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THE DETECTION OF CARBAZOLE UNITS AND POLY N-VINYL CARBAZOLE IN COPOLYMERS DERIVED FROM N-VINYL CARBAZOLE

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Abstract—Carbazole units in copolymers can be cross-linked by reaction with a Lewis acid catalyst in methylene chloride. The reaction initially causes gel formation, followed by the development (with $BF_3.Et_2O$) of a characteristic blue colour. The blue product has been shown to be a cationic dye of the diaryl-methyl type, derived from the dye base, bis-(9-alkyl-3-carbazolyl)-methane.

Acrylic or vinyl ester homopolymers are unaffected by this reaction, and can be extracted from the gel; N-vinyl carbazole homopolymer noticeably accelerates the gel forming reaction by cross-linking with copolymers.

A series of free radical copolymerizations of N-vinyl carbazole with methyl acrylate, methyl methacrylate, acrylonitrile and vinyl acetate were conducted in solution at 30°, and the products subjected to this reaction. In no case was any homopolymer formed.

INTRODUCTION

IN ANY copolymerization study it is necessary to be certain that the polymer obtained is, in fact, a true copolymer and not a mixture containing one, or more, homopolymers. This is particularly the case in free radical copolymerizations involving N-vinyl carbazole and weakly electron-accepting comonomers (such as acrylates and methacrylates), since it has been suggested(1) that homopolymers are formed in such systems at temperatures in the region of 80°.

The particular susceptibility of the carbazole unit to Lewis acid catalysed alkylations(2) (often with the formation of highly coloured intermediates) suggested that such a reaction could be used to cross-link carbazole-substituted polymer chains, while leaving non-carbazole containing homopolymers in their original soluble form.

Green–blue intermediates containing more than one carbazole residue are readily obtained from carbazole derivatives in acid media. Indeed, the reaction between carbazole and formaldehyde in strong acids yields a blue–green colouration which is a sensitive spot test for the latter compounds.(3, 4) Recently it has been shown(5) that this reaction initially yields methylene-bis-carbazolyl derivatives, which readily lose hydride ion to give a cationic dye.(6)

In this study we have chosen methylene dichloride (the solvent for the polymers and copolymers) as the bis alkylating agent, and boron trifluoride etherate and ferric chloride as the Lewis acid catalysts.

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EXPERIMENTAL

Materials

Methyl acrylate (M.A.), methyl methacrylate (M.M.A.), vinyl acetate (V.A.) and acrylonitrile (A.N.) were freed from inhibitor by successive washings with 5% NaOH and distilled water and then dried. They were fractionally distilled under a reduced pressure of nitrogen and stored at −10°.

N-vinyl carbazole (N.V.C.) was purified by recrystallization four times from distilled methanol. Tetrahydrofuran (T.H.F.) and methylene chloride were fractionally distilled before use, after preliminary drying over CaH_2.

Ditertiary butyl peroxide was fractionated under 60 mm pressure of dry nitrogen. The fraction boiling at 40° was stored in the dark at −10°.

Boron trifluoride etherate was used as received.

Ferric chloride was the commercial "anhydrous" grade and was used directly as a saturated solution in CH_2Cl_2.

Procedure

All copolymerizations were carried out at 30° with appropriate quantities of both monomers and initiator dissolved in T. H. F. The total monomer concentration was 3·0 moles litre^{-1}, and polymerizations were allowed to continue until conversion of the more reactive monomer reached 5–10 per cent. The polymers were then isolated by repeated precipitation from methanol.

Compositions of polymers were determined by elemental analysis, and the presence of carbazole units confirmed by means of u.v. and i.r. spectra.(1, 7)

The bis-methylation cross-linking reaction was conducted by refluxing 20–100 mg polymer in 4·0 ml methylene chloride with the appropriate amount of Lewis Acid. The resulting gel was extracted in a micro Soxhlet, and the filtrate evaporated to dryness to allow examination of any soluble material. 0·4 mg of extracted homopoly methyl methacrylate could be detected by the i.r. carbonyl absorption.

RESULTS

The results observed when the bis methylation reaction was carried out on a series of copolymers are summarized in Table 1. In this table are recorded visual estimates of

TABLE 1. CROSS-LINKING OF POLYMERS, CONTAINING CARBAZOLE UNITS, IN CH_2Cl_2

Copolymer	Composition (mole % NVC)	[Added poly. NVC] (g./l.)	[Total Polymer] (g./l.)	Catalyst*	Gel time
—	100	—	15	$BF_3.Et_2O$	Instantaneous
—	100	—	15	$FeCl_3$	1 min
NVC-VA	64	—	100	$BF_3.Et_2O$	20 hr
NVC-VA	64	10	100	$BF_3.Et_2O$	5 min
NVC-VA	81	5	100	$FeCl_3$	15 hr
NVC-VA	81	5	200	$FeCl_3$	7 hr
NVC-VA	81	—	200	$FeCl_3$	no reaction
NVC-MMA	27	—	100	$BF_3.Et_2O$	20 hr
NVC-MMA	60	—	100	BF_3Et_2O	3 hr
NVC-MMA	60	5	100	BF_3Et_2O	5 min
NVC-MMA	35	10	100	$FeCl_3$	6 hr
NVC-MMA	35	—	100	$FeCl_3$	24 hr
NVC-MMA	55	5	100	$FeCl_3$	30 min
NVC-MMA	55	—	100	$FeCl_3$	1 hr
NVC-MA	45	—	100	$BF_3.Et_2O$	3 hr
NVC-MA	45	5	100	$BF_3.Et_2O$	5 min
NVC-AN	56	—	100	$BF_3.Et_2O$	3 hr
NVC-AN	56	5	100	$BF_3.Et_2O$	5 min

* $BF_3.Et_2O$ was used at a concentration of 0·1 M and the reaction conducted under reflux in CH_2Cl_2 as solvent (40°).

$FeCl_3$ was used at a concentration of 5×10^{-3} M (saturated soln. in CH_2Cl_2) at 20°.

the time required to form the gels. When using BF_3Et_2O it was not possible to distinguish between the time required for initial gel formation and that for the formation of blue dye. With this catalyst all the carbazole-containing polymers gave products which in methylene chloride had a strong absorption between 620 and 640 mμ. Ferric chloride was a much more efficient gelling agent than BF_3Et_2O but did not always give rise to the characteristic blue dye.

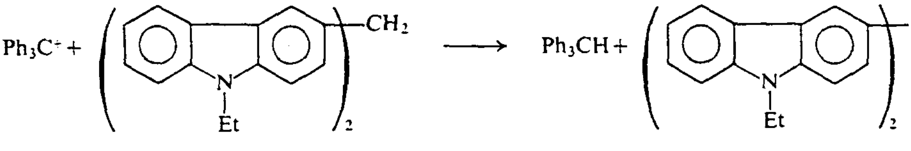
It was noted that the cross-linking reaction occurred only with difficulty when small amounts of vinyl carbazole were present in a strongly electron-accepting environment, or when adjacent to an ester group. Under these circumstances the reaction was greatly facilitated by the addition of traces of homopoly N-vinyl carbazole. The quantities of poly N-vinyl carbazole required for this purpose were so small, that the inefficiency of the original reaction (in polymeric material known to contain carbazole units) can be taken as evidence for the absence of homopoly N-vinyl carbazole in the copolymer sample. These results are also summarized in Table 1. For all systems studied 2 per cent insoluble residue could be detected with certainty.

DISCUSSION

The experiments on the homopolymers show that this bis methylation reaction causes cross-linking of poly N-vinyl carbazole, but does not affect the other homopolymers. In every copolymerization studied, the yield of extractable homopolymer was negligible, so that it is possible to state with confidence that no homopolymerization of acrylic ester, acrylonitrile or vinyl acetate had taken place.

If any electron transfer process leading to cationic homopolymerization of N-vinyl carbazole were to occur, it would be in the presence of the most electrophilic monomers methyl acrylate and acrylonitrile. However, in these copolymers the proximity of the electron-withdrawing side groups appears to deactivate to some extent the carbazole nucleus so that in this system the rate of cross-linking is quite markedly reduced. However, the reaction is greatly assisted by traces of N-vinyl carbazole homopolymer, so that the velocity of gelation can be used as a particularly sensitive test for the presence of homopolymer. In all the copolymer systems studied, the original polymer always reacted much more slowly than when traces of homopoly N-vinyl carbazole were added. Consequently, we deduce that this homopolymer, also, was absent in the original copolymer product. This conclusion appears to contradict recent reports concerning initiation of N-vinyl carbazole polymerization by methyl methacrylate and acrylonitrile.(1, 7)

Independent work(6) has established that the reaction between triphenyl methyl cation and bis-(9-ethyl-3 carbazolyl) methane (I) gives a quantitative yield of the corresponding diaryl methyl dye (II):

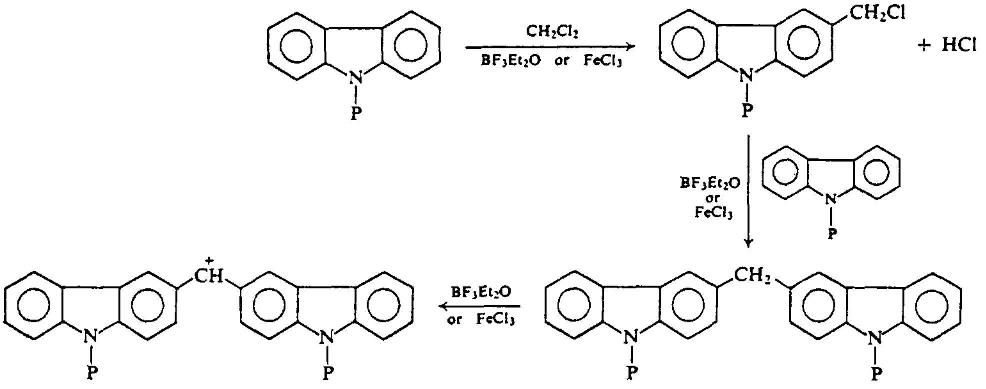


(I) (II)

The blue dye (II) has $\lambda_{max} = 625$ mμ and $\epsilon_{max} = 65{,}000$ in CH_2Cl_2 and its visible spectrum is identical with that of the blue dye formed by cross-linking poly N-vinyl carbazole with $BF_3.Et_2O$ in CH_2Cl_2.

It is reasonable to assume therefore that the gel and colour-forming reactions of poly N-vinyl carbazole occur via similar mechanisms:

(P = polymer chain)



Many other Friedel-Crafts type halides can be used to catalyse these alkylations but offer no particular advantages over $BF_3.Et_2O$ and $FeCl_3$.

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Résumé—Il est possible de réticuler les motifs carbazole dans un copolymère en les faisant réagir en présence d'un catalyseur acide de Lewis dans le chlorure de méthylène. La réaction conduit d'abord à la formation d'un gel puis a l'apparition d'une couleur bleue caractéristique (en présence de $BF_3.Et_2O$). On a pu montrer que le produit bleu est un colorant cationique de type diaryl-diméthyle, dérivé de la leuco-base, bis (alkyl-9)-carbazolyl-3-méthane.

Les homopolymères des esters acryliques ou vinyliques ne sont pas sensibles à cette réaction et peuvent être séparés du gel. L'homopolymère du N-vinylcarbazole accélère notablement la réaction de formation de gel dans les copolymères.

On a préparé par voie radicalaire en solution à 30° une série de copolymères du N-vinylcarbazole avec l'acrylate de méthyle, le methacrylate de méthyle, l'acrylonitrile et l'acétate de vinyle et les produits obtenus ont été soumis à la réaction décrite ci-dessus. Dans aucun cas on n'a pu déceler la présence d'homopolymère.

Sommario—Le unità di carbazolo possono reticolare per reazione con un catalizzatore tipo acido di Lewis in cloruro di metilene. La reazione dà inizialmente un gel e poi (con $BF_3.Et_2O$) un colore blù caratteristico. Si é visto che il prodotto blù é un colorante cationico del tipo diarilmetilico, che deriva dalla base colorante, bis-(9-alchil-3-carbazolil)-metano.

Gli omopolimeri degli esteri acrilici e vinilici non vengono influenzati da questa reazione, e possono essere estratti dal gel; gli omopolimeri del N-vinil carbazolo accelerano notevolmente la formazione del gel reticolandosi con i copolimeri.

Sono state effettuate varie copolimerizzazioni per radicali liberi in soluzione a 30° del N-vinilcarbazolo, e i prodotti sono stati sottoposti a questa reazione. In nessun caso si é formato un omopolimero.

Zusammenfassung—Carbazoleinheiten in Copolymeren können durch Reaktion mit einer Lewissäure als Katalysator in Methylenchlorid vernetzt werden. Die Reaktion führt anfänglich zur Gelbildung, danach kommt es (mit BF_3-Ätherat) zur Ausbildung einer charakteristischen blauen Farbe. Es wurde gezeigt, daß das blaue Produkt ein kationischer Farbstoff vom Diaryl-methyl Typ ist, der sich von der Farbstoffbase Bis-(9-alkyl-3-carbazolyl)-methan ableitet. Homopolymere aus Acryl- oder Vinylester zeigen diese Reaktion nicht und können aus dem Gel extrahiert werden. Homopolymeres N-Vinylcarbazol beschleunigt die Gelbildungsreaktion durch Vernetzung mit Copolymeren merklich.

Eine Reihe von radikalischen Copolymerisationen von N-Vinylcarbazol mit Methylacrylat, Methylmethacrylat, Acrylnitril und Vinylacetat wurden in Lösung bei 30° durchgeführt und der beschriebenen Reaktion unterworfen. In keinem Falle wurde Homopolymeres gebildet.