

Study of the Thermal Degradation of Acrylic Copolymers

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Synopsis

The thermal degradation of the following copolymers prepared by radical polymerization: acrylonitrile–butyl acrylate–vinylidene chloride, acrylonitrile–butyl acrylate–vinylidene chloride–styrene, and acrylonitrile–methacrylic acid–vinylidene chloride–styrene was investigated. The techniques of thermogravimetry and differential thermal analysis were used. The IR spectra of degraded copolymers are discussed.

INTRODUCTION

There are numerous papers¹⁻⁵ devoted to the influence of comonomers on the exothermic oligomerization of nitrile groups, characteristic of acrylonitrile homopolymers.^{6,7} Acrylate and methacrylate comonomers^{3,4} have a diluent effect on the exothermic reaction without inhibiting or initiating the nitrile rearrangements. Acidic comonomers³ have a strong initiating effect on the exothermic reaction. Chlorinated comonomers as vinylidene chloride⁴ reduce the intensity of the exothermic reaction, but do not effectively block the reaction. Styrene² and other comonomers of this have a marked inhibiting effect on the nitrile reaction.

The present paper describes the effect of comonomers on the thermal degradation of polyacrylonitrile in the systems: acrylonitrile (AN)–butylacrylate (BA)–vinylidene chloride (CV), acrylonitrile–butylacrylate–vinylidene chloride–styrene (S) and acrylonitrile–methacrylic acid (AM)–vinylidene chloride–styrene.

The results concerning copolymers synthesis, compositional distribution, spectral characterization, and some potential industrial application are given elsewhere.⁸⁻¹²

EXPERIMENTAL

Copolymers

The copolymers and poly(acrylonitrile) (PAN) used were prepared in solution at 60°C using 0.1% azoizobutironitrile. Polymerizations were carried out in an inert atmosphere. The copolymer composition was determined by nitrogen, chlorine, and carboxylic groups analysis, using the micro Kjeldhal, Schöniger, and potentiometric titration methods, respectively.

Copolymers compositions are summarized in Table I.

TABLE I
Copolymers Composition Data

Copolymer code	AN	Composition, wt %		
		BA or AM	CV	S
AN-BA-CV	70.29	26.91	2.80	—
AN-BA-CV-S	18.39	43.31	25.00	13.30
AN-AM-CV-S	53.80	13.56	10.50	22.14

Thermal Analysis

A derivatograph MOM-Budapest type Paulik–Paulik–Erdely was used. In both DTA and TG analysis the samples were heated at 10°C/min in argon flow and in air.

Infrared Spectra

A UR-10 Karl Zeiss Jena spectrophotometer (range 400–5000 cm^{-1}) and a Unicam SP 1000 IR spectrophotometer (range 625–3800 cm^{-1}) were used.

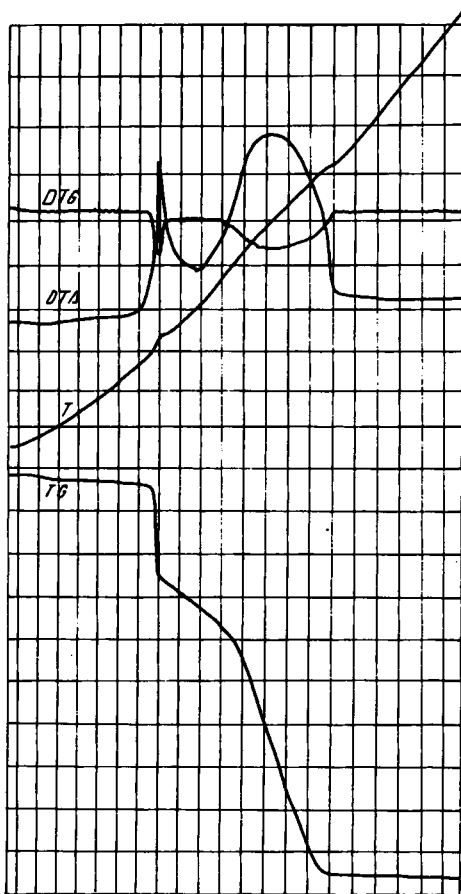
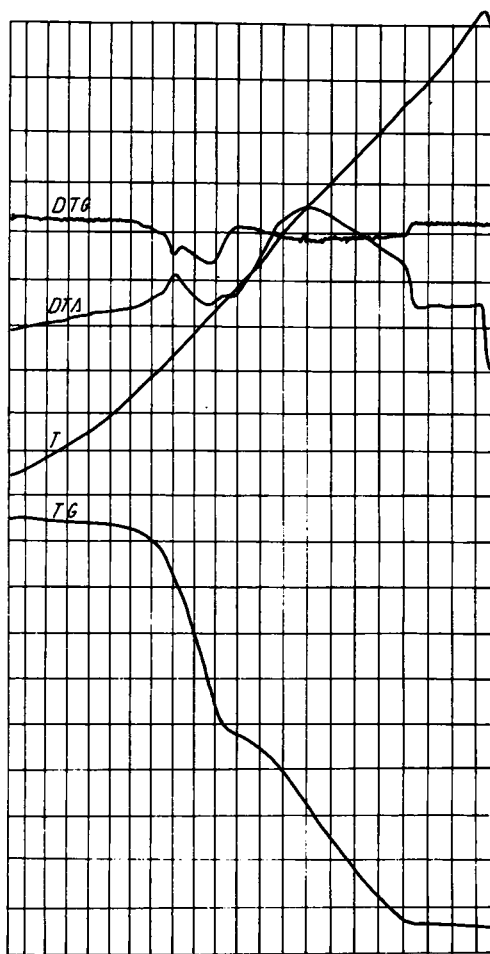


Fig. 1. DTA, TG, and DTG curves for poly(acrylonitrile) in air.



(a)

Fig. 2. DTA, TG, and DTG curves for acrylonitrile-butylacrylate-vinylidene chloride copolymer: (a) under argon; (b) in air.

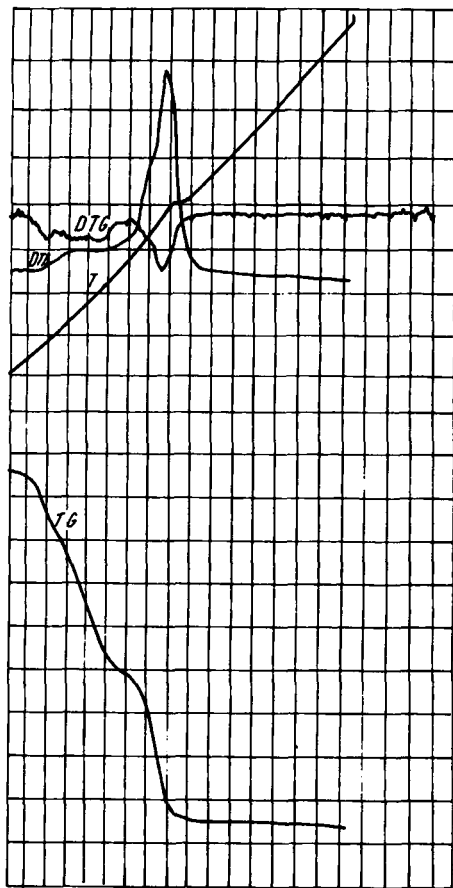
RESULTS AND DISCUSSIONS

DTA and TG results concerning copolymers and PNA in air and in argon flow are presented in Figures 1-4. The IR spectral changes of the degraded copolymers are illustrated by Figure 5.

Polyacrylonitrile

The DTA curve (Fig. 1) obtained for PAN in air is consistent with that observed in Refs. 6 and 7 showing a strong and sharp exotherm which peaks at 340°C. The sharp exothermic reaction is an important feature of PAN pyrolysis, caused by nitrile group oligomerization.¹³

TG curves clearly show the two stages of the oxidative degradation. The fast weight loss of 20% in the temperature range of the exotherm may be explained by chain scission which occurs concurrently. The second stage degradation is clearly oxidative.



(b)

Fig. 2. (Continued from previous page.)

AN-BA-CV Copolymer

The thermal behavior of degraded copolymers is clearly different from that of PAN.

The DTA curve in air (Fig. 2) shows a reduced exothermicity associated with nitrile rearrangement from AN sequences in the copolymer. The curve is still sharp, although it is less intense and broader than that of PAN.

The temperature at which the exothermic effect occurs is the same as in PAN, so that there is no marked retarding or initiating effect on the acrylonitrile cyclization.

The exothermic effect associated with nitrile groups reaction is followed by a very small exothermic one. During the early stage of pyrolysis the exotherm is affected by concurrent processes, the most important being the chain scission. The dehydrochlorination of some units of vinylidene chloride occurs too.

The DTA curve in argon flow reveals a broader and less pronounced exothermic peak at the same temperature as in PAN. The difference between the curves obtained in argon and air can be assigned to the easier volatilization of chain fragments and to the decomposition of acrylate taking place in argon flow.

The TG curve indicates a stable copolymer up to 240°C.

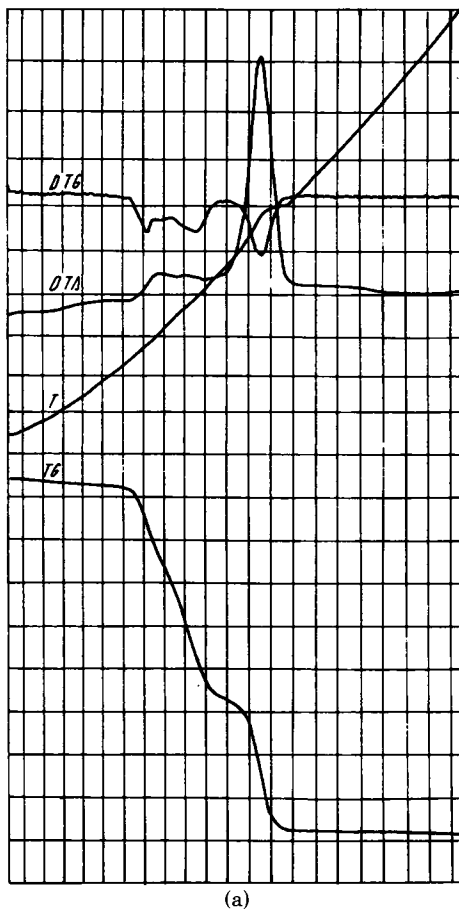


Fig. 3. DTA, TG, and DTG curves for acrylonitrile-butylacrylate-vinylidene chloride-styrene copolymer: (a) under argon; (b) in air.

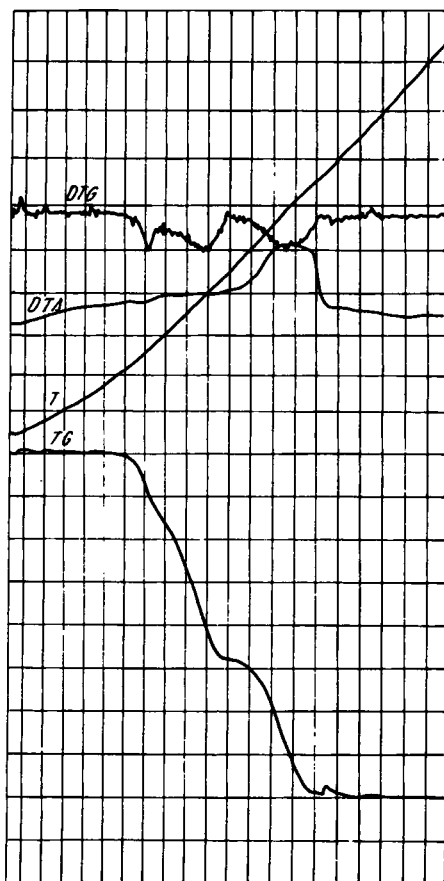
Infrared spectra of heating copolymers in air up to 200°C and 320°C, respectively, show the following changes.

The spectrum of pale yellow heated copolymer at 200°C shows the complete disappearance of the chlorine absorption, which accounts for the vinylidene chloride units dehydrochlorination at lower temperatures.

The original acrylate carbonyl absorption at 1740 cm^{-1} and 1705 cm^{-1} and the original C—O—R absorption at 1260 cm^{-1} disappears completely in the spectrum of the black residue at 320°C. It is concluded that the acrylate comonomers are decomposed by similar reactions as proposed in literature^{2,14,15} for poly(butylacrylate) and their copolymers.

The free nitrile absorption at 2240 cm^{-1} is gradually reduced. The IR spectrum of black residue exhibits a very small residual absorption at 2240 cm^{-1} showing that the nitrile rearrangement at this temperature is only partial. In the black residue are observed the methylene absorptions at 2940 cm^{-1} , 2880 cm^{-1} , and the shoulder at 1450 cm^{-1} , similar to the starting copolymer. New absorption at 3180 cm^{-1} was exhibited by degraded poly(acrylonitrile).

The thermal behavior of terpolymer is in agreement with Grassie's and all observations with respect to the acrylate and vinylidene chloride comonomer influence.



(b)

Fig. 3. (Continued from previous page.)

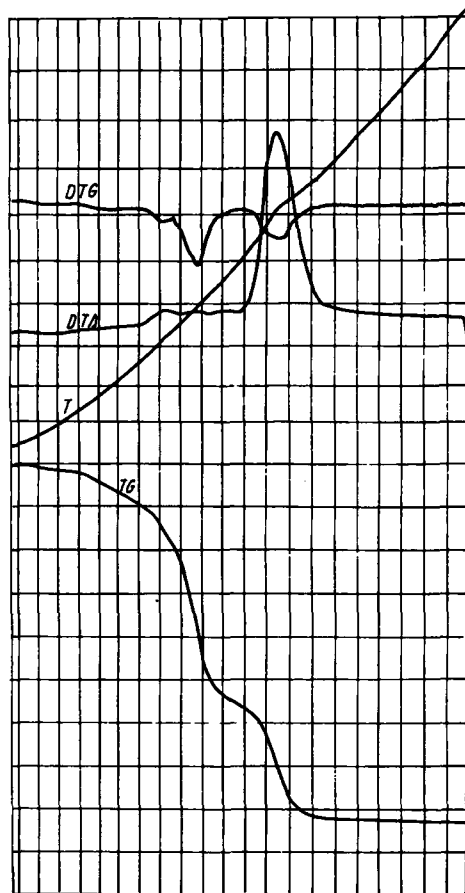
As the chlorine comonomer content is small (only 2.8%), its influence on the thermal destruction of terpolymer is reduced.

AN-BA-CV-S Copolymer

The DTA curves of the copolymer with the composition presented in Table I reveal a quite different curve in air and in argon flow (Fig. 3).

The DTA curve obtained in air shows a broad and complex exothermic peak with two distinct maxima at 310°C and 380°C, preceded by a small endothermic one. The shape of the DTA curve suggests the numerous reactions taking place concurrently during the early stage of decomposition. In argon flow the exothermic reaction is covered by the endothermic dehydrochlorination of CV units, by depolymerization of styrene units and also by acrylate chain scission processes. All these processes take place more intensely than in air.

The DTA curve in argon flow does not exhibit sharp peaks. The TG behavior is similar in both atmospheres, in argon flow and in air. Up to 240°C, the copolymer is completely stable. The TG curve shows two decomposition stages quite clearly defined. In the first stage, up to 470°C, the copolymer is almost destroyed. The IR spectra of the black residue of the copolymer heated at 320°

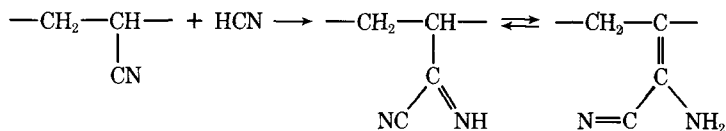


(a)

Fig. 4. DTA, TG, and DTG curves for acrylonitrile-methacrylic acid-vinylidene chloride-styrene copolymer: (a) under argon; (b) in air.

for 20-min is almost identical with that of pure spectral carbon. Slight methylene absorptions at 2935 cm^{-1} , 2875 cm^{-1} , and 1460 cm^{-1} remain. There are also some slight new absorption peaks at 3270 cm^{-1} , 3340 cm^{-1} , and 1650 cm^{-1} .

The N-H bands about 3200 cm^{-1} have been explained by Grassie and McGuchan⁶ by an α -iminonitrile structure or by corresponding τ -tomic form, which can be produced during degradation of AN units.



The broad 1650 cm^{-1} band is going to support such a structure. In fact, this polymer contains 25% CV, so the 1650 cm^{-1} band can be partially done also by isolated C=C-structure.

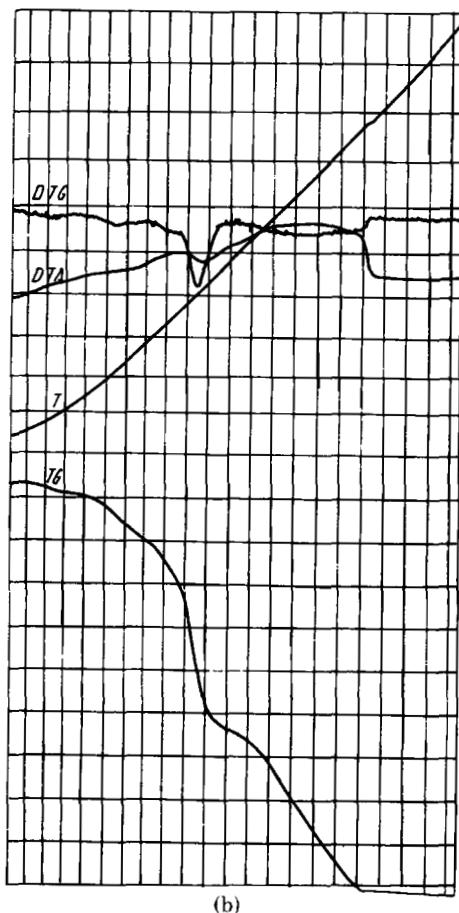


Fig. 4. (Continued from previous page.)

AN-AM-CV-S Copolymer

The thermal analysis data for examined copolymer in air and in argon flow are shown in Figure 4. The DTA curve in air shows many small peaks. The exotherm at about 320°C, associated with a little weight loss, is probably due to the nitrile group oligomerization. The exotherm is affected by a concurrent endothermic reaction with it, corresponding to CV unit dehydrochlorination.

The small weight loss in the region of the exothermic reaction suggested that, initially, chain fragmentation occurred in the copolymer to a smaller extent than in pure polyacrylonitrile.

It is possible that crosslinking reactions by HCl intermolecular elimination from chlorine groups and by H₂O intermolecular eliminations from acidic groups would oppose the formation of the chain fragments. This observation is in agreement with Grassie et al. references with respect to thermal degradation of pure polymethacrylic acid¹⁶ and of acrylonitrile copolymers.^{3,4} The shape of the DTA curve in the region 360–490°C associated with an important loss of weight is the sum of exothermic and endothermic processes: comonomers chain scission and some decomposition of the acid structure units.

In argon flow the thermal behavior is quite similar.

The copolymer shows pale, yellow coloration after 20 min pyrolysis at 200°C. Above 250°C the color changes gradually from brown to black.

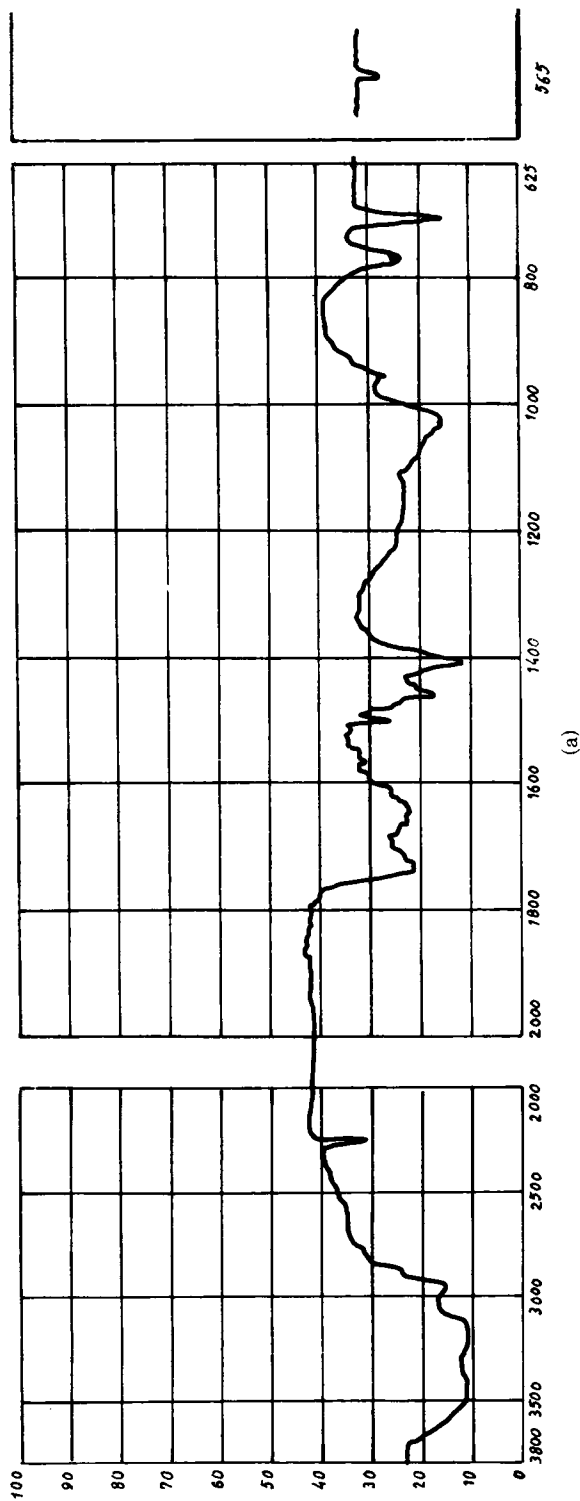
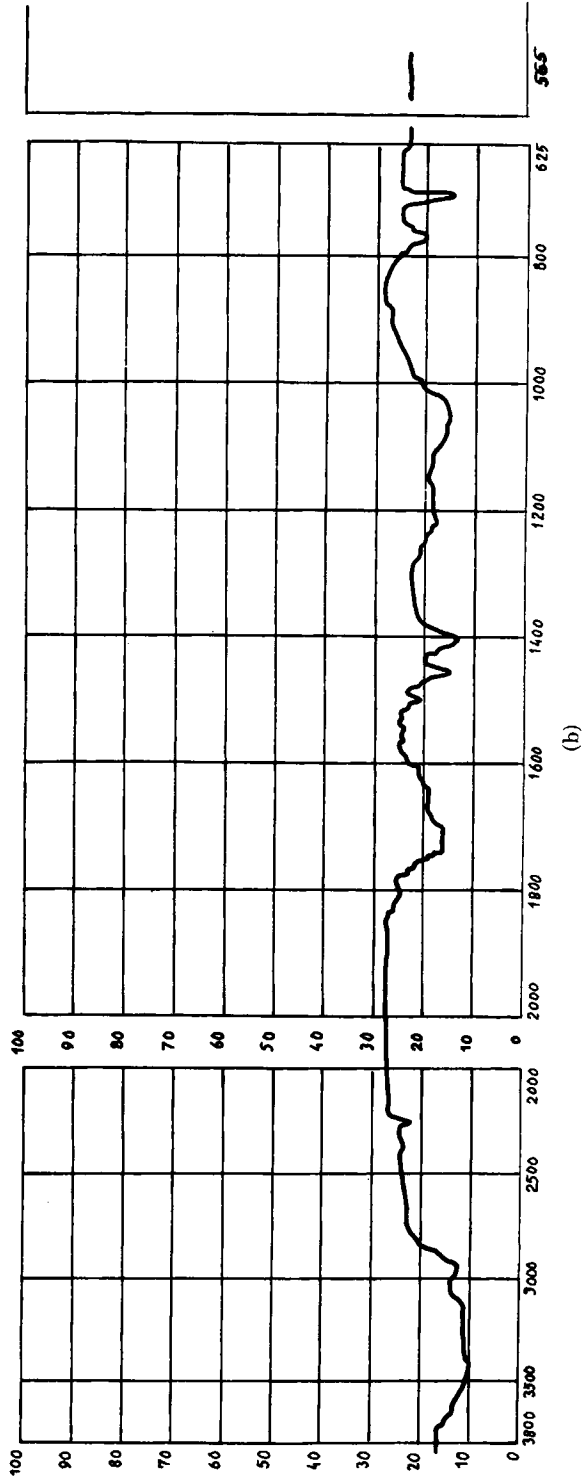
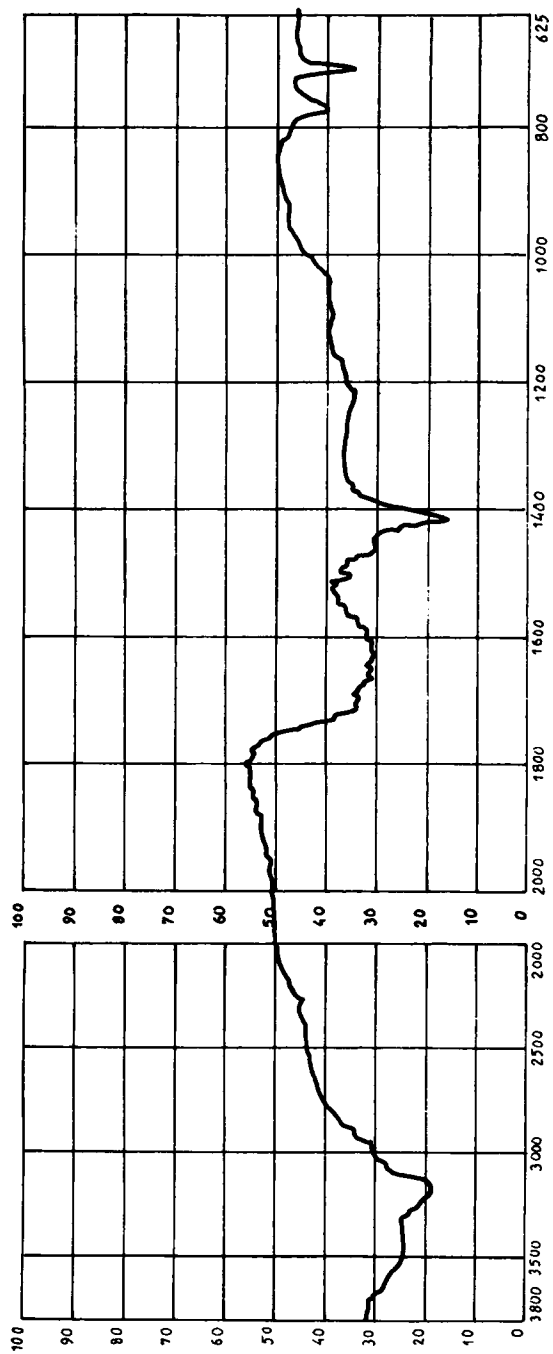
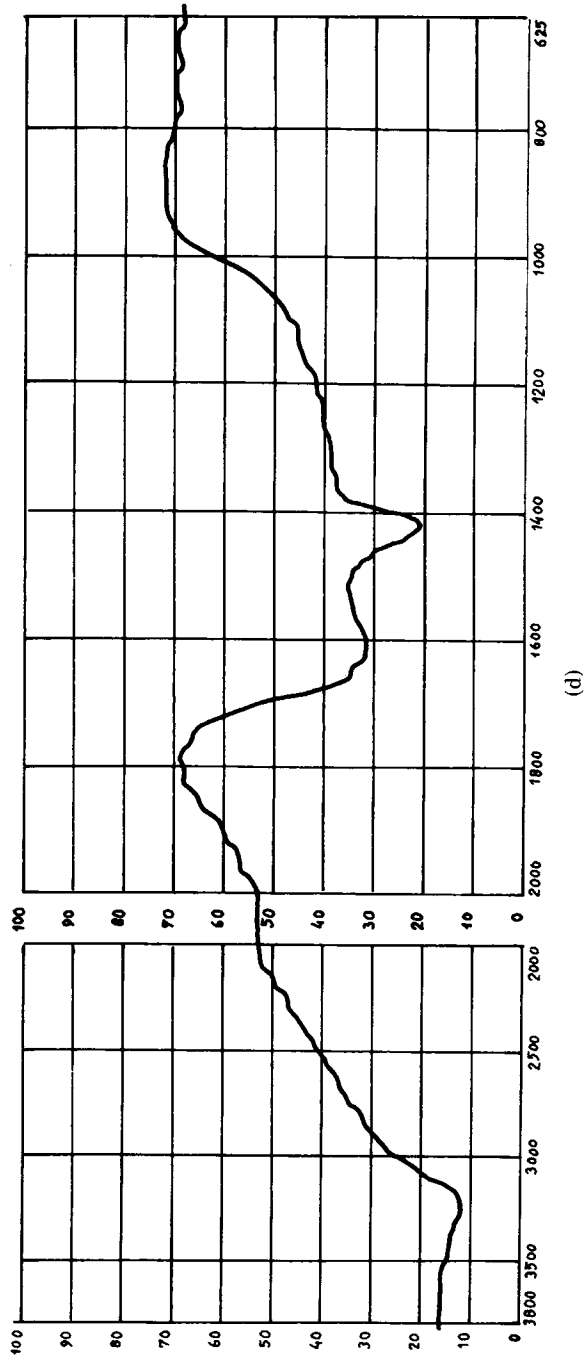


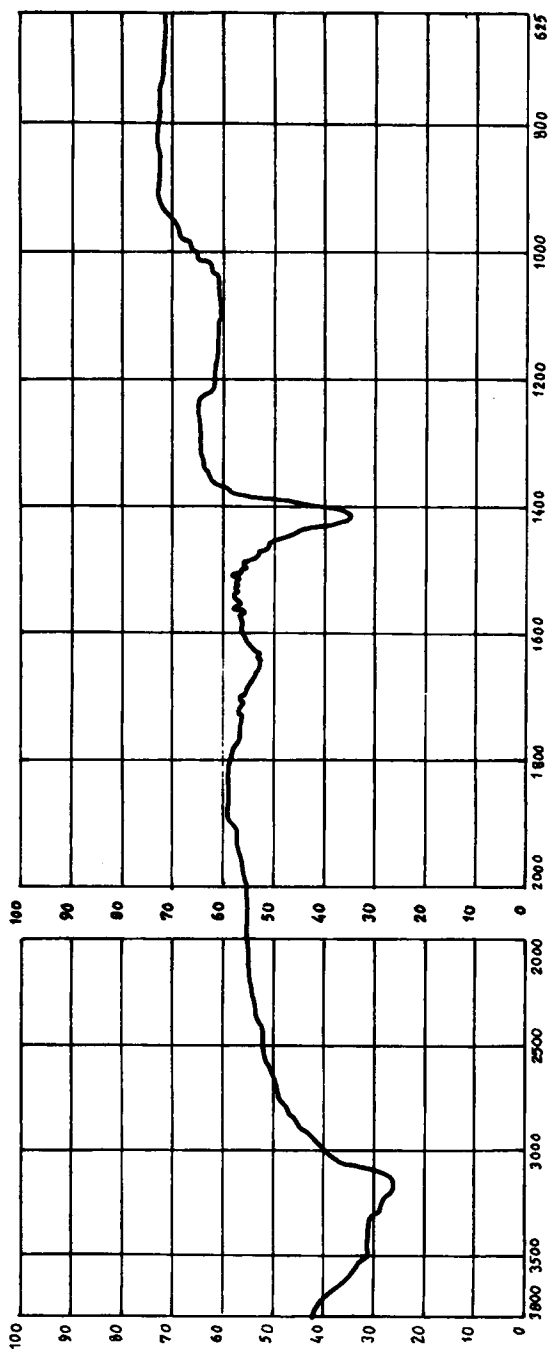
Fig. 5. Infrared spectra of: acrylonitrile-methacrylic acid-vinylidene chloride-styrene copolymer: (a) initial; (b) heated 20 min to 200°C; (c) heated 20 min to 320°C; (d) heated 20 min to 500°C, and (e) spectral carbon.





(c)
Fig. 5. (Continued from previous page.)





(e)
Fig. 5. (Continued from previous page.)

Changes in the IR spectra of heated copolymers are shown in Figure 5, in comparison with the original copolymer spectrum and with the pure carbon spectrum.

The initial free nitrile absorption at 2240 cm^{-1} is gradually reduced, in the heated copolymer spectrum. The carbonil absorption due to acidic groups disappears completely. There are some new, very slight absorptions at 1800 cm^{-1} and 1830 cm^{-1} . This can be a suggestion that a transient intermolecular anhydride species similarly of that reported in literature³ is formed during degradation. The free acid band due to AN sequences at 3480 cm^{-1} does not appear in the spectrum of heated copolymer at 200°C .

The chlorine absorption due to CV units disappears in the spectrum of the heated copolymer at 200°C .

An interesting feature here is the absorption at 710 cm^{-1} and 770 cm^{-1} assigned to C-H vibrations in phenyl rings still remaining in the spectrum of the residue at 320°C and even in residue at 500°C . Also CH_2 bands at 2940 cm^{-1} , 2880 cm^{-1} , and 1460 cm^{-1} persist in all the spectra studied.

CONCLUSIONS

(1) Thermogravimetry and differential thermal analysis were used in order to investigate the following copolymers: AN-BA-CV, AN-BA-CV-S, and AN-AM-CV-S.

(2) Thermal analysis data are in agreement with spectra of heated copolymers at various temperatures.

(3) The comonomer effects on thermal degradation are discussed, with special emphasis on oligomerization of nitrile groups.

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