Thermal Behavior of Polymethacrylonitrile

SHIGEO NAKAMURA, TAKAO OTAKE,* and KEI MATSUZAKI,
*Department of Industrial Chemistry, Faculty of Engineering, University of
Tokyo, Bunkyo-ku, Tokyo, Japan*

Synopsis

The intramolecular cyclization by heating and the thermal degradation of polymethacrylonitrile samples prepared with various initiators, AIBN (A), BPO (B), BuLi (C), Et₂Mg (D), and methacrylonitrile–methacrylic acid copolymer (E), were investigated by DTA, TGA, and infrared spectroscopy. The rate of formation of —C≡N— linkages determined by IR was in the order of E > C > D > B > A. An endothermic peak of DTA thermogram due to thermal degradation was observed at approximately 345°C for the ionically initiated samples, whereas two endothermic peaks were observed at approximately 315°C and 365°C for the radically initiated ones. In the TGA thermograms, although the ionically initiated samples decomposed continuously in a single stage, the radically initiated ones showed weight loss in two steps, with an inflection point at about 330°C. The first stage of thermal degradation of radically initiated samples was concluded to be initiated at the terminal double bonds formed as a result of termination by disproportionation, and the second one at higher temperatures is initiated at random in the polymer. The ionically initiated samples without terminal double bond decompose exclusively by random scission.

INTRODUCTION

Grassie et al.[1-8] have extensively examined the behavior of polymethacrylonitrile when it is subjected to heat and observed three different reactions in three different temperature ranges, namely, the disappearance of ketene-imine structures in the range 20–120°C, the coloration through yellow and orange to red in the range 120–220°C, and the depolymerization to monomer above 220°C.

Grassie and co-workers have concluded that the coloration is a result of formation of conjugated double bonds of naphthyridine-type structure resulting from the intramolecular cyclization of adjacent nitrile groups. It has also been observed that the thermal coloration of polymethacrylonitrile remarkably depends on the method of preparation of polymers and their impurities. Namely, polymers obtained from thoroughly purified monomer with 2,2′-azobisisobutyronitrile (AIBN) is very stable to the coloration reaction, whereas the coloration reaction is accelerated by the use of insufficiently purified monomer of benzoyl peroxide (BPO) as

* Present address: Mizushima Refinery, Nihon Mining Co., Kurashiki-city, Okayama, Japan.

initiator. Accordingly, it has been confirmed that the carboxyl groups in polymer resulting from benzoyl peroxide or impurities in monomer act as a starting point of the coloration reaction.

In this report, several types of polymethacrylonitrile samples were prepared by various polymerization techniques, and the intramolecular cyclization reaction by heating and the thermal degradation of these polymers were investigated by infrared spectroscopy, differential thermal analysis, and thermogravimetric analysis. Based on the results, the effects of different polymerization methods on these reactions were discussed.

EXPERIMENTAL

Preparation of Polymers

Polymerization with AIBN, BPO, and BuLi was carried out according to the method reported in the previous report.[9] Polymerization with diethylmagnesium (Et$_2$Mg) was carried out in toluene solution at $-78°$C for 2 hr under nitrogen. The reaction was terminated by the addition of methanol containing a small amount of HCl, and the precipitated polymer was washed several times with methanol and vacuum dried. Dried polymer was immersed in dimethylformamide (DMF) overnight, and the DMF-insoluble fraction was isolated from the DMF-soluble fraction by means of a centrifuge. In the experiments to be described, the DMF-insoluble fraction with high isotactic content was used.

Methacrylonitrile–methacrylic acid copolymer was obtained according to the following procedure: a mixture of 14 g methacrylonitrile and 0.1 g methacrylic acid was polymerized at 80°C for 2 hr. After the reaction was terminated by the addition of methanol, the polymer was purified by repeated reprecipitation using acetone and methanol.

Before the characterization of polymers, all the samples were heated to 80°C under vacuum for several days to remove occluded solvents completely. The polymerization conditions are summarized in Table I.

TABLE I
Polymerization Conditions of Polymethacrylonitrile
and Methacrylonitrile–Methacrylic Acid Copolymer

Sample	Initiator	Solvent	Temp., °C	Time, hr	Conversion, %
A	AIBN	none	80	6	23.9
B	BPO	none	80	7	34.6
C	BuLi	toluene	-78	2	34.9
D	Et$_2$Mg	toluene	80	5	46.6
E (copolymer)[a]	AIBN	none	80	4	27.3

[a] Copolymer of methacrylonitrile (93.8 mole-%) and methacrylic acid (6.2 mole-%).

Characterization of Polymers

Infrared absorption spectra of polymers were measured by means of the KBr disk method using a Nihon Bunko DS 301 spectrophotometer with NaCl prism, and on films prepared on NaCl plate using a Nihon Bunko DS 403G grating spectrophotometer. NMR spectra were obtained with a JEOL 4H-100 spectrometer on CF_3COOH solutions at 60°C.

Viscosities of polymers were determined in dimethylformamide solution at 29.2°C except for Et_2Mg-initiated polymer, for which the viscosity was determined in dichloroacetic acid solution at 30°C. The molecular weight of polymers was calculated by the following relationships:

$$[\eta] = 3.06 \times 10^{-3} M^{0.503} \qquad (DMF, 29.2°C)^{11}$$

$$[\eta] = 2.27 \times 10^{-4} M^{0.754} \qquad (CCl_2HCOOH, 30°C)^{12}$$

Heat Treatment

Each sample was subjected to heat treatment for a predetermined time at 200°C under nitrogen, and the change in its infrared spectrum was followed by means of the KBr disk method.

Thermal Analysis

Thermogravimetric Analysis. An Ohyo Rika automatic-recording thermobalance programmed for a linear heating rate of 5°C/min was used in both dynamic air and nitrogen. A 100-mg sample was employed in each experiment.

Differential Thermal Analysis. A Rigaku Denki thermal analyzer was used. A 50-mg sample was sandwich-packed using α-alumina as diluent. The analysis was carried out in dynamic nitrogen using a heating rate of 5°C/min.

RESULTS AND DISCUSSION

The stereoregularity of polymethacrylonitrile samples was determined from the relative area of peaks due to the isotactic methylene protons (quartet) and syndiotactic ones (singlet) in the main chain.[10] As shown in Table II, the polymer obtained with Et_2Mg was 70% isotactic, whereas those obtained with other initiators were atactic. The polymer obtained with Et_2Mg was confirmed to be crystalline from the x-ray diffraction pattern as previously reported by Joh et al.,[12] and other samples were all amorphous. The solubility of the polymers varied considerably depending on the methods of preparations; namely, radically initiated polymers were soluble in methylene chloride, acetone, and nitromethane, the polymer obtained with BuLi did not dissolve completely in methylene chloride, and that obtained with Et_2Mg was insoluble in all of these solvents. This is attributed to the stronger intermolecular interactions as a result of the increased isotactic content, as indicated by its crystallinity and a higher glass transition temperature of the Et_2Mg-initiated polymer.
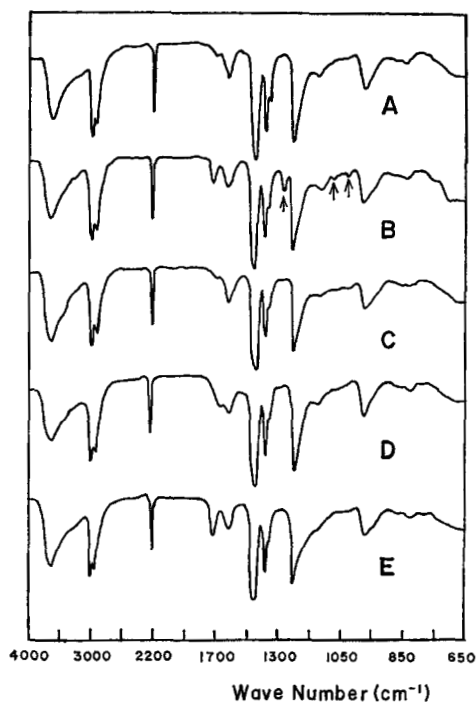
Fig. 1. Infrared spectra of polymethacrylonitrile samples (KBr disk method): (A) AIBN; (B) BPO; (C) BuLi; (D) Et$_2$Mg; (E) copolymer with methacrylic acid.

The infrared spectra of polymethacrylonitrile samples measured by the KBr method are given in Figure 1.   The spectra in the C=O region were recorded on films cast on NaCl plates (Fig. 2), as the absorption band of C=O at 1720 cm^{-1} is sometimes overlapped by that of the water in KBr. In addition to the bands observed for AIBN-initiated sample (A), the bands due to C=O stretching and C—O stretching vibrations were observed at 1720 and 1270 cm^{-1}, respectively, for BPO-initiated sample (B). The absorption bands at 1073 and 1025 cm^{-1} observed in the spectra of sample B did not appear in other samples.   No appreciable difference was observed among samples A, C, and D, except for a broad absorption observed in the neighborhood of 1720 cm^{-1} for sample D.   The absorption spectrum of copolymer E was characterized by a strong band at 1720 cm^{-1} due to C=O stretching and a very broad absorption at 1210 cm^{-1}.

Each sample was subjected to heat treatment for a predetermined time at 200°C under nitrogen, and the infrared spectra were recorded.   The most remarkable changes in the IR spectra were the decrease in the intensity of the 2220 cm^{-1} band due to C≡N stretching vibration and the increase in the intensity and broading of 1625 cm^{-1} band due to C=N stretching vibration as previously reported by Grassie et al.[2]   In order to compare the rate of the intramolecular cyclization reaction of the samples,
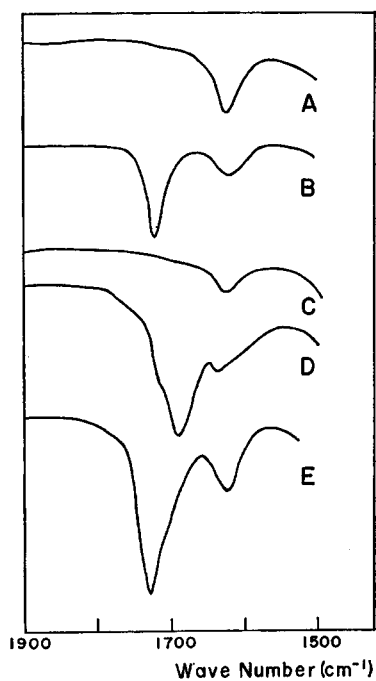
Fig. 2. Infrared spectra of polymethacrylonitrile samples in C=O and C=N regions (films on NaCl plates): (A) AIBN; (B) BPO; (C) BuLi; (D) Et₂Mg; (E) copolymer with methacrylic acid.
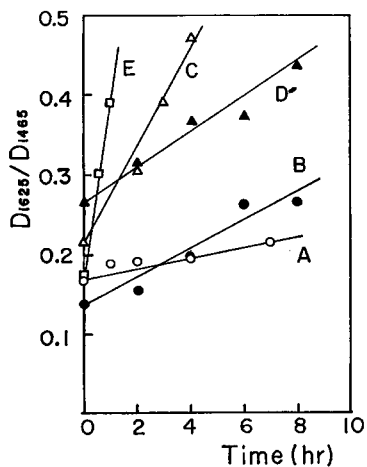

Fig. 3. Relation between D_{1625}/D_{1465} and heating time of polymethacrylonitrile heat treated at 200°C in nitrogen: (A) AIBN; (B) BPO; (C) BuLi; (D) Et₂Mg; (E) copolymer with methacrylic acid.
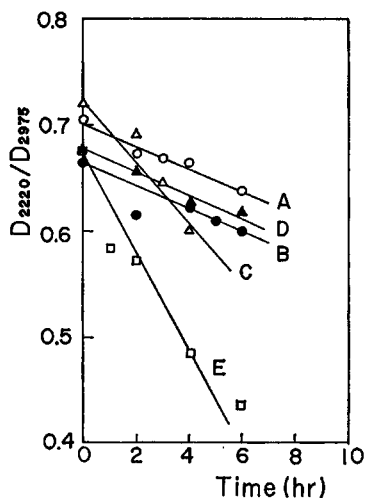
Fig. 4. Relation between D_{2220}/D_{2975} and heating time of polymethacrylonitrile heat treated at 200°C in nitrogen: (A) AIBN; (B) BPO; (C) BuLi; (D) Et$_2$Mg; (E) copolymer with methacrylic acid.
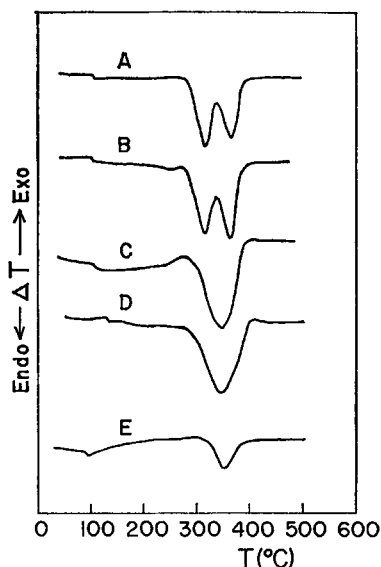

Fig. 5. DTA curves of polymethacrylonitrile in nitrogen: (A) AIBN; (B) BPO; (C) BuLi; (D) Et$_2$Mg; (E) copolymer with methacrylic acid.

the ratios of absorbance, D_{1625}/D_{1465} and D_{2220}/D_{2975}, were plotted against time. It was found that the plots were linear at the early stage of heat treatment. As seen from the slopes of the D_{1625}/D_{1465}-versus-treating time plots in Figure 3, the rate of increase of D_{1625}/D_{1465}, namely the rate of formation of —C=N— linkages, decreased in the order of E > C > D > B >

TABLE II
Characterization of Polymethacrylonitrile and
Methacrylonitrile–Methacrylic Acid Copolymer

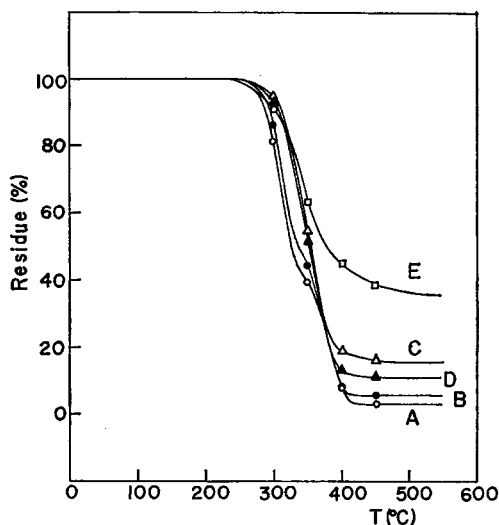| Sample | Initiator | NMR data | | T_g, °C | $\bar{M}_v$ |
		Iso, %	Syndio, %		
A	AIBN	42	58	102	3.44×10^3
B	BPO	46	54	101	4.27×10^3
C	BuLi	53	47	103	8.79×10^4
D	Et₂Mg	70	30	120	3.65×10^5
E (copolymer)	AIBN	—	—	90	—

Fig. 6. TGA curves of polymethacrylonitrile in nitrogen: (A) AIBN; (B) BPO; (C) BuLi; (D) Et₂Mg; (E) copolymer with methacrylic acid.

A. Accordingly, the intramolecular cyclization reaction occurs more easily in the order mentioned above. The rate of decrease of D_{2220}/D_{2975}, namely the rate of disappearance of the nitrile group, was in the same order (Fig. 4) as that of intramolecular cyclization.

DTA measurements were carried out at a linear heating rate of 5°C/min in dynamic nitrogen. As seen in Figure 5, an endothermic shift of the baseline due to glass transition was observed for each sample (Table II). An endothermic peak due to thermal degradation was observed at approximately 345°C for the ionically initiated samples and the copolymer, whereas two endothermic peaks were observed at approximately 315°C and 365°C for the radically initiated ones.

In the TGA thermograms obtained at a programed rate of 5°C/min in dynamic nitrogen (Fig. 6), the weight losses of radically initiated samples started at a little lower temperature than those of ionically initiated ones, and each polymer showed its characteristic weight loss curve at higher
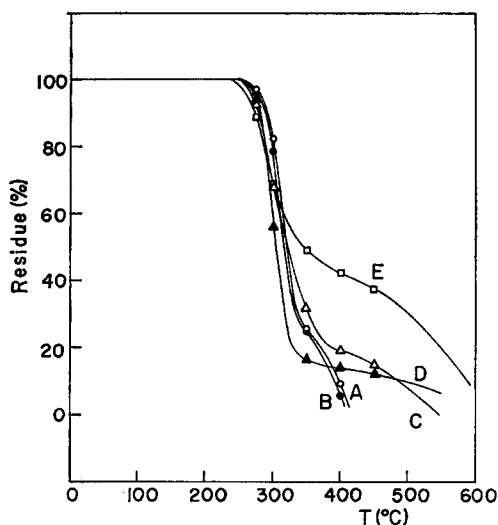
Fig. 7. TGA curves of polymethacrylonitrile in air: (A) AIBN; (B) BPO; (C) BuLi; (D) Et₂Mg; (E) copolymer with methacrylic acid.

temperatures. Although the ionically initiated samples and the copolymer decomposed continuously in a single stage, the radically initiated ones showed the weight loss in two steps, with an inflection point at about 330°C. The second stage of degradation of radically initiated polymers (>ca. 340°C), however, coincides with that of ionically initiated ones, and the weight loss-versus-temperature curves of all the samples lie on the same line. All the samples did not decompose completely as a result of formation of thermally stable naphthylidine structure, and the weight of each sample approached its individual constant value. The residue amounted to as much as 35% in the case of the copolymer for which the rate of formation of —C=N— linkages was fastest. The order of the amount of residue, E > C > D > B > A, shows the same tendency as the rate of formation of —C=N— linkages.

The TGA thermograms obtained in dynamic air are very different from those obtained in dynamic nitrogen, as shown in Figure 7. Even if the temperature at which the weight loss began and the height of the plateau corresponding to the formation of naphthylidine structure did not vary from those in nitrogen, the whole thermograms shifted to lower temperatures, and the weight of the residues approached zero with increasing temperature as a result of the oxidative degradation of thermally stable naphthylidine structures. In addition, the weight loss of the radically initiated samples occurred in a single stage, and the decomposition of the ionically initiated polymers was more remarkable at lower temperatures than the radically initiated ones.

It has been observed that the thermal degradation of poly(methyl methacrylate) proceeds by a two-stage reaction mechanism and the relative prevalence of the reactions depends on the heating temperature. It was

concluded that the first reaction at lower temperatures is initiated at the unsaturated chain ends formed as a result of termination by disproportionation and proceeds by a chain reaction mechanism, and the second reaction at higher temperatures is initiated at random in the polymer molecules.[13] McNeill[14,15] investigated the thermal degradation of polymethacrylonitrile by a thermal volatilization analysis and observed two peaks in the thermograms of the radically initiated polymers which he used. From the structural similarity of these two 1,1'-substituted polymers, it is supposed that the first stage of thermal degradation is initiated at the terminal double bonds of the radically initiated samples formed as a result of termination by disproportionation, and the ionically initiated polymers without terminal double bond decompose exclusively by random scission. The reason why the copolymer decomposes by the one-stage mechanism may be attributed to the rapid intermolecular cyclization, by which further propagation of scission reaction from chain ends may be prevented at an early stage. The faster rate of intramolecular cyclization of the ionically initiated samples, especially the one obtained with Et$_2$Mg, may be attributed to the reactive groups formed during polymerization, purification, and drying, and acting as initiating sites, since the Et$_2$Mg-initiated sample contains many labile bonds in the molecule as indicated by the very fast weight loss observed in the TGA thermogram in air (Fig. 7). The effect of stereoregularity on thermal behavior was not clear in our study.

On heating polymethacrylonitrile in air, oxidative degradation occurs together with depolymerization to monomer, and some of the oxidized sites supposedly act as the starting points of intramolecular cyclization. The combined effect of these reactions shifted the TGA thermograms to lower temperatures, degraded the radically initiated samples in apparently single stage, and degraded the ionically initiated samples with many labile groups formed during preparation more rapidly than the radically initiated samples.

References

1. N. Grassie and I. C. McNeill, *J. Chem. Soc.*, 3929 (1956).
2. N. Grassie and I. C. McNeill, *J. Polym. Sci.*, **27**, 207 (1958).
3. N. Grassie and I. C. McNeill, *J. Polym. Sci.*, **30**, 37 (1958).
4. N. Grassie, J. N. Hay, and I. C. McNeill, *J. Polym. Sci.*, **31**, 205 (1958).
5. N. Grassie and I. C. McNeill, *J. Polym. Sci.*, **33**, 171 (1958).
6. N. Grassie and J. N. Hay, *J. Polym. Sci.*, **39**, 211 (1959).
7. N. Grassie, *J. Polym. Sci.*, **48**, 79 (1960).
8. N. Grassie and J. N. Hay, *Soc. Chem. Ind., Monograph No. 13*, 184 (1961).
9. H. Sobue, T. Uryu, K. Matsuzaki, and Y. Tabata, *J. Polym. Sci. A*, **2**, 3333 (1964).
10. K. Ishigure, Y. Tabata, and K. Oshima, *J. Polym. Sci. B*, **4**, 669 (1966).
11. C. G. Overberger, E. M. Pearce, and N. Mayes, *J. Polym. Sci.*, **34**, 109 (1959).
12. Y. Joh, T. Yoshihara, Y. Kotake, F. Ide, and K. Nakatsuka, *J. Polym. Sci. B*, **4**, 673 (1966).
13. J. R. MacCallum, *Makromol. Chem.*, **83**, 137 (1965).
14. I. C. McNeill, *J. Polym. Sci. A-1*, **4**, 2479 (1966).
15. I. C. McNeill, *Eur. Polym. J.*, **3**, 409 1967).