

764. *The Thermal Degradation of Polymethacrylonitrile. Part I. Separation of Coloration and Depolymerization Reactions.*

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The colour which develops in polymethacrylonitrile at 120° is due to a reaction initiated at impurities in the polymer chains. These are eliminated by suitable purification of the monomer and by carrying out the polymerization in a vacuum in presence of $\alpha\alpha'$ -azoisobutyronitrile as catalyst.

By using such polymers the depolymerization reaction, which occurs at 220° and affords quantitative yields of monomer, can be investigated in absence of the complications due to coloration.

The coloration reaction is most conveniently studied in copolymers of methacrylonitrile with traces of methacrylic acid. The methacrylic acid units act as centres of initiation, the concentration of which can be closely controlled in the preparation of the material.

SINCE polymethacrylonitrile is derived from a 1:1-disubstituted monomer it would be expected, like poly(methyl methacrylate), poly- α -methylstyrene, poly(vinylidene cyanide), etc., to be capable of decomposing quantitatively to monomer.¹ Appreciable yields of monomer can indeed be obtained thermally from polymethacrylonitrile although these have never approached 100%.² Simultaneously the polymer develops colour and becomes insoluble. The principal features of this coloration reaction prove it to be quite unusual and of considerable chemical interest. Superficially it appears to be similar to the coloration produced in solution by alkali.³ This paper describes some preliminary experiments which define the conditions under which the depolymerization and coloration reactions take place and shows how they can be separated for individual study.

Results and Discussion.—When the temperature of a methacrylonitrile polymer which is liable to develop colour is slowly raised in a vacuum, the following general behaviour is observed. At 110° the polymer remains clear and colourless but has softened to such an extent that volatile material readily escapes. Above 120° the material rapidly changes colour through yellow, orange, and red to deep red. Simultaneously it gradually becomes insoluble and infusible. No further appreciable evolution of volatile material is discernible till monomer is evolved at approximately 220°. Fig. 1 shows how the rate of evolution of volatile material varies as the temperature of such a polymer sample is slowly raised to 270° in the dynamic molecular still.⁴

While the coloration of polymethacrylonitrile has always been regarded as characteristic of the polymer, it was quite clear that the ease and extent of coloration were liable to vary widely from sample to sample. Investigation of the factors involved proves that the method of purification of the monomer, the nature of the catalyst, and the method of polymerization may all have an effect as shown in Table I.

¹ Grassie, "The Chemistry of High Polymer Degradation Processes," Butterworths Scientific Publications Ltd., London, 1956, Chapters 1 and 2.

² Kern and Fernow, *J. prakt. Chem.*, 1942, **160**, 296.

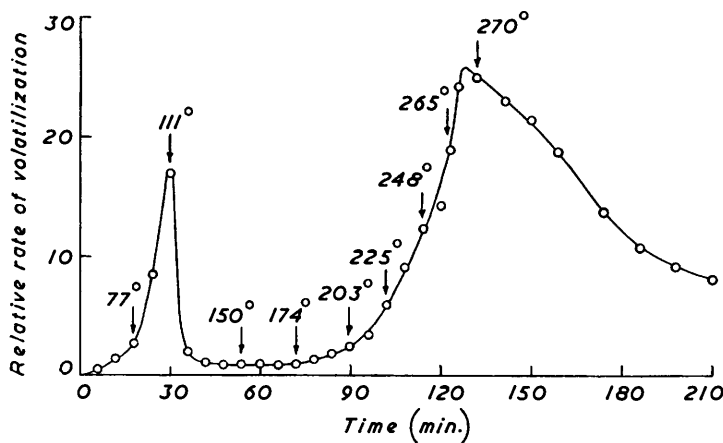
³ McCartney, U.S. Nat. Bur. Stand. Circ. No. 525, 1953, p. 123.

⁴ Grassie and Melville, *Proc. Roy. Soc.*, 1949, **A**, **199**, 1; Grassie, *Trans. Faraday Soc.*, 1952, **48**, 379.

It is also quite clear that the tendency for polymer to develop colour is closely linked with the ultimate yield of monomer which can be obtained at high temperatures; *e.g.*, when the polymer referred to in Fig. 1 (which colours readily) is heated rapidly to 310°, yields of only 58% are produced, but this is reduced to 52% when the colour is first increased by preheating to 160° for 30 min. On the other hand, polymer D (Table 1) is converted almost quantitatively into monomer under the same conditions. Thus when coloration is eliminated the material behaves precisely as one would predict by comparison with other polymers derived from 1 : 1-disubstituted monomers.

The data in Table 1 suggest that the ease of coloration may be associated in some way with the presence of impurities. The infrared spectra of the polymers in Table 1 are shown in Fig. 2 (A—D). The main difference between them resides in the band at 1720 cm^{-1} , the intensity of which runs closely parallel to the ease of coloration of the polymers at high temperatures. The region of this band, the fact that it can be eliminated by washing the monomer with alkali, the obvious possibility of cyanide groups'

FIG. 1. Rate of evolution of volatile material from polymethacrylonitrile which becomes coloured (copolymer of methacrylonitrile with traces of methacrylic acid).



being converted into carboxyl, and the fact that reprecipitation of the polymers affects neither the intensity of the band nor the coloration properties, all suggest that the 1720 cm^{-1} band is due to carbonyl groups incorporated in one way or another into the molecular chains. It is therefore concluded that structures involving carbonyl groups act as centres of initiation for the coloration reaction.

TABLE 1. Factors involved in the coloration of polymethacrylonitrile.

| Polymer preparation | Coloration at 160° |
|--|--------------------|
| A. Monomer purified by distillation (Method a) | Rapid |
| Monomer purified by washing with alkali (Method b) : | |
| B. Polymerized in air | Rapid |
| C. Polymerized <i>in vacuo</i> with benzoyl peroxide as catalyst | Slight |
| D. Polymerized <i>in vacuo</i> with $\alpha\alpha'$ -azoisobutyronitrile as catalyst | None |

Beaman reported a strong peak at 1710 cm^{-1} in the infrared spectrum of polymethacrylonitrile prepared by anionic catalysis and he attributed this to residual acetone in the polymer film.⁵ This cannot be the explanation in the polymers under discussion, however, since reprecipitation does not affect the coloration properties.

Strause and Dyer⁶ have shown that oxygen readily copolymerizes with methacrylonitrile. Primarily, peroxidic structures are undoubtedly formed. Being labile, however,

⁵ Beaman, *J. Amer. Chem. Soc.*, 1948, **70**, 3115.

⁶ Strause and Dyer, *ibid.*, 1956, **78**, 136.

FIG. 2. Infrared spectra of polymers A—D in Table 1 and a copolymer of methacrylonitrile with traces of methacrylic acid (E).

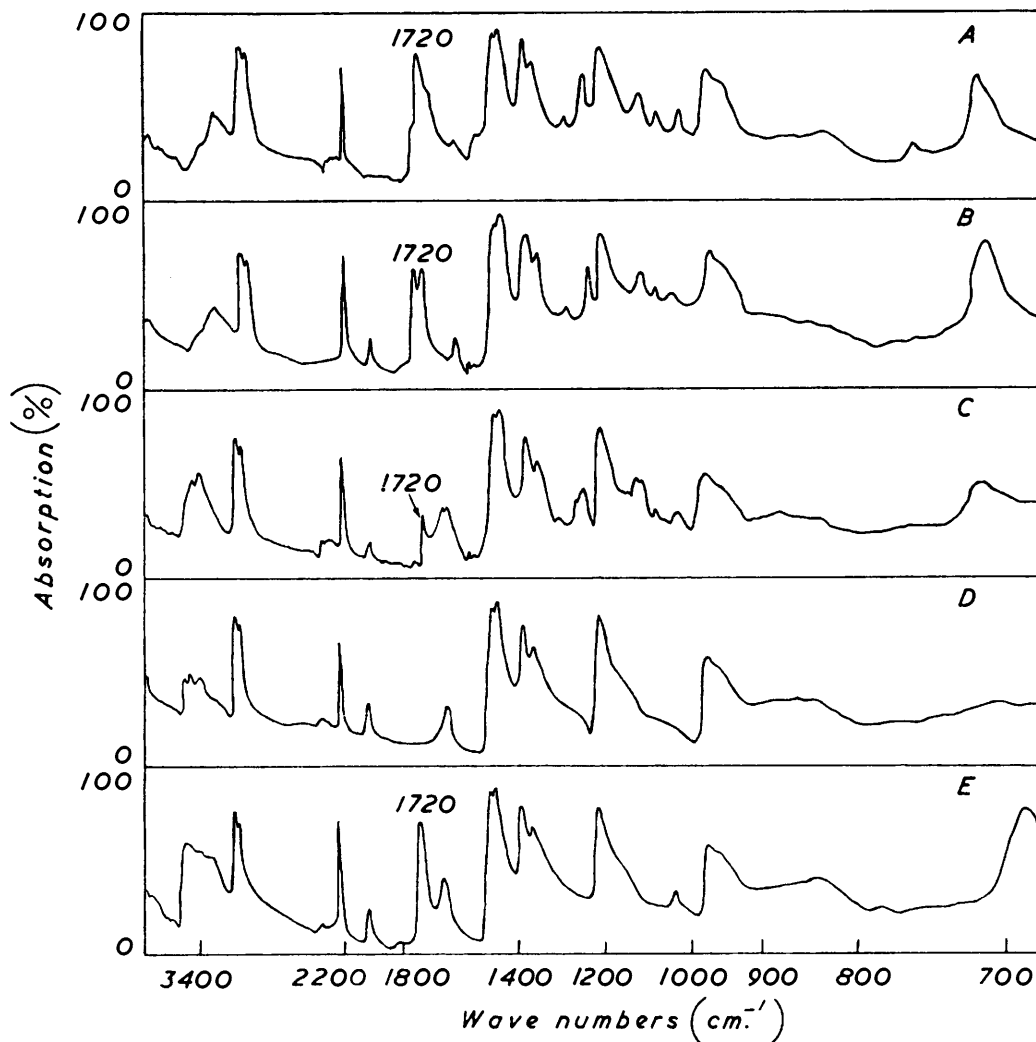
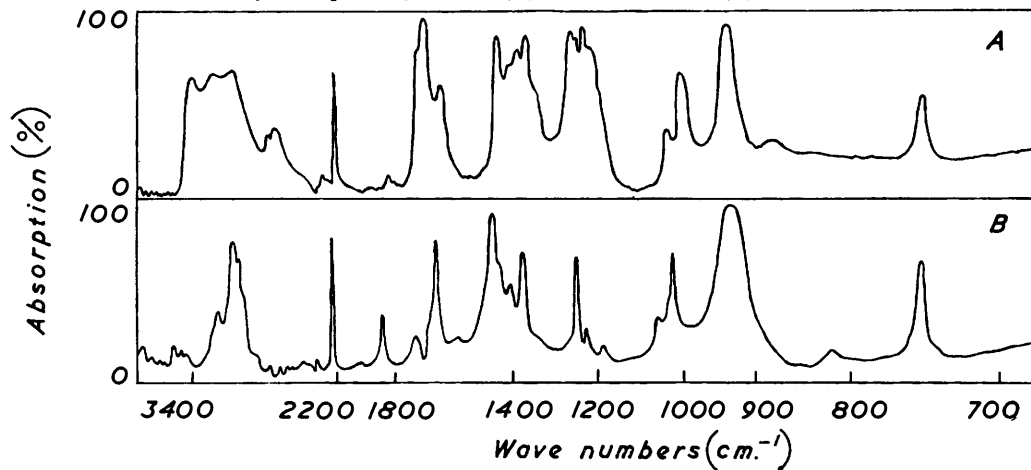


FIG. 3. Infrared spectra of distilled (A) and alkali-washed (B) monomers.



these will decompose to produce other oxygenated structures including carbonyl groups. The double carbonyl peak in Fig. 2B is probably due to products of different modes of peroxide decomposition. The carbonyl groups in benzoyl peroxide-catalysed polymers are also easily accounted for since they occur in the catalyst. Since monomer washed with alkali and polymerized in presence of an azo-catalyst results in a polymer free from carbonyl groups it is reasonable to suppose that polymer prepared from monomer not so washed is really a copolymer of methacrylonitrile with traces of methacrylic acid. Copolymers prepared from alkali-washed monomer with traces of methacrylic acid do in fact have identical thermal coloration properties and similar infrared spectra (Fig. 2E).

The infrared spectra of distilled and alkali-washed monomers are presented in Fig. 3. The former, from which colourable polymer may be prepared, absorbs in the carbonyl region; yet it seems most unlikely that a sufficient quantity of methacrylic acid could have persisted through a careful distillation process (methacrylonitrile, b. p. 89°; methacrylic acid, b. p. 163°). The principal impurities in the methacrylonitrile being distilled can only be water and acetic acid, and the latter could be responsible for the carbonyl absorption. The results of degradation experiments on polymer prepared from alkali-washed monomer together with traces of acetic acid and water both separately and together are shown in Table 2, from which it may be deduced that the methacrylic acid units which

TABLE 2. *Effect of monomer impurities on coloration properties of polymethacrylonitrile.*

| Impurity | Effect on polymer |
|--------------------------|-------------------|
| None | No colour |
| Water (5%) | No colour |
| Glacial acetic acid (5%) | No colour |
| Water + acetic acid (5%) | Colours |

appear in polymer from unwashed monomer are produced by the hydrolysis of methacrylonitrile units by the combined action of acetic acid and water at the high temperature at which polymerization is carried out. It is not clear whether this occurs more readily in unpolymerized monomer or in monomer units after they have been incorporated in polymer chains.

From these results it is possible to make some tentative suggestions about the nature of the coloration reaction. Because of the small concentration of carbonyl groups involved it is unlikely that their reaction alone can cause such extensive changes in the physical properties of the bulk material. Since the colour of the reacting polymer changes from yellow to red it is more probable that structures involving carbonyl groups act only as centres of initiation for a process which results in conjugated structures which gradually increase in length and are characteristic of the methacrylonitrile units rather than of the carbonyl groups.

Polymer initiated by $\alpha\alpha'$ -azoisobutyronitrile does develop colour very slowly at 250°. This represents a rate of reaction many orders of magnitude less than that of the other polymers mentioned above. It does not appear to be the result of impurity in the polymer and is probably due to some initiation process occurring within the methacrylonitrile units themselves, or possibly at terminal structures. This slight coloration does not affect the depolymerization reaction seriously since yields of monomer close to 100% can be obtained.

As a result of these experiments it is now quite clear how the coloration and depolymerization processes may be separated for individual study. For depolymerization investigations at high temperatures it is only necessary to prepare polymer, by means of an azo-catalyst, from monomer which has been thoroughly washed with alkali, while coloration can be studied at 120–150° in copolymers of such monomer with traces of methacrylic acid. In this way a very close control can be kept over the concentration of the centres of initiation. The mechanisms of these two processes will be discussed more fully in later papers.

EXPERIMENTAL

Preparation of Methacrylonitrile.—Methacrylonitrile was prepared as previously described⁷ and isolated by two methods. (a) It was washed with water, dried, and distilled as before⁷

⁷ Grassie and Vance, *J.*, 1954, 2122; *Trans. Faraday Soc.*, 1956, 52, 727.

(b. p. 91—93°; yield 60% on acetone cyanohydrin). (b) Ammonia solution (d 0.88) was added with vigorous stirring to the pyrolysis mixture in a separating funnel until the lower, aqueous layer become alkaline to litmus. After separation, the monomer layer was washed repeatedly with water, dried (CaCl_2), and twice distilled (b. p. 89—90°). Further quantities of monomer were obtained by ether extraction of the aqueous layer (yield 50% on acetone cyanohydrin).

Methacrylic acid. Methacrylic acid (Imperial Chemical Industries Limited) was distilled once at atmospheric pressure (b. p. 163°).

Catalysts. $\alpha\alpha'$ -Azobisisobutyronitrile (Eastman Kodak) was recrystallized from toluene. Benzoyl peroxide was purified by solution in chloroform followed by reprecipitation by methanol.

Preparation of Polymers.—Monomer prepared as above was degassed by freezing and thawing in a vacuum, twice distilled, and sealed off under vacuum in Pyrex dilatometer tubes containing catalyst.

In the preparation of the copolymer, methacrylic acid (2.5% of the total volume of monomers) was poured directly into the dilatometer and degassed before distillation of the methacrylonitrile.

Approximately 0.7% of catalyst was used in each case and polymerizations were continued to 5—10% conversion at 65°.

The air-polymerized sample was prepared, from monomer purified by method (b), in an open flask at 50° with benzoyl peroxide.

In each case polymer was isolated by precipitation in methanol and purified by reprecipitation from acetone solution. The resulting powder was dried in a vacuum at room temperature.

Degradation Experiments.—These were carried out in the dynamic molecular still described by Grassie and Melville.⁴

Infrared Measurements.—These were made on a Perkin-Elmer Model 13 double-beam spectrophotometer with sodium chloride prism. Monomers were examined in a 0.05-mm. sodium chloride cell, and polymers by the standard potassium chloride disc technique (7 mg./300 mg. of KCl).

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