

THE THERMAL DEGRADATION OF COPOLYMERS OF METHYL METHACRYLATE AND ACRYLONITRILE

N. GRASSIE and (MRS.) E. FARISH

Chemistry Department, University of Glasgow, Glasgow, Scotland

(Received 24 May 1967)

Abstract—The thermal degradation of four methyl methacrylate/acrylonitrile copolymers with molar ratios 410/1, 40/1, 16/1 and 8/1 has been studied at 280°. Volatilization of the copolymers to give a mixture of the constituent monomers is accompanied by a rapid decrease in the molecular weight of the residue. The same mol. wt. vs. % volatilization relationship is observed for all four copolymers. The rate of decrease of molecular weight and the rate of volatilization are more rapid the smaller the acrylonitrile content of the copolymer. These findings are interpreted in terms of random scission in the methyl methacrylate segments of the copolymer molecules, followed by depolymerization of the resulting radicals. Previous experiments, carried out at 220° on the 410/1 and 40/1 copolymers, have been reinterpreted in order to give a unified picture of the reaction at the two temperatures.

INTRODUCTION

THE THERMAL degradation reactions which occur in poly(methyl methacrylate) and polyacrylonitrile have been studied in detail.^(1,2) In the course of these investigations the influence of small concentrations of the second monomer copolymerized into the polymer chains was observed. Thus the effect of methyl methacrylate in polyacrylonitrile is to inhibit coloration by blocking the condensation of long sequences of adjacent nitrile groups.⁽²⁾ On the other hand, the presence of acrylonitrile units in poly(methyl methacrylate) causes an induction period in the production of methyl methacrylate monomer at 220°. ⁽¹⁾ Simultaneously a large decrease in molecular weight occurs which led Grassie and Melville to believe that the acrylonitrile units constitute "weak links" in the polymer structure.

Since these latter results were reported in 1949, further clarification of the decomposition of poly(methyl methacrylate) has been achieved,^(3,4) and Grassie and Melville's observations⁽¹⁾ on the influence of small concentrations of acrylonitrile units in poly(methyl methacrylate) chains are seen in a new light. It thus appears profitable to re-examine their work and to extend it to copolymers containing higher proportions of acrylonitrile.

EXPERIMENTAL

Preparation of copolymers

The 410/1 and 40/1, methyl methacrylate/acrylonitrile copolymers are those previously described by Grassie and Melville.⁽¹⁾ Those with the molar ratios 16/1 and 8/1 were prepared similarly. The molecular weights of these polymers are presented in Table I. The values in brackets are those obtained previously by Grassie and Melville.

TABLE I. MOLECULAR WEIGHTS OF THE COPOLYMERS

Molar ratio (MM/A)	Mol. wt.	
410/1	570,000	(617,000)
40/1	510,000	(547,000)
16/1	598,000	
8/1	470,000	

Molecular weight measurements

Number average molecular weights were measured using a Mechrolab high speed membrane osmometer.

Degradation experiments

Degradations were carried out in a dynamic molecular still, similar in principle to that described originally by Grassie and Melville.⁽¹⁾ The extent of volatilization was measured by loss in weight and the total liquid products by volume. Griffin and George Mark II G.L.C. equipment and a Perkin Elmer Model 237 i.r. spectrophotometer were used for the examinations of the liquid products.

RESULTS

Changes in molecular weight

The most suitable temperature for studying the whole range of copolymer compositions was found to be 280°. The changes in mol. wt. which occur during volatilization of the four copolymers at 280° are seen in Fig. 1 to be independent, within experimental error, of the composition of the copolymers. This implies that the same amount of monomer is produced per chain scission in each material.

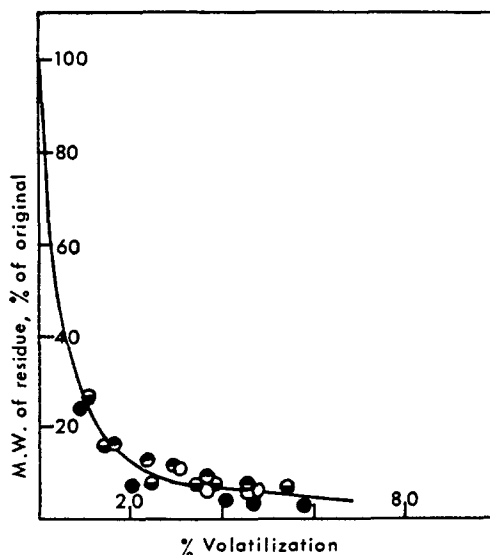


FIG. 1. Changes in mol. wt. with volatilization at 280° of methyl methacrylate/acrylonitrile copolymers. (○, 410/1; ●, 40/1; ⊖, 16/1; ⊕, 8/1).

The influence of copolymer composition on the changes in mol. wt. with time of degradation at 280° is illustrated in Fig. 2. Although the experimental points for the two copolymers of lowest acrylonitrile content lie on the same curve, it is clear that for higher acrylonitrile contents the rate of decrease of mol. wt. is less the greater the

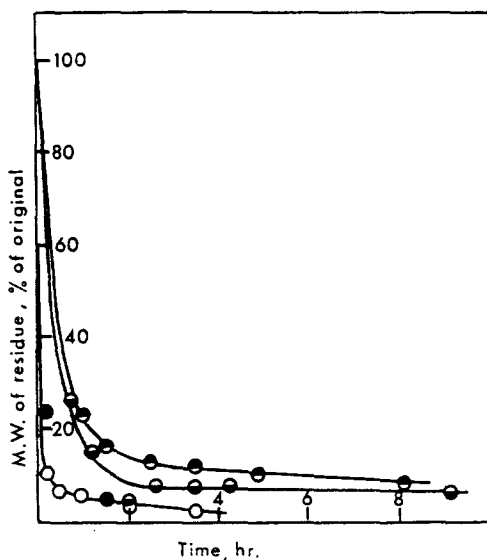


FIG. 2. Changes in mol. wt. with time at 280° of methyl methacrylate/acrylonitrile copolymers. (○, 410/1; ●, 40/1; ◐, 16/1; ●, 8/1).

acrylonitrile content of the copolymer. This observation is at variance with Grassie and Melville's⁽¹⁾ suggestion that chain scission occurs most readily in the vicinity of acrylonitrile units.

Volatile products of degradation

For all four copolymers, the weight loss during degradation was always found to correspond quantitatively with the amount of liquid products recovered. Examination of these volatile products from the 410/1 and 40/1, methyl methacrylate/acrylonitrile copolymers using g.l.c. and i.r. spectroscopy revealed only pure methyl methacrylate. However, small peaks were present at 2225 cm^{-1} in the i.r. spectra of the volatile material from the 16/1 and 8/1 copolymers, indicating the presence of an α , β -unsaturated alkyl nitrile.⁽⁵⁾ That this is due to acrylonitrile monomer was confirmed by g.l.c. analyses, which revealed that the 8/1 copolymer yields a 20/1 monomer mixture. The g.l.c. measurements were not sufficiently sensitive to allow the ratio of monomers obtained from the 16/1 copolymer to be determined accurately, but this ratio was clearly somewhat greater than 16/1. The amounts of acrylonitrile to be expected from the 40/1 and 410/1 copolymers are too small to be detected by these analytical techniques.

Rates of production of volatile material

The occurrence of induction periods and rate maxima of the type reported by Grassie and Melville⁽¹⁾ at 220° was confirmed. These tend to be less well defined as the acrylonitrile content of the copolymer is raised and to occur earlier in the reaction as the

temperature is raised. At 280° they have disappeared. The dependence of volatilization upon time of degradation for the four copolymers at 280° is illustrated in Fig. 3. The rate of volatilization is seen to be lower, the higher the acrylonitrile content.

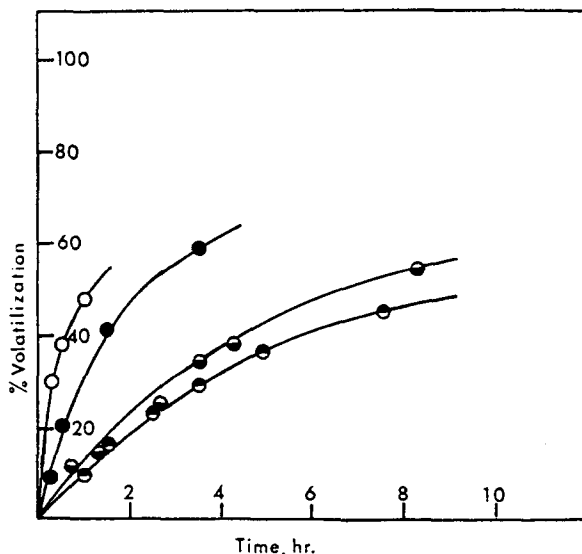


FIG. 3. Volatilization/time relationships for methyl methacrylate/acrylonitrile copolymers at 280°. (○, 41/1; ●, 40/1; ◐, 16/1; ◑, 8/1).

DISCUSSION

Grassie and Vance⁽³⁾ demonstrated that the depolymerization to monomer, which occurs at 220° in poly(methyl methacrylate) prepared using a free radical initiator, is initiated at the unsaturated chain terminal structures formed in the disproportionation termination step during polymerization. Once these are eliminated from the system, the residual polymer is much more stable and, like samples of poly(methyl methacrylate) which do not incorporate unsaturated chain terminal structures,^(1,6) only decomposes at higher temperatures. The way in which this high temperature decomposition is initiated was not clear until recently but the consensus of opinion now is that random scission of the polymer molecules occurs, followed by liberation of monomer from the resulting radicals.⁽⁴⁾

Grassie and Melville⁽¹⁾ observed that the incorporation of small amounts of acrylonitrile (0.25–2.5 mole %) into poly(methyl methacrylate) affects its depolymerization at 220° in a number of ways. Initially, monomer production is almost completely inhibited. During the inhibition period, however, the molecular weight decreases rapidly. Later, the rate of monomer production builds up, passing through a maximum 2–3 hr after heating is commenced. These workers explained the initial inhibition in terms of blockage of the chain end initiated depolymerization reaction by the first acrylonitrile unit encountered, the resulting acrylonitrile terminated radicals ultimately mutually destroying each other or rearranging to form stable chain terminal structures. They believed that the decrease in molecular weight is due to the acrylonitrile units acting as weak links at or near which chain scission occurs, and further that the scission

results ultimately in molecules rather than radicals. Since a proportion of these new terminal structures must be unsaturated and thus degradable at 220°, the increase in the rate of monomer production is also explained. One possible mechanism whereby chain scission may occur can be represented as follows:

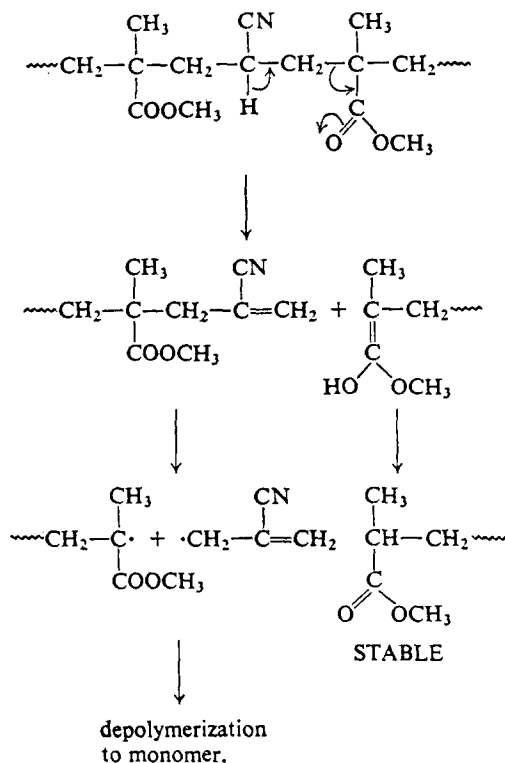
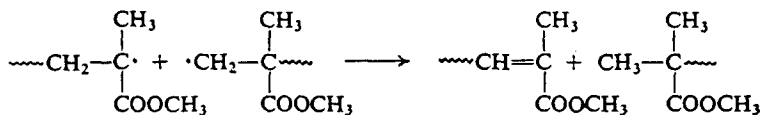


Figure 2 demonstrates that the rate of decrease in mol. wt. observed at 280° decreases with increasing acrylonitrile content. This is directly at variance with the concept of acrylonitrile units as weak links. The random chain scission which is now accepted as part of the degradation process at 280° in pure poly(methyl methacrylate) allows an alternative explanation of the decrease in molecular weight and a unified picture of reaction at 220° and 280° can be given as follows.

Like Grassie and Melville, we believe that at 220° radical depolymerization to monomer cannot pass through acrylonitrile units. Thus degradation initiated at unsaturated chain ends is stopped at the first acrylonitrile unit thereby accounting for the almost complete inhibition of monomer production early in the reaction. Chain scission can occur at random, however, although at a very slow rate at 220°. The ultimate effect of this random scission is to produce molecules although radicals may be formed initially followed by disproportionation in a cage.



The concentration of unsaturated chain ends formed in this way gradually builds up and since they are unstable at 220°, being identical with these formed during polymerization, the rate of volatilization increases. Since depolymerization cannot pass through acrylonitrile units, however, the chain length of the residue tends to decrease to the average length between adjacent acrylonitrile units, as shown by Grassie and Melville. The initiation of depolymerization at unsaturated chain ends is so rapid compared with random scission at 220° that the latter can not reveal itself in pure poly(methyl methacrylate).

When the degradation temperature is raised to 280° two fundamental changes in the nature of the reaction occur. Firstly, random chain scission is effectively into radicals which immediately depropagate. This may be due to a decrease in the influence of the cage effect owing to the very much lower viscosity of the molten polymer at the higher temperature. Alternatively, disproportionation may still occur, to be followed by immediate decomposition of the unsaturated structure. It will be extremely difficult to distinguish between these alternatives. In either case, as observed experimentally (Fig. 3), the initial inhibition will no longer occur. Secondly, at the higher temperature, depropagation can pass more efficiently through the acrylonitrile units which are thus liberated as monomer.

The close interdependence of chain scission and production of monomers is illustrated by a comparison of Figs. 2 and 3, which demonstrate that both are decreased by an increase in the acrylonitrile content of the copolymer. Since chain scission occurs at random in the methyl methacrylate segments of the copolymer molecules and since depolymerization can pass through acrylonitrile units, the zipp length of depolymerization should be independent of acrylonitrile content, thus accounting for the data in Fig. 1. The fact that chain scission is inhibited by the acrylonitrile units is the one experimental fact which cannot be fitted readily into this simple qualitative picture. It may be due to the fact that the copolymer molecules become less flexible as the acrylonitrile content is increased due to the kind of interaction between acrylonitrile units which results in the generally poor solubility of polyacrylonitrile. This may result in a greater probability of recombination in the cage if radicals are the initial products of scission, or to a reduced probability of achieving the conformation necessary if chain scission is initially to molecular species.

Acknowledgements—This research work has been sponsored by the United States Air Force under Grant AF EOAR 62-78 through the European Office of Aerospace Research, OAR, United States Air Force.

REFERENCES

- (1) N. Grassie and H. W. Melville, *Proc. R. Soc. A* **199**, 1 (1949).
- (2) N. Grassie and J. N. Hay, *J. Polym. Sci.* **56**, 189 (1962).
- (3) N. Grassie and E. Vance, *Trans. Faraday Soc.* **49**, 184 (1953).
- (4) J. R. MacCallum, *Makromolek. Chem.* **83**, 137 (1965).
- (5) L. J. Bellamy, *The Infra-Red Spectra of Complex Molecules*, p. 263, Methuen, London (1958).
- (6) I. C. McNeil, to be published.

Résumé—On a étudié la dégradation thermique à 280° de quatre copolymères méthacrylate de méthyle/acrylonitrile ayant des rapports molaires 40/1, 40/1, 16/1 et 8/1. La volatilisation des copolymères en un mélange des deux monomères constituants est accompagnée d'un abaissement rapide de la masse moléculaire du résidu. On trouve pour les quatre copolymères la même relation entre la masse moléculaire en fonction du degré de volatilisation. La vitesse de décroissance de la

masse moléculaire et la vitesse de volatilisation sont d'autant plus rapides que la teneur en acrylonitrile dans le polymère est plus petite. On interprète ces résultats en admettant qu'il se produit des coupures au hasard dans les segments méthacrylate de méthyle des copolymères qui sont suivies par la dépolymérisation des radicaux formés. On réinterprète des résultats antérieurs obtenus à 220° avec des copolymères ayant les rapports molaires 410/1 et 40/1 de manière à rendre compte de façon homogène de la réaction à ces deux températures.

Sommario—E' stata studiata la degradazione termica a 280°C di quattro copolimeri tra metilmetacrilato e nitrile acrilico con rapporti molari 410/1, 40/1, 16/1 e 8/1. Insieme alla volatilizzazione dei copolimeri con formazione di una miscela dei monomeri che li costituiscono, si ha un rapido abbassamento del peso molecolare del residuo. Per tutti i quattro copolimeri si osserva lo stesso andamento del peso molecolare rispetto al % di volatilizzazione. Le velocità di diminuzione del peso molecolare e quella di volatilizzazione sono tanto più alte quanto più piccolo è il contenuto di acrilonitrile nel copolimero. Questi risultati sono interpretati amettendo una scissione caotica nei segmenti di metilmetacrilato delle molecole di copolimeri seguita da una depolimerizzazione dei radicali formati. Sono stati riesaminati i lavori precedenti fatti a 220°C sui copolimeri 410/1 e 40/1 in modo da dare una visione unica delle reazioni alle due temperature.

Zusammenfassung—Der thermische Abbau von vier Methylmethacrylat-Acrylnitril-Copolymeren mit den Molverhältnissen 410/1, 40/1, 16/1 und 8/1 wurde bei 280° untersucht. Bei der Crackung der Copolymeren zu einer Mischung der zugrunde liegenden Monomeren findet eine rasche Abnahme im Molekulargewicht des Rückstandes statt. Für alle vier Copolymeren ist die Beziehung Molekulargewicht gegen % Verflüchtigung dieselbe. Je kleiner der Gehalt an Polyacrylnitril im Copolymeren ist, desto größer ist die Geschwindigkeit der Molekulargewichtsabnahme und der Geschwindigkeit der Verflüchtigung. Diese Ergebnisse werden gedeutet im Sinne einer statistischen Spaltung in den Methylmethacrylat-Segmenten der Copolymermoleküle mit nachfolgender Depolymerisation der dabei gebildeten Radikale. Frühere Versuche, die mit Copolymeren von 410/1 und 40/1 bei 220° durchgeführt worden waren, wurden erneut diskutiert, um eine einheitliche Interpretation der Reaktion bei beiden Reaktionstemperaturen zu geben.