

Thermal Degradation of Polymethacrylonitrile. Part II. The Coloration Reaction

N. GRASSIE and I. C. McNEILL, *Chemistry Department, The University, Glasgow, W. 2, Scotland*

Most progress in the understanding of polymer degradation processes has been made with reactions which result in volatile products. These can usually be identified so that a good deal of purely chemical evidence can be accumulated. Very much less progress has been made with reactions in which the products remain attached to the polymer chains, principally because of the difficulties of identification of low concentrations of chemical groupings in that particular environment.

Coloration reactions in polymers, which are of intense interest industrially, are often of this latter type. In the present paper an attempt is made to elucidate some of the details of the thermal coloration of polymethacrylonitrile by a consideration of the general physical characteristics of the reaction together with some infrared spectral and molecular weight data.

The rapid coloration which occurs in polymethacrylonitrile at temperatures over 120°C. was shown in the first paper of this series¹ to take place in polymers in which traces of certain types of impurities had become incorporated into the macromolecular chains. These impurities act as centers of initiation for the coloration reaction, which thenceforward is concerned with methacrylonitrile units. Methacrylic acid is capable of behaving as such an impurity and its accidental presence in most polymethacrylonitriles hitherto examined has led to the belief that thermal coloration is an inherent property of this polymer. In fact thermal coloration of polymethacrylonitrile below 200°C. can be almost completely suppressed by careful attention to monomer purity and polymerization conditions. Methacrylic acid units can be incorporated very conveniently into polymethacrylonitrile chains in closely controlled amounts by copolymerization techniques and the experiments presently described concern copolymers of methacrylonitrile with methacrylic acid as coloration initiator.

EXPERIMENTAL

Preparation of Copolymers. *Methacrylonitrile* was prepared as previously described¹ (purification by washing with alkali and redistillation).

Methacrylic acid (I. C. I. Ltd.) was freed from inhibitor by distillation under reduced pressure (b.p. 60°/10 mm.) and stored at -16°C.

Azobisisobutyronitrile (Eastman Kodak), recrystallized from toluene, was used as initiator.

Methacrylonitrile was degassed and twice distilled in vacuum, first into a calibrated reservoir and finally into dilatometers containing initiator. These were then removed from the vacuum system and a measured amount of methacrylic acid added. This procedure was adopted since methacrylic acid cannot easily be degassed and distilled because of its low volatility and strong tendency to polymerize when freed from inhibitor. The mixture was finally degassed and sealed off under vacuum. Polymerizations were carried to 5% conversion. Further details are given in Table I. Copolymer compositions were calculated from reactivity ratios determined by Grant.²

$$r_1 = 0.62 \pm 0.05, \quad r_2 = 1.64 \pm 0.05 \quad (65^\circ\text{C.})$$

(subscripts 1 and 2 refer to methacrylonitrile and methacrylic acid, respectively).

TABLE I
Preparation of Copolymers

Copolymer	Initiator (%)	Temp. (°C.)	Composition ratios ^a	
			Monomers	Copolymer
1	0.7	65	39.5	21.2
2	0.7	65	8.11	5.25
3	0.7	65	4.05	2.57

^a (Methacrylonitrile)/(methacrylic acid).

Polymers were precipitated with petroleum ether and reprecipitated from acetone solution. They were then ground to a fine powder and dried under high vacuum at room temperature.

Degradation Experiments

(a) **Molecular Weight and Solubility Changes.** These degradations were carried out in the dynamic molecular still³ on 0.2 g. quantities of copolymer 1. Coloration proceeds at a convenient rate at 140°C. During the course of the reaction the polymer gradually becomes insoluble in acetone. Colored polymers were extracted by refluxing with acetone, and solubilities were calculated from the concentrations of these solutions and the original weights of polymer used. The molecular weights of these colored polymers were measured as described below.

(b) **Changes in Infrared Spectrum.** For these experiments copolymers were heated to 120° in vacuum for five minutes to remove occluded volatile material (solvents etc.). They were ground to a fine powder and incorporated into KCl discs (5.6 ± 0.1 mg./300 mg. KCl) which were heated in

an evacuated Pyrex tube at 140°C. Heating was interrupted at intervals and the infrared spectrum of the disc measured on a Perkin-Elmer model 13 double-beam spectrophotometer with NaCl prism.

Molecular Weight Measurements. Number-average molecular weights were measured using Pinner-Stabin type osmometers⁴ (Polymer Consultants Ltd.) with membranes prepared from undried cellophane. Measurements were made in acetone (Analar) solution at 25°C.

Molecular Models. These were constructed from Catalin atomic models.

RESULTS AND DISCUSSION

Development of Insolubility and Changes in Molecular Weight

While copolymers of methacrylonitrile and methacrylic acid are coloring thermally at 140°C. in vacuum, changes occur in their solubility properties. The data in Table II give some indication of the extent of reaction at which insolubility in acetone develops. Prolonged reaction results in complete insolubility. In general cyclohexanone is a better solvent than acetone for colored material, although the opposite is true for undegraded polymer.

TABLE II
Molecular Weights and Solubilities of Colored Polymethacrylonitrile

Time at 140° (min.)	Color	Soly. (%)	Mol. wt.
0	Colorless	100	14,400 ± 750
15	Yellow-orange	100	11,850 ± 750
45	Orange-red	100	12,950 ± 750
180	Deep red	80	12,750 ± 750

Decreasing solubility suggests the occurrence of a crosslinking reaction either intimately linked with the coloration process or entirely independent of it. It is quite clear, however, that crosslinking is not involved since no increase in molecular weight occurs up to the point of insolubility, as shown in Table II.

It was also established previously that no volatile material is produced during the reaction.¹

This combination of evidence strongly suggests that the reaction consists of an intramolecular rearrangement involving extensive configurational changes which result in insolubility.

A small but definite decrease in molecular weight does occur in the earliest stages of the reaction. This, however, appears to be associated with an independent reaction, involving the destruction of ketene-imine linkages,⁵ which is complete before any significant coloration occurs.

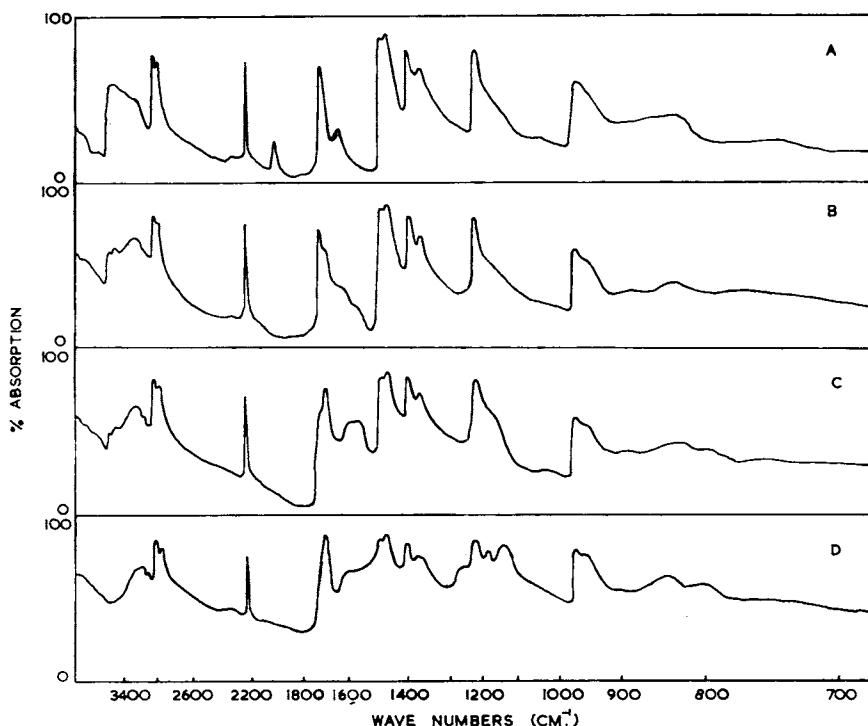


Fig. 1. Changes in infrared spectrum during coloration (copolymer 1): (a) undegraded material, colorless; (b) 3 hours at 140°, yellow-orange; (c) 9 hours at 140°, orange-red; (d) 23.5 hours at 140°, deep red.

Changes in Infrared Spectrum

While these polymers are coloring thermally in vacuum their infrared spectra undergo substantial changes. The spectrum of undegraded copolymer 1 is compared in Figure 1 (A-D) with those of the same material degraded to different extents of coloration. The changes are summarized in Table III.

TABLE III
Changes in Infra-red Spectrum during Color Reaction

Disappearance or reduction of absorption at (cm. ⁻¹)	Structure responsible	Appearance of new absorption at (cm. ⁻¹)	Structure responsible
3480	OH or NH	3180 ^a	=NH ?
2580 w	COOH ?	3070	
2210 m	—C≡N	1693-1490 s	probably (—C=N—) _n
2012 w	C=C=N—	1272	
		1178	
		1133 s	

^a Already present in undegraded copolymers 2 and 3.

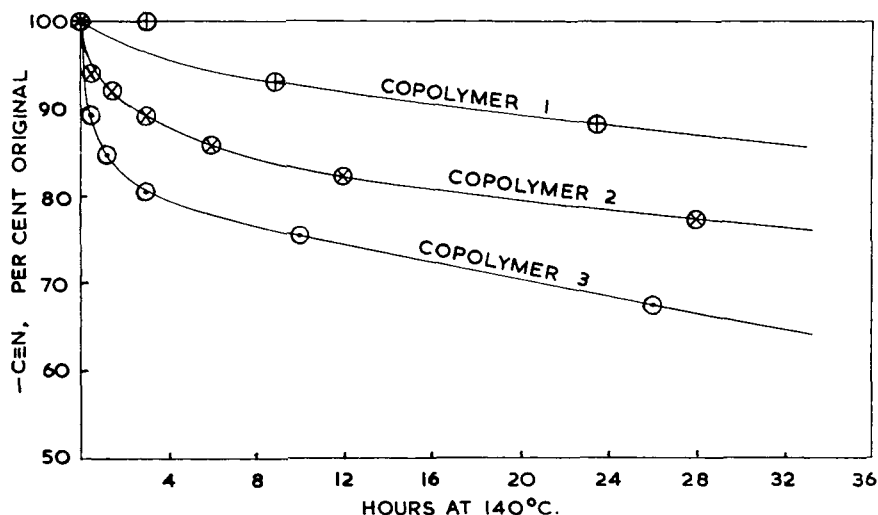


Fig. 2. Decrease in nitrile absorption ($\log I_0/I$) during coloration.

Copolymers 2 and 3 show the same general changes in spectrum as copolymer 1; detail differences are discussed below.

The general broadening of bands in the lower frequency region of the spectrum is to be expected since we are dealing in effect with a mixture of colored and undegraded polymer.

The band at 3480 cm.^{-1} may be due to the hydroxyls of the carboxyl group or more probably to traces of water. Interpretation in this region is confused by possible hydrogen bonding effects and poor resolution of the NaCl prism. It is also possible that the spectrum may be modified by interaction between the carboxyl groups and the KCl disc on heating.⁶ However the spectra of discs prepared from previously colored polymer do not differ appreciably from those obtained as in the present work in which the polymer is colored thermally within the disc. We hope at a later date to clarify the changes in the OH and carbonyl regions through a study of solution spectra. The 2012 cm.^{-1} peak, which disappears as soon as the temperature is raised substantially above room temperature is due to ketene-imine groups, as discussed above, and is not associated with coloration. The 2210 cm.^{-1} band due to the nitrile group decreases steadily and continuously during the course of the reaction.

The interpretation of the peaks which appear during degradation is more difficult. The most significant change appears to be the development of broad absorption in the $1693\text{--}1490 \text{ cm.}^{-1}$ region.

The decrease in intensity of the 2210 cm.^{-1} band during the coloration of all three polymers under discussion has been investigated quantitatively. Results are summarized in Figure 2, from which it is clear that the initial rate of disappearance of $\text{C}\equiv\text{N}$ is roughly proportional to the number of centers of initiation (methacrylic acid units). On the other hand, the development of visible color bears some inverse relationship to the concen-

tration of methacrylic acid units and for different polymers does not at all depend upon the extent of reaction of the nitrile groups. Thus copolymer 1 has become deep red by the time 12% of the nitrile groups have reacted. copolymer 2 is only yellow-orange after 23% reaction, while copolymer 3 is only slightly yellow at 30% reaction.

In Figure 3 the changes which occur in the 1660–1490 cm^{-1} region are shown quantitatively for each polymer. Copolymer 1 exhibits an initial increase in absorption at the higher frequency end of this region. As the color changes from yellow to red there is a gradual shift to lower frequencies

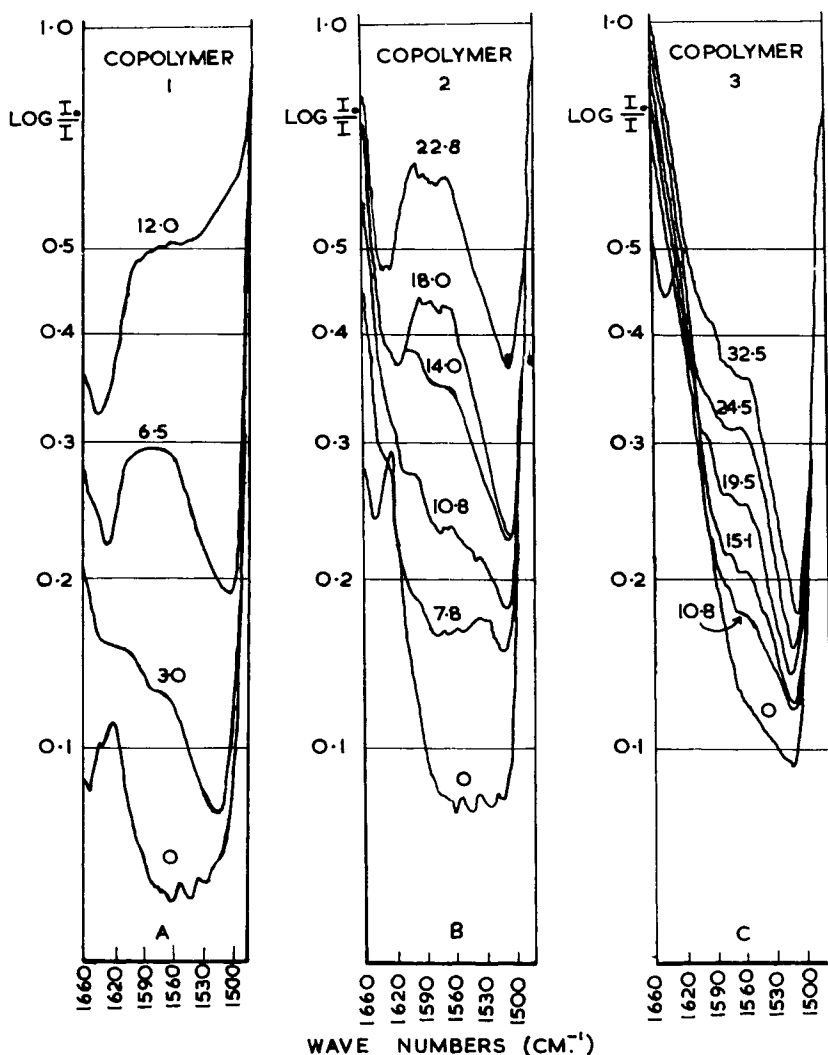


Fig. 3. Changes in the 1660–1490 cm^{-1} region of the infrared spectra of copolymers 1, 2, and 3 during coloration. Extent of reaction (% decrease in $\text{C}\equiv\text{N}$) is indicated for each stage.

as well as a general intensification. This behavior can be accounted for on the basis of the production of conjugated sequences gradually increasing in length. The movement of color through the visible spectrum during degradation rather than the intensification of a single spectral color is additional evidence for the gradual development of conjugation. Since nitrile groups are disappearing without chain scission, crosslinking, or elimination of volatile material, these are probably carbon-nitrogen sequences derived from the linking up of adjacent nitrile groups along the polymer chains. Bircumshaw, Tayler, and Whiffen⁷ have made a similar interpretation of absorption in the same region of the spectrum of paracyanogen.

If the above conclusions are correct, then in copolymers 2 and 3 the length of the conjugated carbon-nitrogen sequences, and hence the development of color, must be severely restricted by the greater proportion of methacrylic acid units (1 in 5.3 and 1 in 2.6, respectively) which break up the long sequences of methacrylonitrile units. We should therefore expect to find very much narrower absorption bands for equivalent extents of reaction and much less general tendency to broaden to lower frequencies as reaction proceeds.

Figures 3B and 3C show that these predictions are realized. Copolymer 3 exhibits very little shift in absorption to lower frequencies as reaction proceeds, and copolymer 2 is intermediate in behavior between 1 and 3.

Further evidence of the close connection between the disappearance of

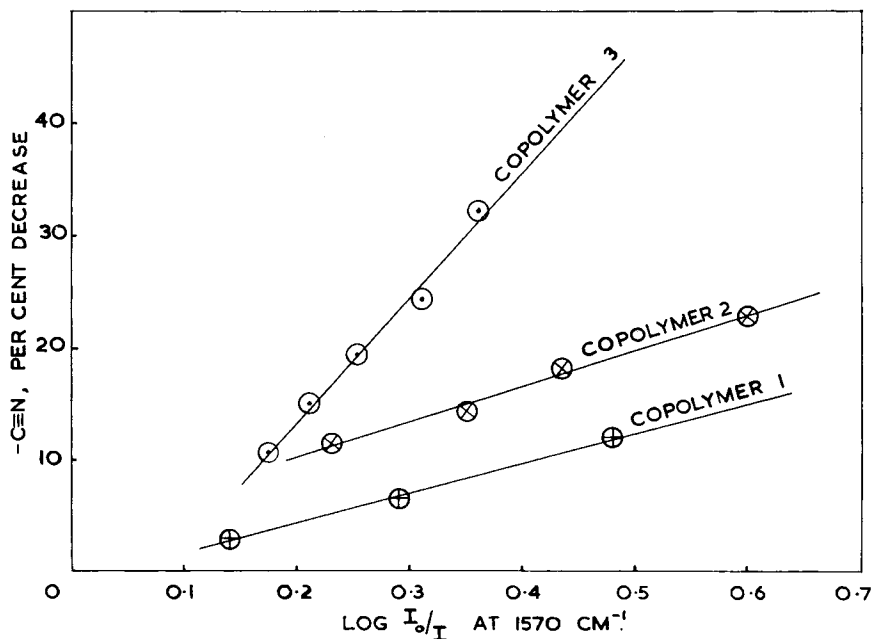


Fig. 4. Linear relationship between decrease in nitrile absorption ($\log I_0/I$) and increase in absorption at 1570 cm^{-1} .

nitrile groups and the appearance of absorption in the region under consideration is given in Figure 4, from which there is seen to be a direct linear relationship.

Reversibility of the Reaction

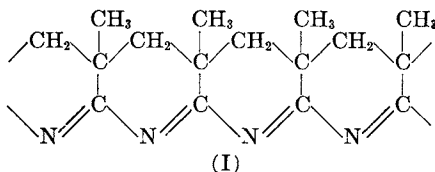
Thermally colored copolymer 1 dissolves in acetone and more readily in cyclohexanone to give a correspondingly colored solution. Gradual reversion occurs, however, and a blood red solution, for example, reverts to orange in two or three days at room temperature. Reversion occurs in colored samples of polymers 2 and 3 as they dissolve and colorless or yellow solutions result. The chemical structure responsible for color is clearly unstable in solution; this is emphasized by the fact that no coloration is obtained when cyclohexanone solutions of copolymer 1 are heated to 140–150°.

Reversion can be accelerated by treatment of solutions in acetone with aqueous solutions of acids, alkalis, or salts (*e.g.*, calcium chloride). Thus a blood red solution of copolymer 1 reverts to pale yellow in a few seconds. From this solution yellow polymer can be precipitated which has an infrared spectrum identical with that of yellow polymer obtained directly by thermal coloration.

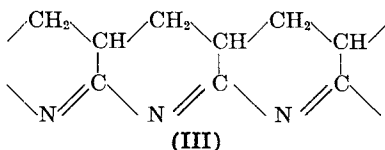
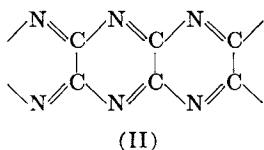
Any mechanism proposed for the reaction must therefore allow of a simple reverse process.

Molecular Structure of Colored Polymer

From the experimental data described above it is proposed that intramolecular linking of nitrile groups occurs, resulting in structure I.



Molecular models indicate that in polymethacrylonitrile the double substituents must impose considerable restriction to free rotation about the chain carbon-carbon bonds and that one of the most probable configurations has nitrile groups all on the same side of the chain so that such an intramolecular reaction would be facilitated. Furthermore no appreciable strain exists in the resulting fused-ring structure. Similar structures have been proposed for paracyanogen⁷ (II), alkali-degraded polyacrylonitrile,⁸ and very recently for thermally degraded polyacrylonitrile⁹ (III). Polymerization of nitrile groups is also well established in the for-



mation of cyclic triazines from nitriles containing no reactive methylene groups.

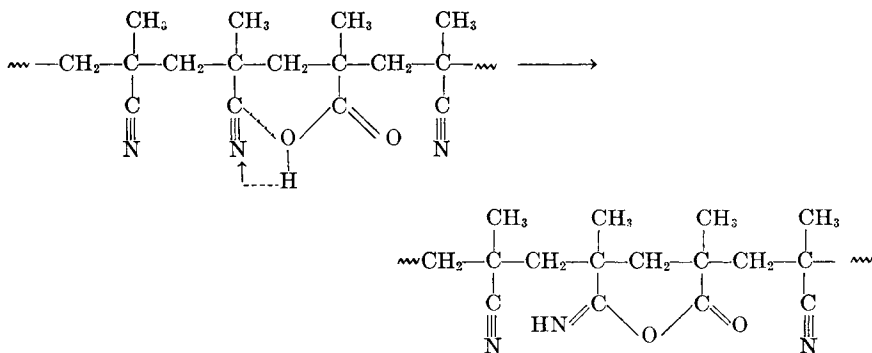
The changes in infrared spectrum which occur on thermal coloration of polymethacrylonitrile are reasonably explained on the basis of I although the assignment of the bands at lower frequencies (see Table III) to naphthyridine type ring systems can only be speculative.

The insolubility in acetone of extensively colored material can be attributed to the rigidity of this fused ring structure.

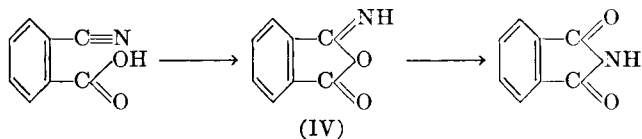
A Possible Mechanism for Coloration

Methacrylic acid units in the chains are necessary for the reaction to occur and the rate of disappearance of nitrile groups increases with the concentration of these units. Initiation of the coloration reaction must therefore be associated with methacrylic acid units. At the same time, increasing concentrations of methacrylic acid inhibit coloration, as do other foreign molecules like methyl methacrylate, so that fairly long sequences of adjacent monomer units must be involved. The relative slowness of the movement of color through the visible spectrum is strong evidence that this chain reaction is not a radical one but that at each stage, probably on production of each double bond, relatively stable structures exist which must be reactivated. The probable ionic rather than free radical type of mechanism is further emphasized by the fact that a superficially similar coloration process occurs in pure polymethacrylonitrile in acetone solution on addition of alkali.⁸ These requirements, together with the infrared, solubility, and other experimental data already discussed, are fairly well satisfied by the following reaction scheme.

It is proposed that initiation is represented by:



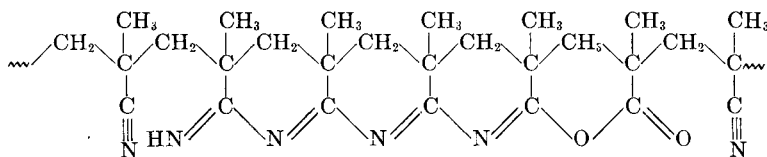
ring closure and proton migration being facilitated by the electromeric dis-



placements in the nitrile and carboxyl groups. Interaction of this sort

has been observed in *o*-cyanobenzoic acid, which can be converted to phthalimide via the isomer (IV) which can be isolated.¹⁰

Propagation may consist of reaction of the imine group in a similar way to reproduce itself one unit further along the chain. Several such additions would result in the structure:



This reaction should be readily reversible as is found experimentally and color reversion might easily be accelerated in an ionic medium, especially by acids and alkalis, by opening of any one of the rings by hydrolysis.

It is of interest to compare these results with those recently published by Burlant and Parsons⁹ on the pyrolysis of polyacrylonitrile, since the overall reactions have similar coloration characteristics. These superficial similarities are emphasized by the facts that their infrared spectra show a decrease in nitrile absorption as reaction proceeds and there is evidence of absorption in the 1650–1490 cm.⁻¹ region. The details of the preparation of Burlant and Parsons' polymers are not quoted but there is little carbonyl absorption apparent in the spectrum of the undegraded material. The initiation process in polyacrylonitrile may therefore be different, possibly being associated with the presence of the relatively reactive tertiary hydrogen atoms which are replaced by methyl groups in polymethacrylonitrile. Molecular weight data on polyacrylonitrile would be of interest in view of the possible part which these tertiary hydrogen atoms might play in either chain scission or crosslinking reactions.

The authors thank Dr. G. Eglinton and his associates for assistance in the measurement and interpretation of infrared spectra and Mr. A. Glennie for general technical assistance. Thanks are also due to the D.S.I.R. for the award of a Maintenance Grant (to I.C.M.).

References

1. N. Grassie and I. C. McNeill, *J. Chem. Soc.*, **1956**, 3929.
2. D. H. Grant, unpublished.
3. N. Grassie and H. W. Melville, *Proc. Roy. Soc.*, **A199**, 1 (1949). N. Grassie, *Trans. Faraday Soc.*, **48**, 379 (1952).
4. S. H. Pinner and J. V. Stabin, *J. Polymer Sci.*, **9**, 575 (1952).
5. N. Grassie and I. C. McNeill, unpublished. M. Talat-Erben and S. Bywater, International Symposium on Macromolecular Chemistry, 1954. Published in *Ric. sci.*, **25A**, 11 (1955). Distributed in the U.S. by Interscience, New York.
6. V. C. Farmer, *Chemistry & Industry*, **1955**, 586.
7. L. L. Bircumshaw, F. M. Tayler, and D. H. Whiffen, *J. Chem. Soc.*, **1954**, 934.
8. J. R. McCartney, *Natl. Bur. Stand. Circ.* **525**, 123 (1953).
9. W. J. Burlant and J. L. Parsons, *J. Polymer Sci.*, **22**, 249 (1956).
10. F. Tiemann, *Ber.*, **19**, 1475 (1886). O. Allendorf, *Ber.*, **24**, 2347 (1891).

Synopsis

The thermal coloration which occurs in copolymers of methacrylonitrile with small amounts of methacrylic acid has been studied at 140°C. The infrared spectra of colored polymers show a decrease in nitrile absorption (which has been followed quantitatively) and new absorption appears, mainly at 1693–1490 cm^{-1} . No volatile material is lost during coloration and molecular weight measurements show that neither chain scission nor crosslinking is involved. Copolymers of different compositions have been used to control the length of sequences of adjacent methacrylonitrile units, and it has been found that coloration is inhibited by larger concentrations of methacrylic acid. Colored polymer slowly reverts to the original material in solution, and rapid decoloration is effected by addition of aqueous solutions of acids, alkalis, and salts. A structure has been deduced for colored polymethacrylonitrile analogous to those proposed previously for paracyanogen and colored polyacrylonitrile. Essentially this is the result of the linking up of adjacent nitrile groups to form conjugated carbon-nitrogen sequences of considerable length. It is suggested that this structure is formed in a nonradical chain process initiated at methacrylic acid units and propagated through adjacent nitrile units. The changes in solubility properties are not the result of crosslinking but of the rigidity of the modified polymer structure.

Résumé

On a étudié la coloration thermique à 140°C du copolymère de méthacrylonitrile contenant de faibles quantités d'acide méthacrylique. Les spectres infrarouges des polymères colorés indiquent une diminution de l'absorption de la bande nitrilique (qui a été suivie quantitativement) et de nouvelles bandes d'absorption apparaissent principalement à 1693–1490 cm^{-1} . Aucune substance volatile n'est éliminée en cours de coloration, et les mesures de poids moléculaires montrent qu'il n'y a ni rupture ni pontage de chaîne. Des copolymères de compositions différentes ont été utilisés pour contrôler la longueur des séquences d'unités méthacrylonitriliques voisines; on trouve ainsi que la coloration est inhibée par de grandes concentrations d'acide méthacrylique. Le polymère coloré retourne lentement au matériel original, en solution, et cette décoloration rapide est obtenue par addition de solutions aqueuses d'acides, bases et sels. Une structure de ce polyméthacrylonitrile coloré a été déduite; elle est analogue à celle proposée pour le paracyanogène et le polyacrylonitrile coloré. Essentiellement elle résulte de la liaison de groupes nitriles voisins avec formation de séquences conjuguées carbone-azote de longueur considérable. On suggère que cette structure résulte d'un processus en chaîne non-radicalaire initié à l'endroit des unités d'acide méthacrylique et propagé le long des unités nitriles voisines. Les variations de propriétés de solubilité ne sont pas le résultat de pontage, mais de la rigidité de la structure du polymère modifié.

Zusammenfassung

Die thermische Färbung, die in Copolymeren von Methacrylnitril mit kleinen Mengen von Methacrylsäure auftritt, wurde bei 140°C untersucht. Die infraroten Spektren von gefärbten Polymeren zeigen eine Abnahme der Nitrilabsorption (die quantitativ verfolgt wurde) und es tritt neue Absorption in der Hauptsache bei 1693–1490 cm^{-1} auf. Während der Färbung wird kein flüchtiges Material verloren und Molekulargewichtsmessungen zeigen, dass weder Kettenspaltung noch Querverbindung auftreten. Copolymere verschiedener Zusammensetzung wurden zur Kontrolle der Länge der Sequenzen von benachbarten Methacrylnitril-Einheiten verwendet, und es wurde gefunden, dass die Färbung durch grössere Konzentrationen von Methacrylsäure inhibiert wird. Das gefärbte Polymer verwandelt sich langsam wieder in die Anfangssubstanz in Lösung und schnelle Entfärbung wird durch Addition wässriger Lösungen von Säuren, Alkalien und Salzen erreicht. Es wurde eine Struktur für gefärbtes Polymethacrylnitril ähnlich denen früher für Paracyanogen und gefärbtes Polyacrylnitril vorgeschlagen abgeleitet.

In der Hauptsache ist dies das Resultat der Verbindung benachbarter Nitrilgruppen, um konjugierte Kohlenstoff-Stickstoff-Sequenzen von erheblicher Länge zu bilden. Es wird vorgeschlagen, dass diese Struktur in einem nicht-Radikal-Kettenvorgang gebildet wird, der an Methacrylsäure-Einheiten initiiert wird und durch benachbarte Nitril-Einheiten propagiert wird. Die Änderungen der Löslichkeitseigenschaften sind nicht das Resultat von Querbindung, sondern von Steifheit der veränderten Polymerstruktur.

Received February 28, 1957