Thermal Studies on the Saponification Products of Acryionitrile Terpolymer

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ABSTRACT

Thermal behavior of saponified products of an acrylic terpolymer was studied by differential scanning calorimetry and thermogravimetry in a nitrogen atmosphere. The exothermic reaction was attributed to the oligomerization of nitrile groups by comparing the extent of the reaction with the number of nitrile groups present. A shift in the position of the exotherm was observed with an increase in the degree of saponification up to 0.730, but further increase in the extent of saponification led to the disappearance of the exotherm though the nitrile content was found to range between 4.5 and 2.2%. The saponified products beyond a degree of saponification of 0.755 showed a broad endothermic peak instead of the exotherm. Thermogravimetric analysis of the products revealed that the exothermic reaction was concurrent with the weight loss. In the polyacrylonitrile homopolymer the threshold decomposition temperature was 248°C as compared to 294.8°C for acrylonitrile terpolymer. The residue at 800°C was less for the terpolymer, and it further decreased with increasing extent of saponification.

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INTRODUCTION

The thermal stability of a polymer is of great importance in de-
termining its processability and application as a material of construc-
tion. The use of acrylonitrile polymers (PAN) and copolymers in the
synthetic fiber industry and as carbon fiber has promoted extensive
studies on the degradation of PAN. That the oligomerization of nitrile
groups, an important step in the manufacture of carbon fiber from
PAN, is influenced by preparation [1], additives [2], preheat treat-
ment [3], and copolymers [3-6] is well established.

Grassie et al. [7] reported that the thermal analysis of acrylo-
nitrile copolymers revealed that 20% acrylate or methacrylate units
exert a diluent effect without inhibiting the reaction, while comonomers
with styrene-type structures behave differently, showing a marked in-
hibiting effect on the nitrile oligomerization. Recently, Ferguson et al.
[8] showed the role of acrylic acid comonomer as accelerator in cycli-
zation, while N-vinylpyrrolidone inhibits it. The termogravimetric
behavior of acrylonitrile-methacrylic acid copolymers and their so-
dium salts has been reported by Guyot et al. [9]. They extended their
studies to various heating rates, using thermogravimetric analysis
coupled with gas-liquid chromatography, thermal volatalization analy-
sis, differential calorimetry, and flash pyrolysis coupled with GLC
and eventually mass spectroscopic analysis to discuss the role of co-
monomers in nitrile oligomerization. Fitzgerald and Nielsen [10] and
Eisenberg [11, 12] have correlated the properties of styrene-meth-
acrylic acid copolymer with the concentration of sodium methacrylate
in the system. Tsutsui et al. [13] made use of dilatometry for the de-
termination of T_g in methyl acrylate-acrylic acid copolymers as a
function of the degree of neutralization, while Ogura et al. [14] inves-
tigated the same in the sodium salt of styrene-methacrylic acid (0.2
M) by means of IR and DSC.

In the ensuing presentation, the thermal behavior of saponified products
of acrylonitrile terpolymers containing methyl acrylate (7-7.5%) and
sodium methallyl sulfonate (1%) is presented. The kinetics of saponi-
fication of PAN and the terpolymer have been reported elsewhere [15].

EXPERIMENTAL

Sample Preparation

The terpolymer (composition: acrylonitrile 91.5-92%, methyl acry-
late 7-7.5%, and sodium methallyl sulfonate 1%) was supplied by Indian
Petrochemicals Limited, Baroda, India. The nitrogen content in the
terpolymer was 24.1% and the intrinsic viscosity of 1.10 dL/g in N,N-
dimethylformamide at 25°C.

TABLE 1. Analysis of Parent and Saponified Polymer Samples

Polymer code	Saponification time, min	% N (Kjeldahl)	% Nitrile[a]	Degree of saponification
H0	0	26.4	–	–
T0	0	24.1	91	–
T1	30	7.4	26.7	0.692
T2	60	6.5	24.4	0.730
T3	90	5.9	4.5	0.755
T4	120	5.5	2.2	0.771
T5	180	5.2	0	0.784
T6	240	5.0	0	0.80

[a]Calculated from CN absorption at 2245 cm^{-1}.

The saponification was carried out at saponification index (S.I.) of 0.5 in aqueous sodium hydroxide at 85°C. The amount of sodium hydroxide was determined by the S.I.:

$$\text{S.I.} = \frac{\text{weight of saponifying agent}}{\text{weight of polymer}} .$$

The saponification products were sampled after 30, 60, 90, 120, 180, and 240 min of saponification. The reaction product was cooled, precipitated with methanol, washed with water, and finally washed with methanol. The product was dried and characterized. The details of the kinetics of saponification and characterization have been reported [15]. The composition of the saponified products is given in Table 1.

Thermal Analysis

A Du Pont 1090 thermal analyzer was used to evaluate the thermal behavior of the products. Differential scanning calorimetric (DSC) studies and thermogravimetric (TG) studies were carried out on the 910-DSC and 951-TG modules of the Du Pont 1090 thermal analyzer. The measurements were done in a nitrogen atmosphere at a heating rate of 10°C/min. The sample size was 10 mg in all experiments.

RESULTS AND DISCUSSION

Differential Scanning Calorimetry Analysis

The DSC traces in Fig. 1 show that the exothermic transition due
to the cyclic oligomerization (T_p) in polyacrylonitrile starts at 244°C
with a peak maximum at 294°C, while in terpolymer (T0) the same re-
action starts at 260°C, with a peak maximum at 304.5°C. The increase
in the exothermic reaction temperature in the terpolymer may be attri-
buted to the presence of methyl acrylate units, which do not initiate or
retard the exothermic reaction but participate in the cyclization, allow-
ing the radical activity to pass through the monomer units (Eq. 1). A
similar observation has been reported by Grassie et al. [7].
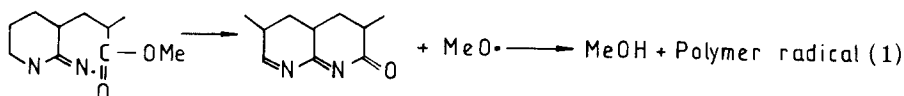
The saponification product T1 with a degree of hydrolysis of 0.692
shows an exotherm at 310.3°C, a temperature higher than the parent
terpolymer, probably due to the formation of imide structures that
hinder the reaction sterically. This was further confirmed by TG,
where the product formed during the exothermic reaction was found
to be more thermally stable.

It was also noted that, on continuing the saponification up to a de-
gree of saponification of 0.730, the exotherms appear at lower tempera-
ture (284.5°C) than that for samples T0 and T1, emphasizing the strong
accelerating effect of neighboring acid groups:
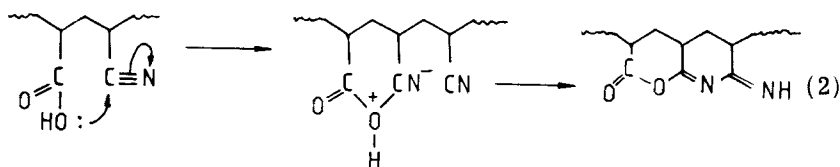
and ionic structures formed during the saponification reaction:
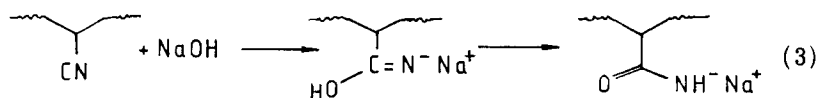
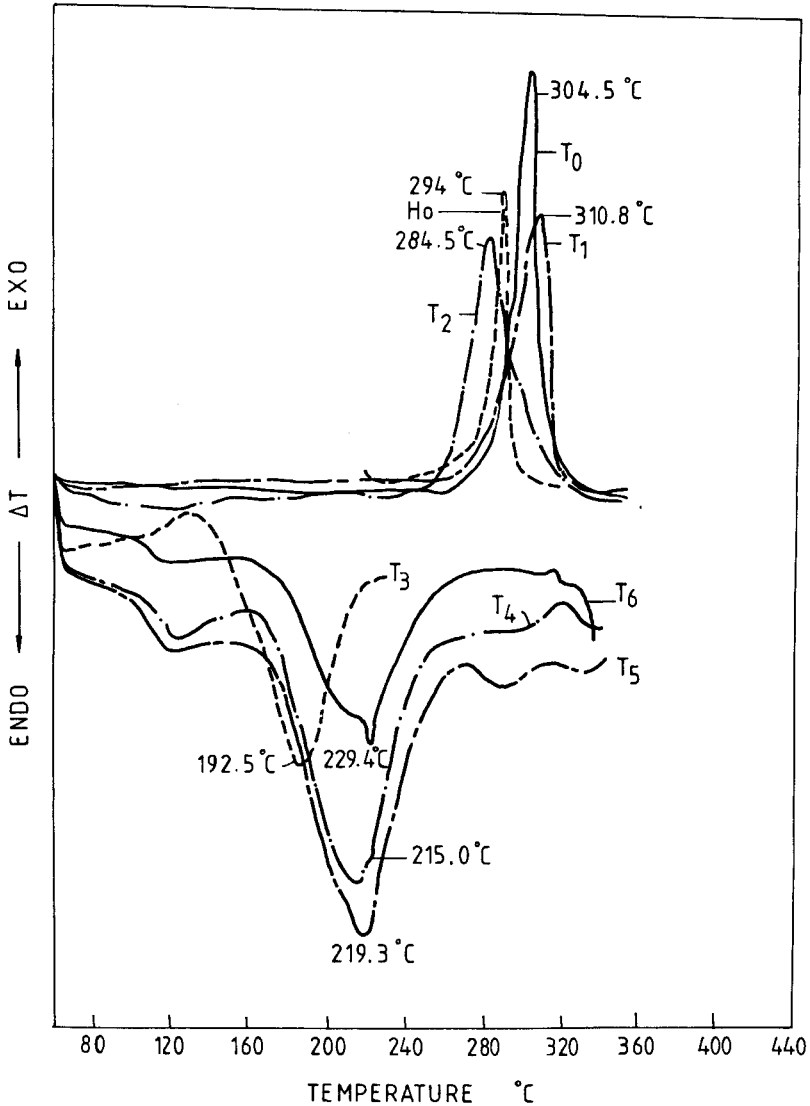FIG. 1. Representative DSC traces of polyacrylonitrile (H0),
acrylic terpolymer (T0), and the saponified products to a degree
of saponification of 0.692 (T1), 0.730 (T2), 0.755 (T3), 0.771 (T4),
0.784 (T5), and 0.80 (T6) in nitrogen.

Such structures are known to change the radical mechanism of the exothermic reaction to an ionic or concerted mechanism. In the free-radical mechanism, self-initiation may occur (Eq. 4), as reported by Grassie [16], or through the abnormal structures resulting from a side reaction during free radical polymerization [17] (Eq. 5):

(4)

(5)
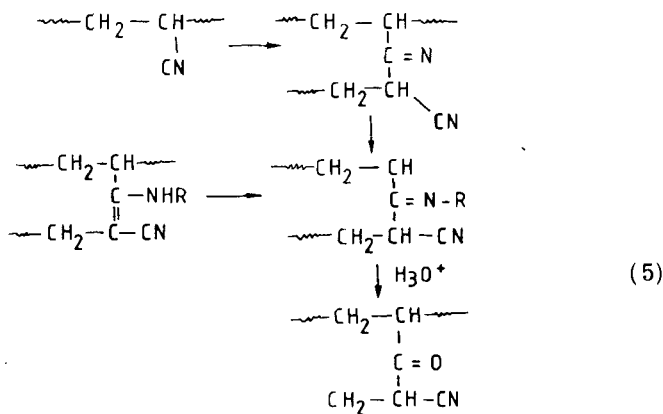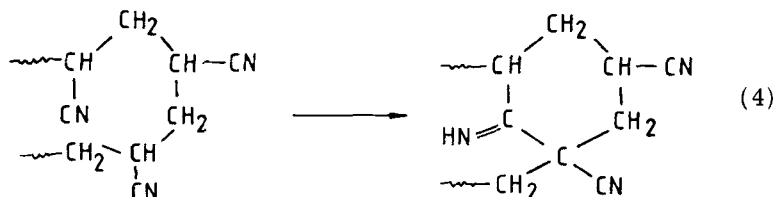
In homopolyacrylonitrile, initiation is a slow step and propagation is very rapid, but in our saponified system (T2), the reverse is true. The slow propagation of T2 is explained by the fact that it would necessitate the separation of electrostatic charges or migration of counterions. The DSC data lend further support to Grassie's proposition [2].

The observed ΔH values, calculated by applying a correction for CN groups [9] (Table 2), show a decline in the extent of exothermic reaction, primarily due to the drop in nitrile content of the saponified product as determined by infrared spectroscopy and nitrogen estimation data.

Interestingly, when the saponification was continued beyond a degree of saponification of 0.755, the exothermic peak for the nitrile group disappeared. This may be correlated with the much lower number of nitrile groups available only at large distances in the polymer chains (4.5 and 2.2%, respectively, in T3 and T4), which can not participate in the oligomerization.

TABLE 2. DSC Analysis of the Parent and Saponified Polymer Samples

Polymer code	Exotherm range, °C	T_p, °C	$-\Delta H$, heat of oligomerization		Endotherm range, °C	T_p, °C	ΔH, J/g
			J/g	kJ/mol, (V)			
H0	244–308	294	448	23.8	–	–	–
T0	260–360	304.5	593	34.5	–	–	–
T1	250–340	310.3	464	71.1	–	–	–
T2	240–340	284.5	436	94.7	–	–	–
T3	–	–	–	–	100–200	192.5	129
T4	–	–	–	–	120–270	215	149
T5	–	–	–	–	160–270	219.3	161
T6	–	–	–	–	160–200	229.4	212

On the contrary, an endotherm was observed at 192.5°C without any weight loss. On further increase in the saponification time, as in T4, T5, and T6, the endotherms observed at 215, 219.3, and 229.4°C are associated with weight losses of 13.29, 10, and 4%, respectively. This indicates that the endotherm is a consequence of two major changes, one of which does not involve any weight loss, while the other is associated with a weight loss. Moreover, the position of the endotherm is dependent on the composition of the saponified product.

The observed increase in the endothermic peak temperature with increasing saponification may be related to an increase in the amount of sodium acrylate and, hence, the degree of ionization. The electrostatic interactions of such bonded ions in the polyelectrolytes limit the segmental mobility of the polymer chain, which is also reflected in the increasing values of ΔH. It is assumed that such an endotherm partially contributes to the electrostatic forces (or T_g) of the polymers. Similar results have also been reported by Eisenberg [19]. It is therefore evident that our results are in conformity with the behavior of acrylate/methacrylate salts reported by the same author [11, 12], according to whom $T_g \propto q/a$, where q is the charge in units of electrons and a is the distance between the bonded ions in Angstrom units. As the sodium acrylate content increases with increasing saponification time, the electrostatic interactions increase and hence account for the shift in endothermic transition to higher temperature.

Thermogravimetric Analysis

The thermogravimetric curves for the polyacrylonitrile (H0), the terpolymer (T0), and its saponification products (T1-T6) are reproduced in Figs. 2 and 3. It is evident from the data in Table 3 that small differences in the chemical structure of the samples cause interesting changes in the thermograms.

The thermal degradation of polyacrylonitrile (H0) begins at 248°C with a rapid loss of 30% between 300 and 350°C, followed by a slower degradation step causing a weight loss of 20% up to 850°C.

The introduction of comonomers does not influence the weight loss but initiates degradation at 294.8°C with a maximum rate of degradation (D_{max}) at 304°C. The second step of degradation begins at 365°C and corresponds to a weight loss of 22.7% with a maximum rate of degradation at 420.5°C, while the total weight loss till 800°C was comparable to that of the homopolymer.

Up to 350°C, low molecular weight compounds containing conjugated carbon-nitrogen sequences are known to be produced. The gaseous products of this reaction are NH_3 and HCN. Ammonia is probably formed from the terminal imine, and hydrogen cyanide is eliminated from the units which have not undergone cyclization, pos-
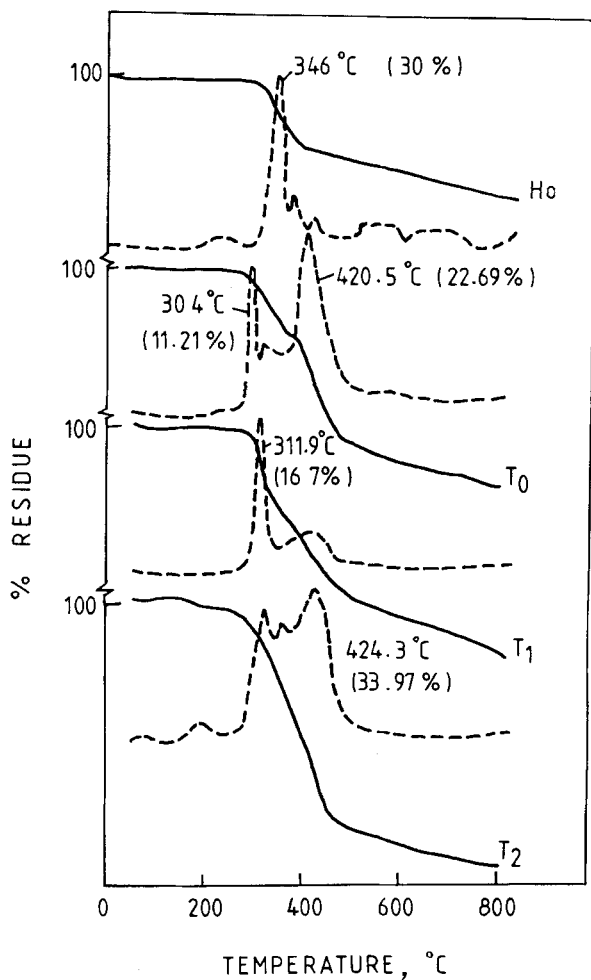
FIG. 2. TG and DTG curves of polyacrylonitrile (H0), acrylic terpolymer (T0), and the saponified products to a degree of saponification of 0.692 (T1) and 0.730 (T2) in nitrogen.
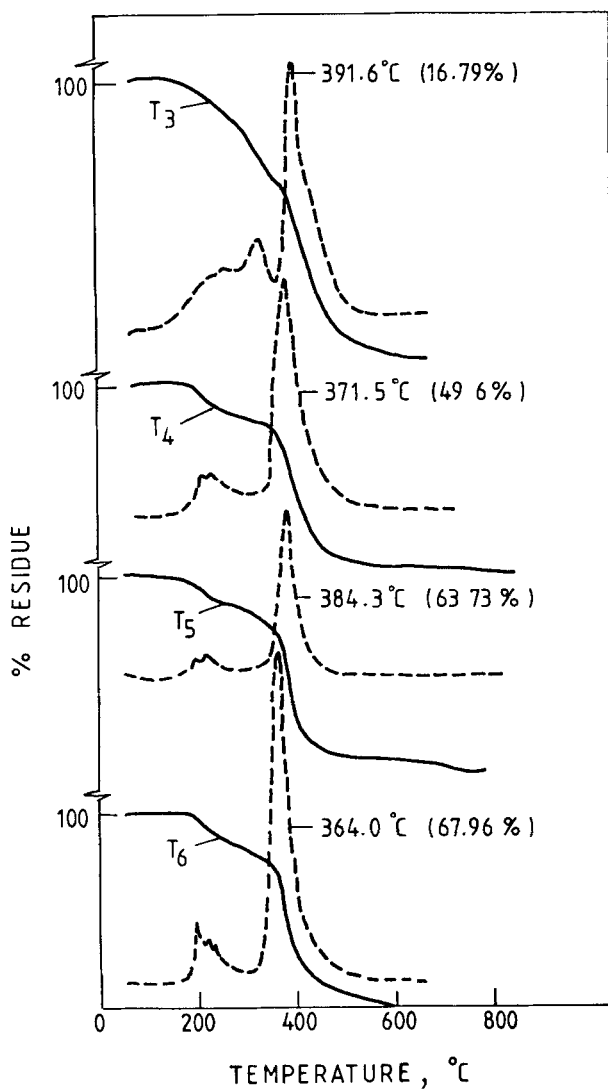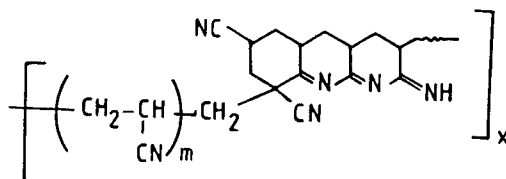
FIG. 3. TG and DTG curves of saponified products of acrylic ter-polymer to a degree of saponification of 0.755 (T3), 0.771 (T4), 0.784 (T5), and 0.80 (T6) in nitrogen.

sibly in conjunction with a chain scission reaction. The structure proposed by Grassie et al. [1] also accounts for such a reaction:

$$\left[\left(CH_2-\underset{\underset{CN}{|}}{CH}\right)_m CH_2 \underset{CN}{\overset{NC}{\diagdown}} \underset{N}{\diagdown} \underset{N}{\diagup} \underset{NH}{\diagdown} \right]_x$$

On the other hand, above 350°C the cyclized structures lose hydrogen and become more aromatic in character. This process continues till 700°C, above which further hydrogen formation may occur due to intermolecular condensation of aromatic structures [20]. Finally, at 900°C, the char begins to lose nitrogen, indicating the production of heterocyclic rings. In the terpolymer (T0) the much lower weight loss may be attributed to the diluent effect of the comonomers [20]. Further, in the saponified product T1, the exothermic weight loss is initiated at 301.8°C. The maximum degradation at 311.9°C corresponds to a weight loss of 16.7%, and the second step of thermal degradation begins at 370°C, resulting in a weight loss of 12.3%. It is evident from the above data that, though the exothermic reaction is

TABLE 3. Thermal Degradation Data of Parent and Saponified Polymer Samples

Polymer code	IDT,[a] °C	Major weight loss region, °C	% Residue	
			At 500°C	At 800°C
H0	248	248–400	68	56
T0	294.8	400–500	66	54.5
T1	301.8	301.8–370	65	55
T2	161.4	300–500	54	50.5
T3	215.2	350–500	47	43.5
T4	174.5	350–500	30	24.4
T5	175	350–500	28	22
T6	140	350–500	23	20

[a]Initial decomposition temperature.

delayed in sample T1, the weight loss corresponding to the exotherm is not affected. On the other hand, the lower degree of weight loss in the second step of degradation confirms the formation of more thermally stable species. When the saponification was continued further as in T2, a slight drop in the weight loss due to the exothermic reaction was observed, indicating the slower propagation rate. Beyond a degree of saponification of 0.755 the exotherm is absent and, hence, there is no weight loss through conjugated ladder-type structure formation.

The saponified products T4, T5, and T6 undergo weight losses of 13.29, 10, and 4%, respectively, at 200-220°C. This may be associated with the evolution of NH_3 from carboxamide groups formed during the saponification, which are known to convert to carboxylic acid groups. The second stage of degradation corresponds to a loss of 49.6% in T4, 63.7% in T5, and 68.0% in T6. This increase in weight loss with increased number of carboxylic acid groups probably means that the two are interrelated, and the degradation may be due to the elimination of small molecular weight fragments like CO, CO_2, etc. from the carboxylate groups and the chain scission.

Finally, it is concluded that both exotherm and weight loss in the range from 280 to 320°C are manifestations of the same reaction, but on increasing the degree of saponification beyond 0.755, the electrostatic interactions and weight loss occur almost simultaneously, showing as a broad endotherm. Also, the extent of degradation increases with increasing extent of saponification.

ACKNOWLEDGMENT

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