10% have given only fairly good results, the moldings being somewhat underexpanded.

Impregnations with a solution of 3% AIBN in benzene (12.5%)–dioxane (12.5%)–acetone yielded granules of molding properties intermediate between the solutions containing either benzene or dioxane.

The lack of cohesion upon molding of rough crushed foamed polyvinylcarbazole granules was also largely overcome by impregnation with AIBN–benzene–acetone solution. The molding of smaller particles seemed desirable, since the liability to failure, especially of the thinner moldings, should be lessened. Foamed polyvinylcarbazole granules (120 g.; relative viscosity, 2.55; size distribution $>1/4$ in., 35%; $1/4$ – $3/16$ in., 45%; $3/16$ – $1/8$ in., 18%; $1/8$ – $1/32$ in., 2%) were crushed to pass through a $3/16$ -in. sieve, and fractions $3/16$ – $1/8$ in. (31 g.) and $1/8$ – $1/32$ (82 g.) were separately impregnated with AIBN–benzene–dioxane solution and dried for 2 hr. at 80°C. Impregnation appeared to improve the molding properties of the crushed granules to a molding quality similar to that shown by the correspondingly impregnated, uncrushed granules (Table XI).

Impregnation by several Porofor blowing agents, which were unfortunately available only as rather colored mixtures with diluents (hydrocarbon or chlorinated hydrocarbon) was examined (Table XII). These blowing agents decompose to give various (often sulfur-containing) products of low volatility. The Porofors were applied as 3% solutions, 25% dioxane in acetone being used as solvent. Several of these blowing agents were insuffi-

TABLE XI
Effect of Impregnation with AIBN (3%)–Benzene (25%)–Acetone Solution upon the Molding Properties of Rough Crushed Foamed Polyvinylcarbazole Granules*

Particle size, in.	Molding			Disk	
	Polymer, g.	Temp., °C.	Time, min.	Thickness, in.	Appearance
Control	2.09	218–225	6	$1/2$	Fairly good, many cavities
Control	1.05	207–228	6	$1/4$	Fairly good, incompletely expanded
$3/16$ – $1/8$	2.09	219–222	—	$1/2$	Fairly good, many cavities
$3/16$ – $1/8$	1.05	210–234	6	$1/4$	Good, few holes
$1/8$ – $1/32$	2.09	219–224	6	$1/2$	Good, small cavities
$1/8$ – $1/32$	1.05	210–224	6	$1/4$	Good expansion, fair cohesion

* A $2\frac{1}{4}$ -in. circular molding frame was used. The density of the moldings was 0.06–0.07 g./cc. Uncrushed, impregnated granules were used in the control experiments.

TABLE XII
Molding of Polyvinylcarbazole Granules Impregnated with Porofor Blowing Agents in
Dioxane-Acetone Solution*

Porofor	Impregnation				Molding		
	Time, hr.	Weight incr., %	Drying time, min.	Wt. incr. after impregna- tion and drying, %	Temp., °C.	Time, min.	Panel
TR	18	79	165	8.5	219-229	4	Very good
TR	20	74	180	10	216-230	6	Good, well fused, shrunk, light brown
BSH paste	18	76	240	9	215-233	4	Very good
BSH paste	19	72	180	10	214-225	5	Very good
B13/CP50	18	66	180	10	210-230	5	Good, fairly well fused
B13/CP50	18	64	90	11.5	216-230	6	Moderate, not very well fused

* Polyvinylcarbazole granules (100 g.; relative viscosity 2.60) were impregnated with 200 ml. solution and were dried at 80°C. The impregnated granules (40 g.) were molded in a 6 × 6 × 1 in. frame.

ciently soluble in the solvent mixture to be used. Several of the Porofors gave rather discolored but otherwise very good moldings.

Impregnation of polyvinylcarbazole granules (50 g.; relative viscosity, 2.70) with a solution of *n*-butyl cyclohexyl phthalate (10 ml.) in acetone (190 ml.) for 2 hr., followed by drying for 3 hr. at 60°C. resulted in no marked improvement of the molding quality of the granules.

Impregnation and Molding of Polymer Beads

It was hoped that the molding of foamed polyvinylcarbazole beads would yield moldings of a finer and more uniform core structure. The solvent-extracted and dried beads could not be molded to satisfactory panels before impregnation, cohesion being even worse than with granules, due probably to the higher molecular weight of the beads. Impregnation with benzene gave considerable improvement, but as in the case of the granules, AIBN-dioxane-acetone proved superior for this purpose. It will be noted that this treatment resulted in good moldings from beads of widely varying molecular weights (Table XIII). However, unsatisfactory moldings were also obtained, and for satisfactory results improved control of the impregnation is still needed.

TABLE XIII
Molding of Polyvinylcarbazole Beads Impregnated with AIBN (3%)–Dioxane (25%)–
Acetone Solution^a

Polyvinylcarbazole, relative viscosity	Molding		Panel appearance
	Temp., °C.	Time, min.	
1.72	240	6.5	Very good
2.12	240	8	Good, smooth surfaces
2.58	210	20	Good
2.99	210	15	Good
3.19	200	18	Very good
5.45	245	7	Fairly good, some rough areas

^a Following 18 hr. impregnation at ambient temperature and atmospheric pressure, the beads were dried at 80°C. to a weight increase of 10%. Panels of density ~ 0.1 g./cc. were molded in a $6 \times 6 \times 1$ in. frame.

Hemispherical Molding

Polyvinylcarbazole granules impregnated with a solution of AIBN (3%) in dioxane (25%)–acetone were molded (Table XIV). Very satisfactory results were obtained when the open mold, preheated to 200–220°C., was charged with the granules and then closed and the clamps set, all within

TABLE XIV
Hemispherical Moldings of Foamed Polyvinylcarbazole^a

Wt. increase on impreg- nation and drying, %	Polymer wt., g.	Charging time, sec.	Molding temp., °C.	Hemisphere	
				Density, g./cc.	Appearance
6.9	76	—	214–215	—	Dome fairly well formed, but uneven flange an- nulus
8.0	104	210	207–210	—	Good, dome well formed, but flange incomplete
8.0	104	120	203–215	0.124	Good, dome and flange fully formed
8.0	104	72	195–215	0.117	Good, dome and flange fully formed

^a The charging time is the interval between removal of the preheated mold from the oven and the return to it of the charged mold. Molding time, 14 minutes.

about 1 min., before being returned to the air oven. Satisfactory moldings were soon obtained, the appropriate edges of the flange being sharp or well rounded. At the end of the molding period the mold was submerged under water for 1 min.

DISCUSSION

The aqueous dispersion polymerization of vinylcarbazole is clearly a complex process in which the disperse phase must be maintained under close control while the monomer polymerizes, its physical properties changing from those of a viscous liquid through those of a tacky gum to those of a hard solid, while the heat evolved is in excess of that needed to raise the temperature of the dispersion from about 70 to 100°C.

The results indicate that polymer granules are built up from monomer droplets, and that the size of these at the outset of the polymerization—intermediate between that corresponding to that of the small monomer crystals and the quantity of monomer required for a single granule—has a critical effect upon the state of the polymer. The once-recrystallized grade monomer appears to contain an impurity facilitating its dispersion in hot water. Whether this is ascribable to anthracene, which is known to be responsible for retarding the polymerization in bulk and which is known to be present in the grade monomer¹⁴ is still uncertain.

The concentration (2%) of azobisisobutyronitrile required for polymerization to granules is much greater than that (0.1%) required for polymerization to beads. A much smaller initiator concentration (0.005–0.01%) suffices for the bulk polymerization of this monomer.¹⁴ The much greater amount of initiator needed in the dispersion polymerization is thought to be due to unfavorable distribution of the initiator between monomer and aqueous phase, but the difference between the concentrations required for granules and beads suggests a more subtle factor, which may include the size of the dispersed monomer particles and the temperature at which initiation sets in. Thus the isolation of a low molecular decomposition product of azobisisobutyronitrile $(\text{CH}_3)_2\text{C}(\text{CN})\text{NHCOCH}(\text{CH}_3)_2$ from the granular polymer indicates that even initiator dissolved in the disperse monomer does not initiate efficiently (unless this product is formed from initiator dissolved in the aqueous phase and then contaminates the wet polymer granules). Whether the lower molecular weight of the polymer made from the once-recrystallized grade monomer is solely ascribable to the presence in it of a little anthracene is also still uncertain. There is no evidence that degradation of the protective colloid by the radicals produced from the initiator occurs and is accountable for some of these complex features.

In forming expandable beads the polymerizing monomer droplets are thought to coalesce to a large degree, depending upon the protective colloid with the formation of voids in the polymerizing phase. With Elvanol (a strongly hydrophilic protective colloid), these beads remain separate during the polymerization despite their tacky surface, but with a more lyophilic protective colloid, the separate particles coalesce forming granules, lumps, or even a single piece of expanded polymer. The conditions required for granules are thus likely to be more exacting than those required for beads, and this is found to apply.

Incorporation of the protective colloid into the granule surface either by solution or grafting does not apparently contribute to the difficulties encountered in molding granules, but may help to account for some inconsistencies applying to the molding properties of the polymer beads.

The effect of oxygen upon the dispersion polymerization is typical for free-radical reactions. The formation of some benzene-insoluble polymer when the polymerization is carried out under an inert atmosphere is particularly interesting. The insolubility in benzene of part of the polyvinylcarbazole product during the cationic polymerization^{20,21} by boron trifluoride etherate in methylene dichloride has been ascribed to crosslinking.²⁰ Insolubility in benzene of part of the polyvinylcarbazole produced by certain Ziegler type initiators has been quoted as evidence for a higher measure of stereoregularity.²² The infrared absorption spectrum of benzene-insoluble polymer made in presence of boron trifluoride etherate in methylene dichloride has been found to be identical with that of benzene-soluble polymer obtained by free radical-initiated polymerization.²³ In the absence of any direct evidence for crosslinking or for Friedel-Crafts polymerization which in any case could not account for the insoluble material obtained upon free-radical initiation, its high molecular weight is taken to account for the low solubility of this material.

The results of analysis of the gas isolated from freshly polymerized granules and the apparent good gas permeability of the granule surface indicate that the nitrogen formed on thermal decomposition of the azobisisobutyronitrile does not contribute significantly to the foaming. Only a small proportion of the azobisisobutyronitrile is thought to be dissolved in the monomer, and this is far from sufficient to account for the quantity of gas contained in the granules. All the nitrogen obtainable from the AIBN used under the conditions required for making granules (137 ml./g.) amounts to about twice that contained in granules (density 0.4 g./cc.), but is insufficient to account for the very much lighter polymer (density ~ 0.1 g./cc.) which has been obtained following failure of the dispersing system, nor does the quantity of nitrogen obtainable from the AIBN used for making beads account for their density. It is considered that the foaming is due to vapor formed mainly from water contained in the dispersed monomer spheres during the exothermic phase of the polymerization, since the temperature in the disperse monomer spheres must rise rapidly to well over 100°C.

The high yield of granules obtained with Nonex 64 is remarkable. Lower yields have been reported with Elvanol,⁵ and this has been confirmed during the course of the present work, when it was shown also that the yield is not improved by the use of more initiator. The results point to some involvement of the Elvanol in the polymerization, but no completely satisfactory explanation is available.

The decomposition product of AIBN $(\text{CH}_3)_2\text{C}(\text{CN})\text{NHCOCH}(\text{CH}_3)_2$ isolated from the acetone used to extract the polymer granules is no doubt the hydration product of the Schiff's base $(\text{CH}_3)_2\text{C}(\text{CN})\text{N}=\text{C}=\text{C}(\text{CH}_3)_2$,

which is a known product of the thermal decomposition of AIBN. No recognizable monomer impurities (e.g., anthracene) have yet been isolated from these extracts, suggesting that they are combined either with the high molecular weight polymer of the granule or bead or with the acetone-soluble polymer of low molecular weight.

There is a strong indication that complete removal of acetone-soluble material from the polyvinylcarbazole granules or beads is desirable if these are to mold well.

If the effect of solvent impregnation is a decrease of the orientation of the polymer molecules during molding, which may explain its beneficial effect upon the molding properties, a more refined interpretation is needed to account for the wide differences in efficacy of various polymer solvents, e.g., dioxane, pyridine, and benzene, being in varying measure beneficial, whereas others such as dimethylformamide and tetrahydrofuran have little if any good effect. Even more remarkable is the specificity of the solute, acetone being suitable while diethyl ether and methanol are not. Thus the effect of impregnation upon the molding properties appears to depend upon polymer, solvent, and solute. Its relation to the flexibility of the polymer molecule is particularly interesting.

The effect of AIBN upon cohesion during molding is thought to be due to the formation from the AIBN of decomposition products which counteract the orientation of the polymer molecules. There is no indication of cross-linking, both solubility and relative viscosity of the polymer being unaffected by molding in presence of AIBN. Addition of monomer to the impregnation solution containing also AIBN may well improve further cohesion and with it especially the tensile properties of the molding. The negligible effect of AIBN upon the expansion during molding is presumably due to the relatively high permeability of the granule or bead surface to nitrogen, so that the latter has a negligible effect compared with that of solvent and solute.

Control of the impregnation by AIBN-dioxane-acetone solution remains a problem requiring further study and particularly needful in the case of beads for which, especially when their molecular weights are high, this is particularly critical.

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Résumé

La polymérisation de vinyl-carbazol en dispersion aqueuse en présence d'azobisisobutyronitrile fournit suivant le colloïde protecteur utilisé des perles ou des granulés de polyvinyl-carbazol. Ceux-ci nécessitent une imprégnation par un solvant du polymère et, de préférence, contenant aussi de l'azobisisobutyronitrile avant qu'ils puissent être moulés en panneaux ou en des formes bien déterminées.

Zusammenfassung

Die Polymerisation von Vinylcarbazol in wässriger Dispersion mittels Azobisisobutyronitril kann je nach dem verwendeten Schutzkolloid Polyvinylcarbazolperlen oder -körnchen liefern. Diese bedürfen einer Imprägnierung durch ein Lösungsmittel für das Polymere und womöglich durch Azobisisobutyronitril vor einer Verpressung zu Platten oder einfachen Formen.

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