Thermal Behavior of Pentachlorophenyl Methacrylate–Acrylonitrile Copolymers

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ABSTRACT: Acrylonitrile was copolymerized with pentachlorophenyl methacrylate (PCPMA) in dimethyl formamide using azobisisobutyronitrile as initiator. The composition of the copolymers was determined by nitrogen analysis and the monomer reactivity ratios (r_1 and r_2) were calculated. Both the homopolymer and the copolymers were characterized by a variety of spectral and thermal methods. Thermogravimetry and differential thermal analysis data showed that the comonomer (PCPMA) initiates the nitrile oligomerization reaction in the copolymer upon heating. A mechanism for the initiation of (PCPMA) units in the nitrile copolymers was also proposed. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 296–302, 2004

Key words: copolymerization; thermal properties; oligomers; crosslinking; pentachlorophenyl methacrylate (PCPMA)

INTRODUCTION

The thermal degredation of polyacrylonitrile (PAN) and its copolymers in air as well as under nitrogen atmosphere was previously investigated by Coleman et al.[1–3] Intramolecular cyclization, intermolecular crosslinking, and water elimination have been proposed.[4–8] Oxidative reactions were a major factor with subsequent heating. Grassie and McGuchan[9,10] investigated the effect of copolymerization on the oligomerization of the nitrile group of PAN on heating.

The technological importance of PAN is known to suffer from several disadvantages: weak modability, color instability, and weak dyeability. Besides other efforts to abolish these difficulties, several monomers have been used as comonomers for the production of acrylonitrile (AN) copolymers[11,12] with improved thermal stability.

The present study was conducted to investigate the effect of introducing a methacryloyloxy unit into the polymer chain of PAN. It was expected that the thermal properties of PAN would be greatly affected and, consequently, it was necessary to investigate the thermal behavior of the copolymers produced.

EXPERIMENTAL

Materials

Acrylonitrile (AN) was obtained from BDH (Toronto, Canada) and was purified by distillation before polymerization; pentachlorophenyl was provided by M&T Chemical Inc. (Rahway, NJ); methacrylic acid (Aldrich, Milwaukee, WI) was distilled twice under produced pressure; N,N-dicyclohexylcarbodiimide (DCCI) and azobisisobutyronitrile (AIBN) were from Merck (Darmstadt, Germany).

Synthesis of pentachlorophenyl methacrylate (PCPMA) monomer

PCPMA was prepared by the reaction of pentachlorophenal with the corresponding acid chloride or through the reaction of pentachlorophenyl with the corresponding acid in the presence of N,N-dicyclohexylcarbodiimide as follows:

Acid chloride method[13]

To a well-stirred solution of 53.3 g (0.2 mol) pentachloro-phenol and 41 mL (0.3 mol) triethanolamine in 350 mL dry methylene chloride, 24.8 mL (0.24 mol) of methacryloyl chloride was added dropwise under cooling in ice bath (0–5°C). After the complete addition of methacryloyl chloride, the reaction mixture was then allowed to stand at room temperature for 2 h. The product was washed with distilled water, 1M sodium hydroxide, and again with distilled water. After drying with anhydrous sodium sulfate the solvent was evaporated. The residue obtained was crystallized from ethanol (yield 80%, m.p. 85°C).

N,N-Dicyclohexylcarbodiimide (DCCI) method[14]

To a well-stirred cooled solution (0–5°C) of pentachloro-phenol 33.4 g (0.1 mol) and methacrylic acid 8.6

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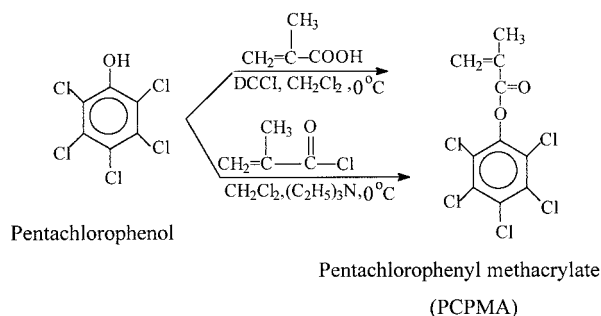
Scheme 1 Preparation of PCPMA monomer.

mL (0.1 mol) in 300 mL of dry methylene chloride, 20.6 g (0.1 mol) of DCCI was added dropwise. The reaction mixture was stirred for 8 h at room temperature and the precipitated dicyclohexyl urea was removed by filtration; after being washed with dilute sodium bicarbonate solution the filtrate was washed with water, dried over anhydrous sodium sulfate, and then filtered. The resulting solution was evaporated under reduced pressure and the solid product was crystallized from ethanol (yield 72%, m.p. 85–86°C).

Polymerization procedures

Ampoules of Pyrex glass were charged with the monomer mixtures, the solvent, and the initiator (AIBN). The ampoules were then cooled under nitrogen. The copolymerization was carried out in a water ultra-thermostat at 65°C with stirring for about 8 h. The contents were poured into a large excess of methanol. The polymers obtained were washed several times with hot methanol and dried at 50°C to constant weight. The nitrogen content of the copolymers was determined by a modified Kjeldahl method.

Spectral measurements

[1]H-NHR spectra were recorded on a Varian EM-390 spectrometer (Varian Associates, Palo Alto, CA) operating at 90 MHz in deuterated $CDCl_3$. IR spectra were recorded in KBr discs using a Shimadzu 470 (4000–400 cm^{-1}) spectrophotometer (Shimadzu, Kyoto, Japan). The mass spectrum was measured on a Hewlett–Packard (Palo Alto, CA) MS 5988 spectrometer at 15 eV.

Thermal analysis

DTA was performed at a heating rate of 15°C min^{-1} using a Shimadzu X-30 thermal analyzer. TG thermograms were obtained at a heating rate of 10°C min^{-1}, using a DT-30 thermal analyzer (Shimadzu).

RESULTS AND DISCUSSION

The pentachlorophenyl methacrylate (PCPMA) monomer was prepared according to Scheme 1. The prepared monomer was a white powder, soluble in most organic solvents. The ^{1}H-NMR spectrum of PCPMA monomer (Fig. 1) shows a singlet peak at δ 2.1 attributed to the presence of (CH_3), two singlet peaks at δ 5.9 and 6.3 corresponding to two nonidentical protons (CH_2=C), and a singlet peak at δ 7.3 corresponding to $CDCl_3$.
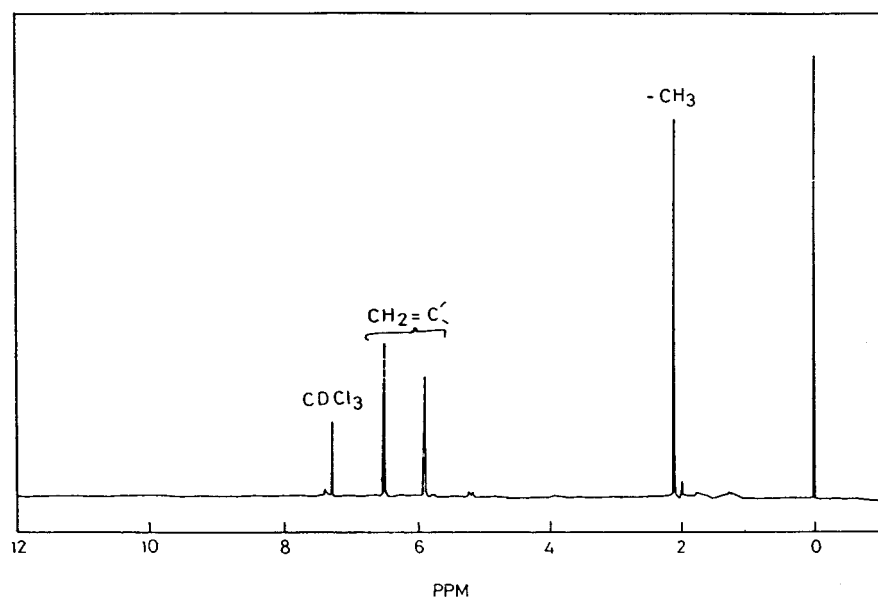

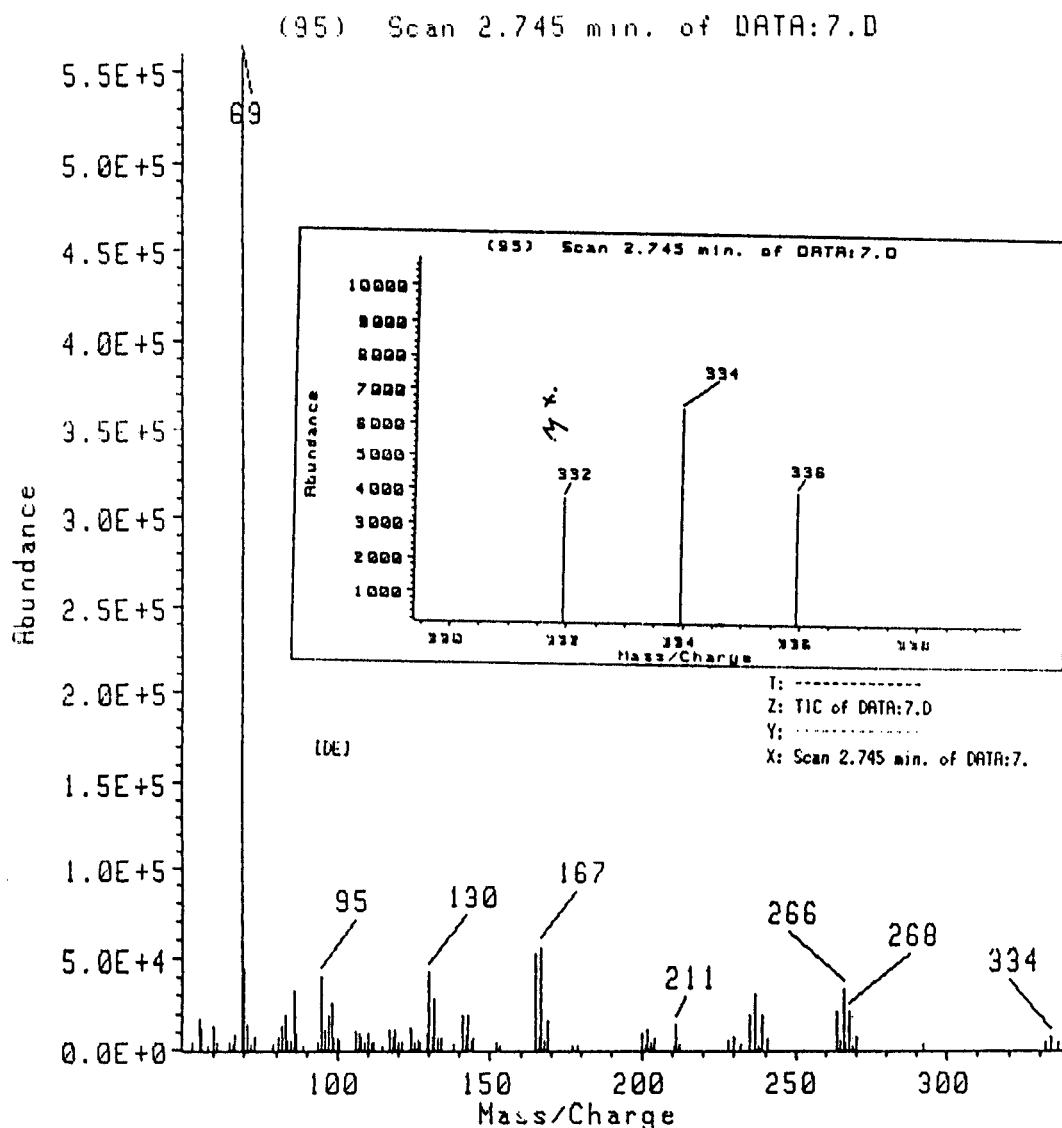**Figure 1** ^{1}H-NMR spectrum of PCPMA monomer.

Figure 2 Mass spectrum of PCPMA monomer.

Structures of the prepared monomer (PCPMA), homopolymer (PPCPMA), and copolymer with AN were investigated by IR spectroscopy. The IR spectra show bands at 3000, 1740, 1630, and 1400 cm^{-1} attributable to $\nu_{(C-H)}$ aliphatic, $\nu_{(C=O)}$, $\nu_{(C=C)}$, and $\nu_{(C-O)}$, respectively. The spectrum of the copolymer shows a new band at 2240 cm^{-1} attributable to $\nu_{(C\equiv N)}$.
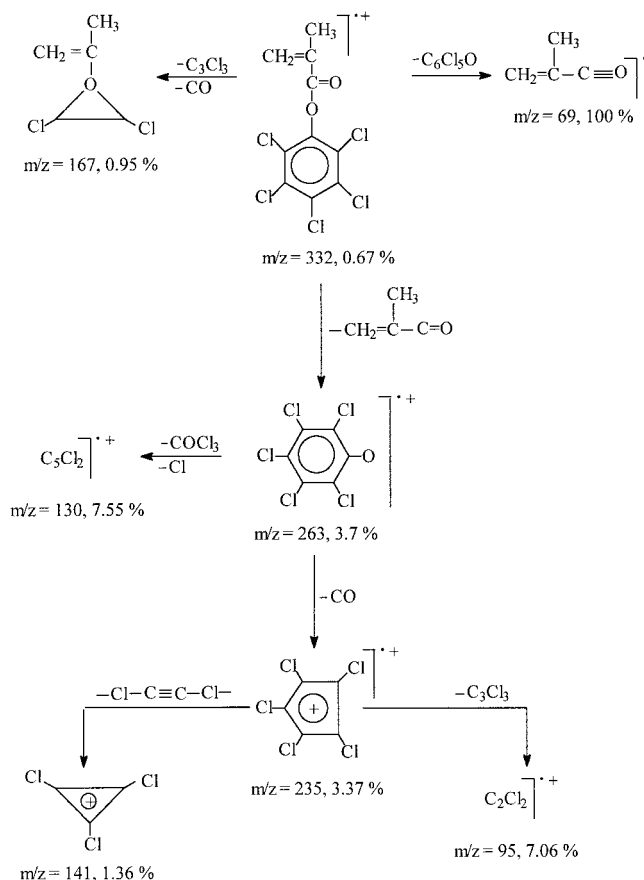
The mass spectrum of PCPMA monomer is shown in Figure 2. The fragmentation patterns are represented in Scheme 2, which illustrates the most abundant fragments of PCPMA monomer.

The copolymerization data of PCPMA with AN in DMF at 65°C are summarized in Table I The reactivity ratios for the comonomer were calculated using the Kelen–Tüdös equation.[15] Figure 3 shows a plot for this system. The intercept at $\zeta = 1.85$ is equal to r_1 (PCPMA) and that at $\eta = 0.015$ is equal to r_2/α,[16] where α is an arbitrary parameter.

Thermal behavior

The thermal behavior of any polymer should be affected appreciably by the introduction of a comonomer in the polymer chain. It was thus important to investigate the thermal behavior of the prepared copolymers. For this purpose four PCPMA–AN copolymers containing 10, 20, 30, and 40% PCPMA were prepared. The thermal characteristics of PAN were previously studied in detail by Grassie.[17] In the present investigation, the thermal analysis of PAN is given as a reference; that is, the comparison of DTA and TG data of PAN and those of the corresponding PPCPMA and copolymers will illustrate the effect of these comonomers on the thermal behavior of the products.

The DTA curves of PAN and PPCPMA and those of the corresponding copolymers with AN are repre-

Scheme 2 Fragmentation of PCPMA monomer.

Figure 3 Kelen–Tüdös plot for copolymerization of PCPMA monomer with AN: $\xi = [a^2/(ab + a^2)]$ and $\eta = \{[a(b - 1)]/(\alpha b + a^2)\}$, where a and b are the molar ratios (M_1/M_2) of the comonomer in the feed and copolymer, respectively; and $\alpha = [(a_{min}a_{max})/(b_{min}b_{max})]^{1/2}$.

sented in Figure 4 The thermal analysis of PAN in air shows the usual thermogram with an initial decomposition at 320°C and a broad exotherm peak with a maximum at 340°C, which results from the oligomerization of the nitrile groups and formation of some aromatic structures.[17] However, the DTA curve of PPCPMA shows exotherms with maxima at 180, 280, and 370°C, respectively, which may represent the homolytic scission and complete decomposition. The

TABLE I
Analytical Data for Copolymerization of PCPMA with AN[a]

Feed composition (a)	Conversion (%)	N (%)	Copolymer composition (b)
0.1111	7.35	3.93	1.1031
0.2500	8.67	4.80	1.4015
0.4286	5.62	5.94	1.8301
0.6667	9.01	6.74	2.1620
1.0000	7.83	8.44	2.9649
1.5000	6.42	10.08	3.8941

[a] (a) and (b) are the molar ratios of M_1/M_2 in the feed and copolymer, respectively, and N (%) values were determined by a modified Kjeldahl method.
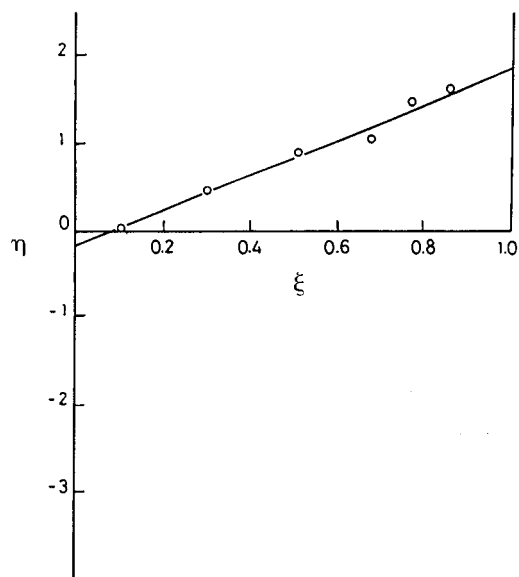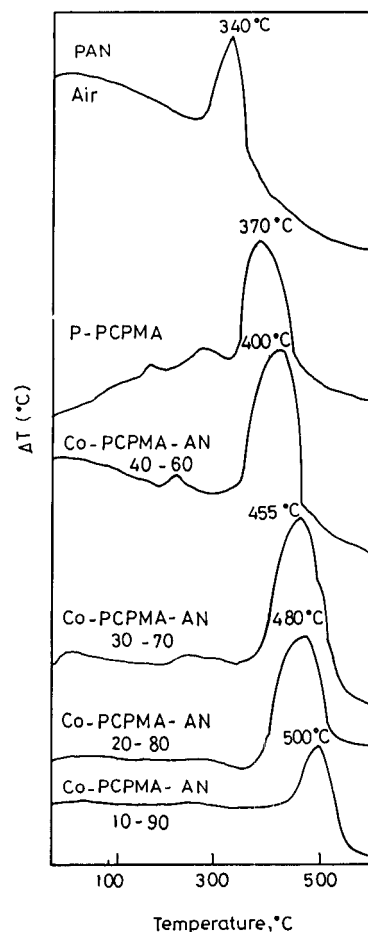

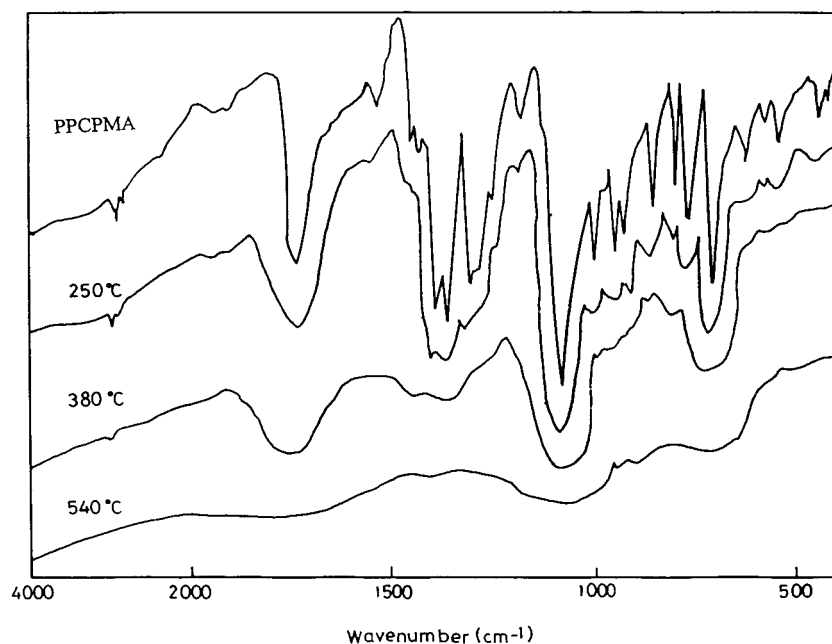Figure 4 DTA curves for PCPMA, AN, and copolymer (PCPMA–AN) in air.

Figure 5 IR spectra of unheated and heated homopolymer *p*-PCPMA at different temperatures.

proposed homolytic scission of PPCPMA was suggested from the fragmentation patterns obtained from the mass spectrum of PCPMA monomer (Fig. 2). As illustrated in Scheme 2, the most abundant fragmentation is cleavage of the C—N bond, giving a parent ion of *m/z* 69 (methacryloyloxy unit). A similar result was obtained previously from the fragmentation patterns of *p*-acryloyloxy-tri-*n*-butyltin benzoate.[18] The exotherm at 370°C may represent a complete decomposition. Moreover, in a separate experiment when PPCPMA was heated at 370°C, a black soluble mass remained, indicating that no crosslinking reaction occurred.

The IR spectra of unheated PPCPMA and PPCPMA samples at different temperatures are shown in Figure 5 The spectra show no change in most of the functional groups present upon heating to 250°C. Above this temperature, the characteristic bands at 1400, 1740, and 3000 cm^{-1} attributed to $\nu_{(C—O)}$, $\nu_{(C=O)}$, and $\nu_{(C—H)}$ aliphatic gradually decrease until they disappear at 540°C. The above arguments indicated that the PPCPMA homopolymer decomposed by increasing the temperature. The exotherm at 540°C represents a complete decomposition and 100% weight loss.

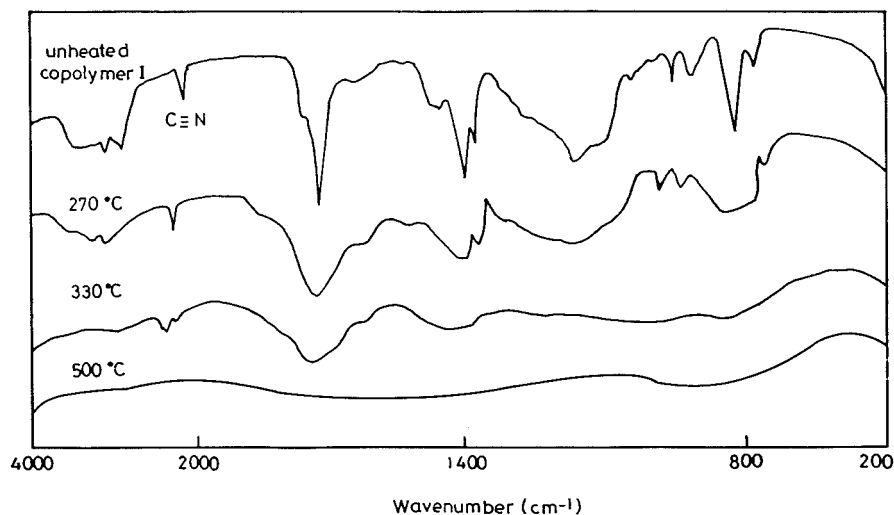The DTA curves of PCPMA–AN copolymers in air (Fig. 4) show exotherms at 400, 455, 480, and 500°C,

Figure 6 IR spectra of heated and unheated copolymer **1** (PCPMA–AN) at different temperatures.

reflecting many processes probably including scission, cyclization, crosslinking, and decomposition at the higher-temperature exotherm. The first stage of decomposition could be attributed to scission of the C—N bond in a manner similar to that occurring in the suggested degradation of homopolymers, followed by cyclization and crosslinking. The DTA peaks of the copolymers were shifted to lower temperatures relative to that of PAN, indicating an initiating effect of the PCPMA comonomers by a cyclization process.

The IR spectra for the unheated and heated PCPMA–AN copolymer **1** (40 : 60) (Fig. 6) show bands for unheated copolymer at 2240, 1720, and 1400 cm^{-1} that are attributed, respectively, to $\nu_{(C\equiv N)}$, $\nu_{(C=O)}$, and $\nu_{(C—O)}$. However, for heated PCPMA–AN copolymer at 270, 330, and 500°C there is an appreciable decrease in the intensity of the C≡N band at 2240 cm^{-1}. The carbonyl band at 1720 cm^{-1} merges with the band at 1700 cm^{-1}. The bands at 1700 and 1630 cm^{-1}, characteristic for the $\nu_{(C=O)}$ and $\nu_{(C=N)}$ groups, are enlarged and broadened.[10] These spectral changes reveal radical changes in the copolymer structure and must also be the result of a direct interaction between the nitrile group and the functional groups of the comonomer. In this interaction an initiation of cyclization and crosslinking reactions will occur.

The TG thermograms for PAN, PCPMA, and the four different concentrations of PCPMA–AN copolymers are given in Figure 7 The analysis shows the existence of two transitions, probably reflecting more
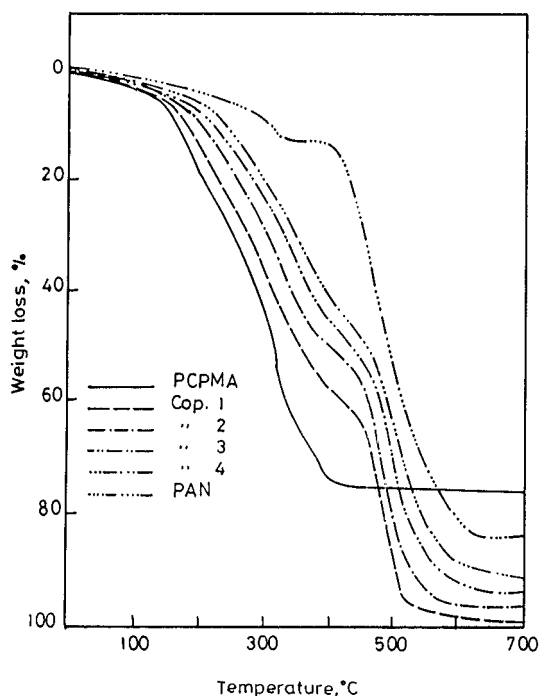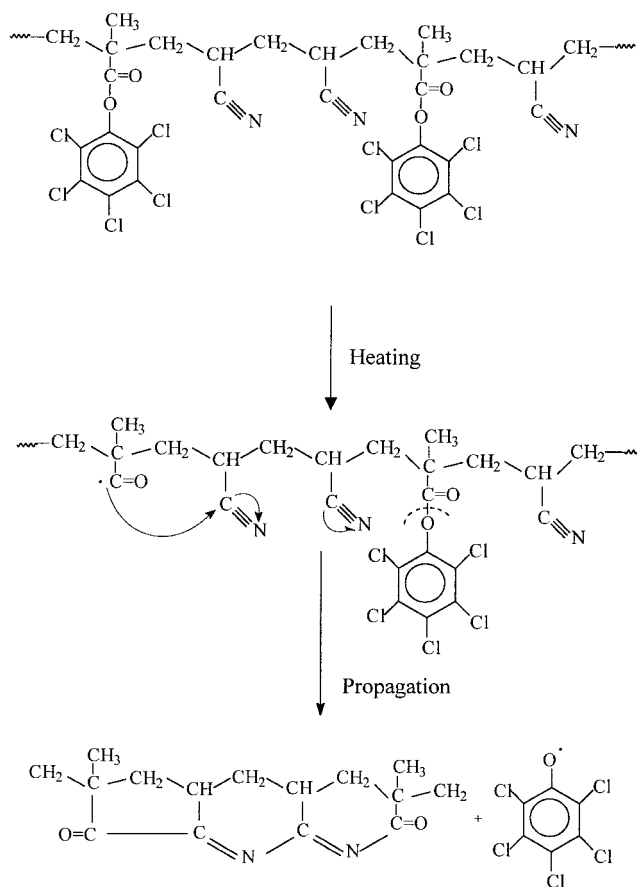
Scheme 3   Thermal degradation of PCPMA–AN copolymer.

Figure 7   TG curves for PAN, PCPMA, and their copolymers. Ratio PCPMA : AN in the copolymer: (1) 10 : 90, (2) 20 : 80, (3) 30 : 70, (4) 40 : 60.

than one process during the thermal degradation reaction. Also, the TG curves show an increase in the weight loss of the copolymer relative to that of PAN. This could be confirmed when the PCPMA–AN copolymer was heated for about 5 min at 330°C; a black insoluble mass remained, indicating an appreciable crosslinking reaction attributed to the cyclization process. Based on the above-mentioned thermal and spectral data, the mechanism in Scheme 3 is suggested for the thermal degradation of copolymers.

CONCLUSIONS

The thermal stability of the PCPMA–AN copolymers showed that the PCPMA comonomer initiates the nitrile oligomerization reaction in the copolymers upon heating and formation of some aromatic compounds.

References

1. Coleman, M. M.; Sivy, G. T. Adv Chem Ser 1983, 203, 559.
2. Coleman, M. M.; Sivy, G. T.; Painter, P. C.; Synder, R. W.; Gordon, B. Carbon 1983, 21, 225.
3. Coleman, M. M.; Gordon, B. Anal Proc London 1983, 20, 572.
4. El-Hamouly, S. H.; Azab, M. M.; El-Kafrowi, S. A. Thermochim Acta 1994, 241, 57.

5. Azab, M. M. J Appl Polym Sci 1994, 51, 1937.
6. Meneill, I.; Mahmoud, T. Polym Degrad Stab 1998, 60, 449.
7. Jang, S. P.; Kim, D. Polym Eng Sci 2000, 40, 1635.
8. Anathalakshmi, N. R.; Wadgaonkar, P. P.; Sivaram, S.; Varma, I. K. Therm Anal Calorim 1999, 58, 553.
9. Grassie, N.; McGuchan, R. Eur Polym J 1972, 8, 243.
10. Grassie, N.; McGuchan, R. Eur Polym J 1972, 8, 862.
11. (a) Grassie, N.; McGuchan, R. Eur Polym J 1971, 7, 1357; (b) Grassie, N.; McGuchan, R. Eur Polym J 1973, 9, 507.
12. Grassie, N.; Heaney, X. Eur Polym J 1974, 10, 415.
13. Ferrnti, P.; Fere, A.; Goltica, G. J Polym Sci 1974, 12, 553.
14. Ferrnti, P.; Goltica, G. J Polym Sci 1975, 13, 2859.
15. Kelen, T.; Tüdös, F. J Macromol Sci Chem 1975, 9, 1.
16. Tüdös, F.; Kelen, T.; Berezsnich, T.; Turcsany, J. J Macromol Sci Chem 1976, 10, 1513.
17. Grassie. N. Developments in Polymer Degradation; Applied Science: London, 1977; p. 137.
18. Azab, M. M. J Appl Polym Sci 1994, 51, 1937.