

THERMAL DEGRADATION STUDY OF GLYCIDYL METHACRYLATE ACRYLONITRILE COPOLYMERS

M. S. Iqbal^{1*}, Yasmeen Jamil¹, T. Kausar² and M. Akhtar²

¹Department of Chemistry, GC University, Lahore 54000, Pakistan

²Pakistan Atomic Energy Commission, P.O. Box 1331, Islamabad, Pakistan

Thermal degradation of copolymers, prepared from glycidyl methacrylate and acrylonitrile in varying molar ratios using 2,2'-azobisisobutyronitrile as an initiator, was studied by thermogravimetry, derivative thermogravimetry, differential thermal analysis and mass spectrometry. The fragmentation patterns in the mass-spectra were interpretable by comparison with the known degradation patterns of the related materials. Thermal kinetic parameters, including activation energies and order of reaction of the degradation of the prepared copolymers, were calculated from their thermoanalytical data. These parameters suggest an overall increase in thermal stability with increasing content of acrylonitrile in the copolymers.

Keywords: acrylonitrile copolymers, glycidyl methacrylate, mass spectrometry, thermal degradation

Introduction

Polymeric materials find an extremely wide range of applications in almost every branch of technology. This is mostly due to the combination of diverse properties in a single material. Polymers with desirable properties and characteristics have been conveniently prepared through copolymerization [1–3]. In recent years glycidyl methacrylate (GMA)-based copolymers received increasing attention due to their versatile applications [4–6]. Syntheses and thermal degradation studies of GMA homopolymers [7] and copolymers with styrene [8], methyl methacrylate [9], vinyl acetate [10] and α -methyl styrene [11] have been carried out extensively, but little work has been done on GMA copolymers with acrylonitrile (AN). The GMA-based copolymers are of great value for binding enzymes and other biologically active species [12, 13]. The sensitivity of the epoxy group to ionizing radiation renders these copolymers as potential candidates for negative electron beam resists [14]. Several workers have studied thermal degradation of acrylonitrile homopolymer by thermal volatilization analysis (TVA) [15, 16]. Preta *et al.* [17] studied thermal behavior of polyacrylonitrile polymers synthesized under different conditions and comonomer composition. In this paper we report the synthesis and thermal degradation behaviour of glycidyl methacrylate–acrylonitrile (GMA–AN) copolymers.

Experimental

Materials

Glycidyl methacrylate (E. Merck) and acrylonitrile (Fluka) were purified before use by drying with anhydrous calcium chloride (E. Merck) and calcium hydride (E. Merck) for 24 h separately and followed by distillation under vacuum (70 mm Hg) at 0°C. The middle fraction was collected and stored at 4°C for use in this study. The initiator 2,2'-azobisisobutyronitrile (AIBN, E. Merck) was purified by recrystallization, after filtration, from absolute ethanol. The recrystallization was affected by allowing the solution to evaporate in air at ambient temperature. The crystals were filtered, dried under vacuum and kept in the dark at 0°C prior to use. Solvents including tetrahydrofuran, methanol and acetone, were purified by drying with calcium hydride (E. Merck) and calcium sulphate (E. Merck) for 24 h and distillation under vacuum (70 mm Hg) at 10°C.

Preparation of homopolymers

Homopolymers of GMA (I) and AN (V) were synthesized, separately, by using AIBN as an initiator according to the reported method [9]. These syntheses involve free radical polymerization. The homopolymers of GMA and AN were precipitated by methanol from THF and acetone solutions, respectively, dried under vacuum at room temperature for 48 h and stored in a desiccator.

* Author for correspondence: saeediq50@hotmail.com

Preparation of copolymers

Copolymers of GMA and AN having compositions II, III and IV (Table 1) were prepared by bulk polymerization using 5 g AIBN in 100 mL of GMA+AN as initiator. The components were mixed and the mixture was degassed by freeze-and-thaw operation three times. The dilatometer containing the mixture was then sealed and removed from the vacuum system and warmed to room temperature and swirled for a few minutes to make the reaction mixture homogeneous. Polymerization was carried out at 60°C in a thermostated bath and during polymerization the reaction mixture was frequently shaken. The copolymers were precipitated by methanol from acetone solution, dried under vacuum at room temperature for 48 h and stored in a desiccator. The purified and dried homo- and copolymers (white in color) were ground, separately, into fine powders.

Measurements

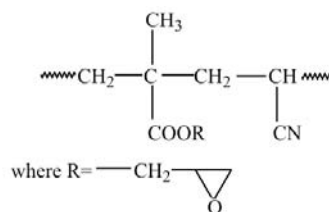
Infrared spectra (4000–400 cm^{-1}) of the synthesized materials were recorded in the transmittance mode on Perkin Elmer Spectrum One FTIR spectrophotometer by using KBr disc technique. Thermal studies, consisting of thermogravimetry (TG), differential thermogravimetry (DTG) and differential thermal analysis (DTA), were carried out by use of Netzsch Simultaneous Thermal Analyzer STA-409. For these studies the powdered sample (10 mg) was heated under dynamic nitrogen atmosphere from ambient to 1000°C at a heating rate of 10°C min^{-1} .

Mass spectrometric measurements were performed on Finnegan Voyager 8000 GC Top/Mass MD800 using direct insertion probe (DIP), electron impact (EI) ionization and quadrupole analyzer. The mass spectra with DIP system provided fast scanning, self-tuning of experimental parameters and a wide mass range. The parameters for DIP were set as: electron energy 70 eV; ion energy 2.0 V; ion energy ramp 2.0 mV amu^{-1} ; detector voltage 350 V; source temperature 250°C; interface temperature 300°C; DIP temperature 50–700°C. The vacuum system produced the required high vacuum and made it possible for ions generated by electron impact in the ion source to move towards the quadrupole analyzer,

where they separated according to their mass to charge (m/z) ratios, and reached the detector without colliding with other ions and molecules. Pyrolysis of the polymers under study was carried out under high vacuum so that the possibility of secondary reactions was minimized. Heating was controlled by a thermocouple attached to the probe tip inside the probe rod and the probe tip was in direct contact with flared glass sample vials that could easily be inserted and removed from the direct probe inlet. The heating rate was 50°C min^{-1} in the range 50–700°C and the maximum temperature of 700°C was kept constant for additional 10 min. The total ion current (TIC) scans for homo- and copolymers were recorded on the DIP-MS system and a library search was performed by using NIST database.

Results and discussion

The copolymers under study were easily obtained by the method given in the experimental section. These polymers containing GMA and AN as monomeric units can be represented by the Scheme 1 which represents bulk polymerization via free radical mechanism.



Scheme 1 Constituent monomeric units of GMA and AN in the copolymer

Characterization

The homo- and copolymers were characterized by FTIR technique. The characteristic FTIR absorption bands appearing in the spectra of homopolymers I and V are listed in Table 2 and shown in Fig. 1. In the FTIR spectrum of homopolymer I the $\nu_{\text{C=C}}$ band at 1639 cm^{-1} is absent which indicates that polymerization has taken place [18]. The bands appearing at 1148 and 840 cm^{-1} indicate the presence of ester and epoxy groups, respectively. Similarly in case of

Table 1 The overall composition of each homopolymer (I, V), copolymers (II, III and IV) and an initiator (AIBN)

GMA–AN copolymer	GMA/v/v%	AN/v/v%	GMA/mol%	AIBN/w/v%	Polymerization temperature/°C
I	100	0	70	0.0500	60
II	75	25	53	0.0500	60
III	50	50	35	0.0500	60
IV	25	75	18	0.0500	60
V	0	100	0	0.0500	60

Table 2 Comparative thermogravimetry (TG), derivative thermogravimetry (DTG), differential thermal analysis (DTA), activation energies and order of reaction data for GMA-AN homo- and copolymers

GMA/AN/%	FTIR/cm ⁻¹	TG/°C		Mass loss at 400°C/%		DTG (peak)/°C		DTA (peak)/°C		E ₀ /kcal mol ⁻¹		Order of reaction	
		T ₀	T ₅₀	T _{max}	1 st step	2 nd step	1 st step	2 nd step	1 st step	2 nd step	1 st step	2 nd step	1 st step
100/0 (I)	2962-3000 ν _{-CH} , 1720 ν _{>C=O} , ^a	230	276	460	92	285	416	386 (exo) ^c	522 (exo)	26	03	0.5	1
	840-909 (epoxide ring), ^b												
	1148 ν _{C-O ester} , 1450 γ _{C-H}												
75/25 (II)	2962-3000 ν _{-CH} , 1738 ν _{C=O} ,	250	338	570	72	326	404	438 (exo)	530 (exo)	11	04	0	2
	840-909 (epoxide ring),												
	1150 ν _{C-O} , 2235 ν _{C=N}												
50/50 (III)	2962-3000 ν _{-CH} , 1720 ν _{C=O} ,	270	353	640	70	338	410	336 (exo)	568 (exo)	12	04	0	2
	840-909 (epoxide ring),												
	1120 ν _{C-O} , 2235 ν _{C=N}												
25/75 (IV)	2962-3000 ν _{-CH} , 1721 ν _{C=O} ,	300	384	680	60	328	400	324 (exo)	590 (exo)	13	04	0	3
	840-909 (epoxide ring),												
	1120 ν _{C-O} , 2235 ν _{C=N}												
0/100 (V)	2925 ν _{-CH} , 2235 ν _{C=N} ,	310	620	810	12	337	460	333 (exo)	584 (exo)	28	12	1	2
	1448 γ _{as(C-H)} , 1360 γ _{s(C-H)}												

^astretching vibration, ^bbending vibration, ^cExotherm, T₀ shows temperature at which degradation starts, T₅₀ shows temperature at which 50% mass loss occurs and T_{max} shows temperature at which maximum mass loss occurs

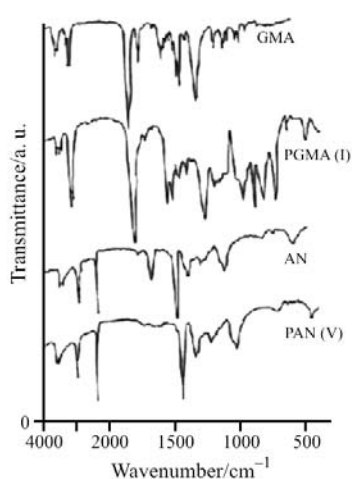


Fig. 1 FTIR spectra of monomers and homopolymers (I, V)

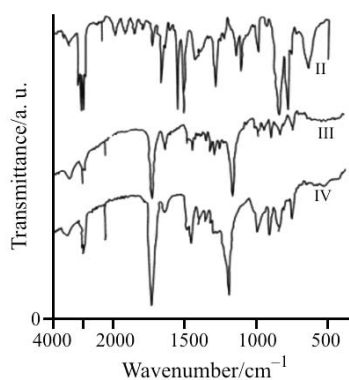


Fig. 2 FTIR spectra of GMA-AN copolymers (II, III and IV)

homopolymer V the $\nu_{C=C}$ band at 1630 cm^{-1} was absent which indicated the conversion of the monomer to the polymer [19]. The bands at $3324\text{--}3177\text{ cm}^{-1}$ due to ν_{N-H} asymmetric and symmetric vibrations, 2235 cm^{-1} due to $\nu_{C\equiv N}$, $2925\text{--}2853\text{ cm}^{-1}$ due to $\nu_{s(C-H)}$ and $1448\text{--}1386\text{ cm}^{-1}$ due to δ_{C-H} were also present. For the copolymers II, III and IV the characteristic FTIR bands are listed in Table 2 and shown in Fig. 2. The absorption band at 840 cm^{-1} indicates the presence of epoxy groups showing that GMA has been incorporated into the copolymer chain. All the copolymers showed strong absorption at $1720\text{--}1740\text{ cm}^{-1}$ due to ν_{COO^-} and strong band at $1400\text{--}1150\text{ cm}^{-1}$ due to ν_{C-O} vibrations. The absorption intensity of these bands was proportional to the amount of GMA present in the sample. The band at 2235 cm^{-1} due to nitrile group was also observed in the spectrum of copolymer. The absence of the absorption band at $1630\text{--}1640\text{ cm}^{-1}$, characteristic of vinyl group ($>C=C<$) stretching, also showed that copolymerization had taken place.

Thermal studies

Thermogravimetric traces of homopolymers and GMA-AN copolymers are shown in Fig. 3. Thermal degradation of homopolymer I appears to proceed in two steps. In the first step depolymerization starts mainly at the unsaturated chain ends followed by random chain scission at higher temperatures [7]. Similarly degradation of homopolymer V proceeded in two steps; in the first step at $310\text{--}380^\circ\text{C}$ evolution of volatile materials like NH_3 , HCN and non-condensable hydrogen gas took place. At higher temperatures (around 480°C) nitrogen gas evolved [20]. The total mass loss in homopolymer I was 97% (85% at first stage of degradation and 12% at second stage) at 460°C as compared to 16% that in homopolymer V (13% at first stage of degradation and 3% at the second stage) at 460°C .

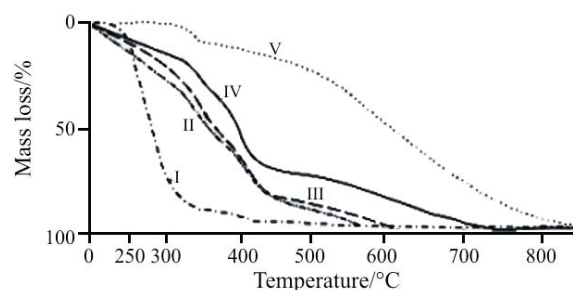


Fig. 3 TG curves (dynamic nitrogen atmosphere, heating rate $10^\circ\text{C min}^{-1}$) for GMA-AN homo (I, V) and copolymers (II, III and IV)

In order to compare the thermal stability of the homo- and copolymers the mass loss of polymers I-V was determined at 400°C . The results are given in Table 2. Thermal parameters T_0 (temperature at which degradation starts), T_{50} (temperature at which 50% mass loss occurs) and T_{max} (temperature at which maximum mass loss occurs) obtained from TG curves are also given in Table 2. These parameters were plotted against the % v/v of AN added and the plots are shown in Fig. 4. The value of T_0 indicated that degradation of AN homopolymer started at higher temperature relative to GMA homopolymer and their copolymers. For the copolymers containing 50% v/v or more acrylonitrile T_{50} and T_{max} showed a substantial increase in thermal degradation temperature with increase in AN concentration, possibly due to nitrile cyclization reaction in polyacrylonitrile structure [20].

DTG and DTA traces are shown in Figs 5 and 6, respectively. The DTG curves for both GMA and AN homopolymers showed two peaks with rate maxima at 285 , 416 and 337 , 460° , respectively. The later rate maxima are due to evolution of NH_3 , HCN and non-condensable hydrogen gas [20]. DTG curves for

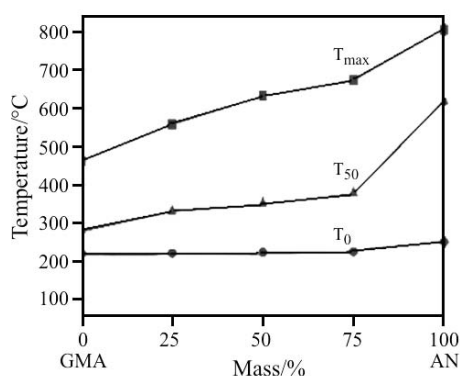


Fig. 4 Plots of thermal parameters vs. AN (% v/v) added

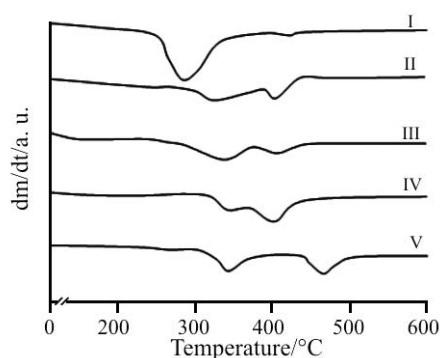


Fig. 5 DTG curves (dynamic nitrogen atmosphere, heating rate $10^{\circ}\text{C min}^{-1}$) for GMA-AN homo (I, V) and copolymers (II, III and IV)

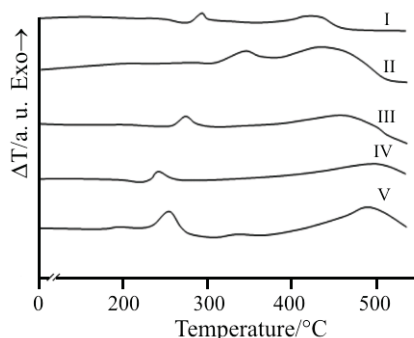


Fig. 6 DTA curves (dynamic nitrogen atmosphere, heating rate $10^{\circ}\text{C min}^{-1}$) for GMA-AN homo (I, V) and copolymers (II, III and IV)

copolymers of GMA-AN showed intermediate values of rate maxima relative to individual homopolymers. The first peak in GMA-AN curve shifted slightly to a higher temperature with an increase in AN concentration. The curves of other copolymers showed degradation with very slow increase in rate maxima values with an increase in the AN concentration.

DTA of GMA homopolymer produced two exotherms. The first was a very small peak at 386°C due to depolymerization at unsaturated chain ends

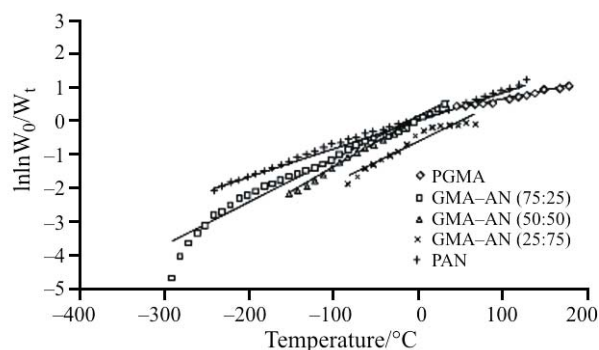


Fig. 7 Plots for determination of activation energies of thermal degradation of GMA-AN homo (I, V) and copolymers (II, III and IV)

followed by the second at 522°C which related to random decomposition of the main chain. This result is in line with those of earlier TG and DTG studies [7]. The AN homopolymer exhibited two exotherms; one at 333°C and the other at 584°C corresponding to monomer formation and nitrile cyclization reaction, respectively [21]. In case of copolymers the exotherms due to degradation of GMA and AN were similar, which shifted to higher temperatures with increase in the AN concentration. In case of copolymer IV, formation of thermally stable conjugated carbon-nitrogen system with an increase in AN concentration is indicated [22].

Activation energies and order of degradation reaction were calculated from the TG curves using the Horowitz and Metzger method [23] by plotting $\ln \ln W_0/W_t$ vs. θ (Fig. 7), where W_0 is the initial mass of polymer and W_t is the mass of polymer at temperature T . The $\theta = T - T_s$, where T_s is the temperature at which $W_t/W_0 = 1/e$ (it is the temperature where the maximum mass loss occurs). The θ values were found to be negative because the initial values of T for the mass loss were lower than T_s (Fig. 8). Similar graphs have been used for calculation of activation energy of polymixed alkyl methacrylate ester [23]. The gradient of the straight line ($\ln \ln W_0/W_t$ vs. θ) thus obtained is given by the expression: $\text{Gradient} = E_0 / RT_s^2$, where R is the gas constant and E_0 the energy of activation. The activation energies of degradation calculated from TG curves were based on mass loss and not on the individual products formed during degradation. The data are listed in Table 2. The results show an overall increase in activation energies with an increase of AN concentration in the copolymer.

Mass spectrometry

The comparative TIC curves (temperature vs. abundance) for GMA-AN homo- (I, V) and copolymers (II, III and IV) are shown in Fig. 8. The GMA

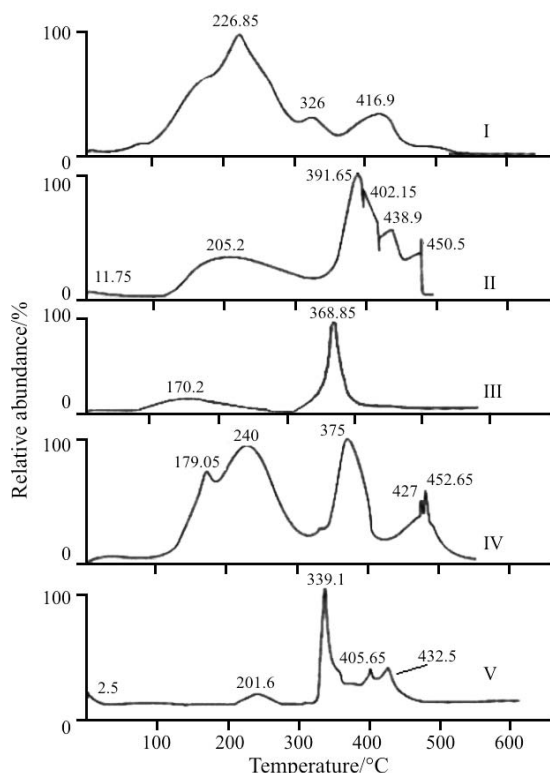
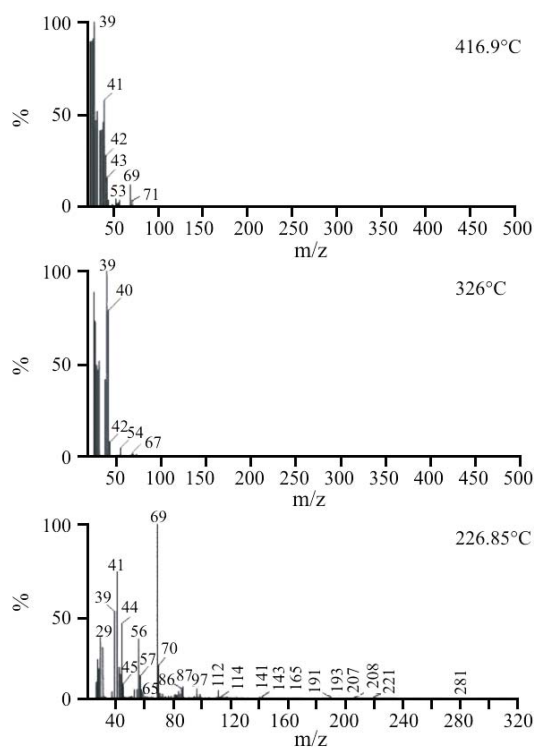
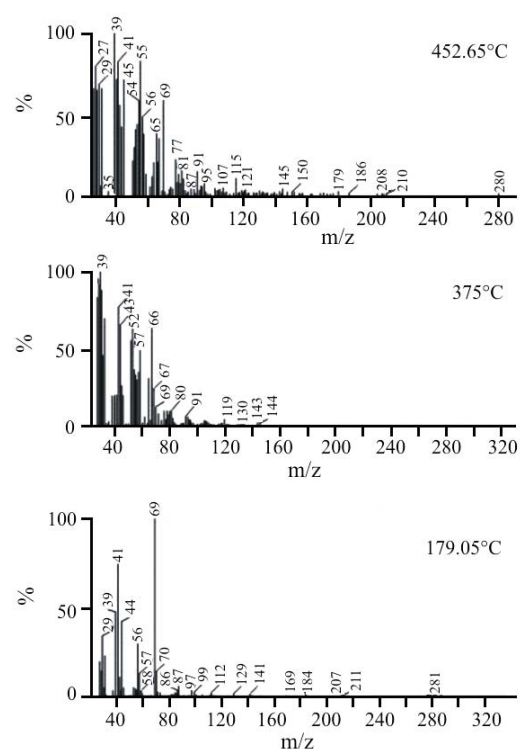
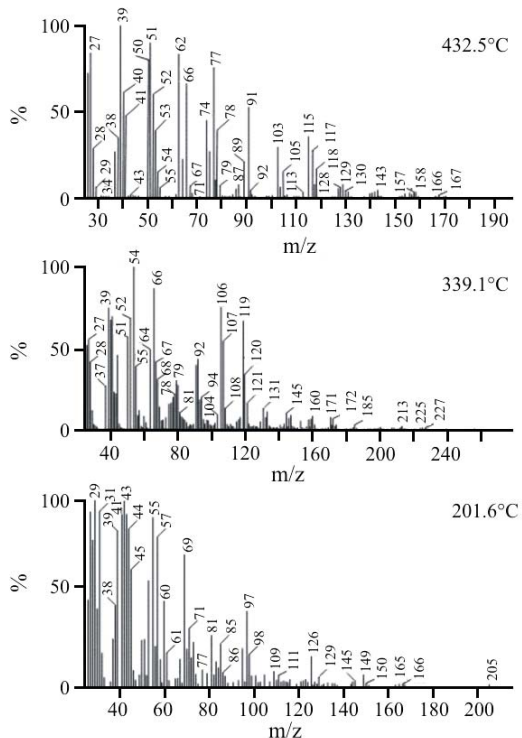


Fig. 8 Comparative TIC curves for GMA–AN homo (I, V) and copolymers (II, III and IV)

and AN homopolymers both showed up one major peak at 226.85 and 339.1°C, respectively, along with several small humps at other positions. In case of GMA–AN copolymers it was observed that the TIC curves shifted to higher retention times with an increase of AN concentration. The fragmentations at particular retention times were analyzed and the mass spectra were identified by using the NIST library. The MS scans at these temperatures for GMA, AN homo- and copolymer IV are shown in Figs 9–11, respectively. The analysis of mass spectra of GMA homopolymer I at 226.85, 326 and 416.9°C showed that these peaks are due to carbon monoxide ($m/z=28$), propene ($m/z=42$), carbon dioxide ($m/z=44$), acrolein ($m/z=56$), allyl alcohol ($m/z=58$) dimethyl ketene ($m/z=70$), glycidol ($m/z=74$), glycidyl methacrylate ($m/z=142$) and glycidylmethyl ether ($m/z=88$). The evolution of the above-mentioned degradation products suggests that the decomposition occurs via two reactions, i.e., *i*) depolymerization to monomer and oligomers and *ii*) decomposition of ester [7]. The presence of acrolein in the degradation products is the convincing evidence for the proposed isomerization of the epoxy group to the carbonyl group. The MS data related to this is summarized in Table 3.

Table 3 The characteristic mass spectral data of homo- and copolymers

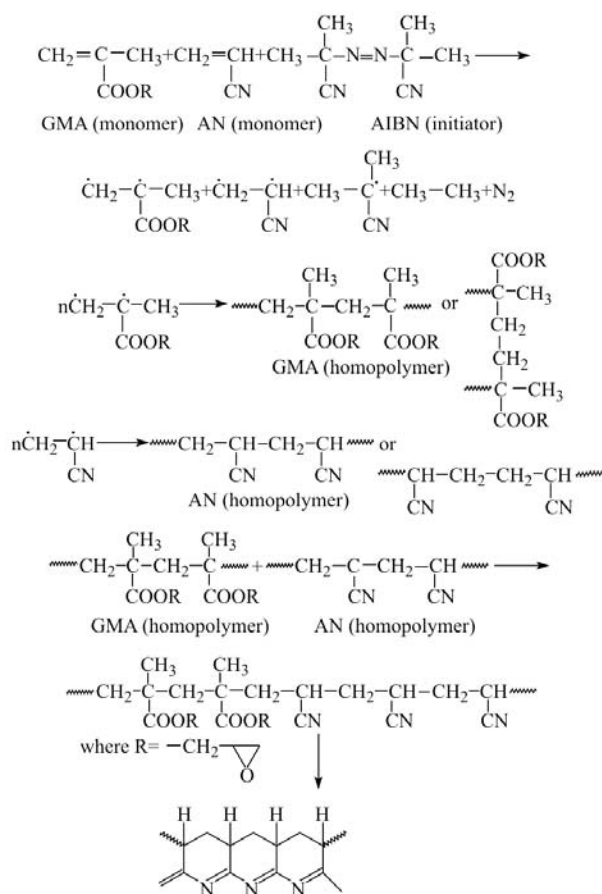
GMA (I) homopolymer		AN (V) homopolymer		GMA–AN (IV) copolymer	
m/z	assignment	m/z	assignment	m/z	assignment
44	CO ₂	26	acetylene	27	CO, HCN
42	propene	27	HCN	28	ethylene
56	acrolein, isobutene	28	ethylene	30	ethane
58	allyl alcohol	30	ethane	41	acetonitrile
70	dimethyl ketene	41	CH ₃ CN, C ₃ H ₃ , NC ₂ H ₃	42	propene
88	glycidylmethyl ether	42	propene	43	CO ₂
142	GMA	44	CO ₂ , propane	44	propane
		54	(C ₂ H ₃ CN)H1,3-butadiene	53	acrylonitrile
		55	ethylnitrile	54	1,3-butadiene
		67	vinylacetonitrile	55	ethylnitrile
				56	isobutene, acrolein
				58	allyl alcohol
				67	vinylacetonitrile
				70	dimethylketene
				74	glycidol
				78	benzene
				91	pyridine
				106	dicyanobutene
				108	adiponitrile
				128	dicyanobenzene, naphthalene
				142	GMA


Fig. 9 MS scans for GMA (I) homopolymer

Fig. 11 MS scans for GMA-AN (IV) copolymer

Fig. 10 MS scan for AN (V) homopolymer

In case of AN homopolymer (V) the peaks at 201.6, 339.1 and 432.5°C were identified as due to $\text{CH}_2\text{CH}_2\text{CN}$ ($m/z=54$), $\text{CH}(\text{CH}_2\text{CHCN})$ ($m/z=66$), $(\text{CH}_2\text{CHCN})_2 \text{H}$ ($m/z=107$) and $\text{CH}(\text{CH}_2\text{CHCN})_2$

($m/z=119$). Furthermore, the peaks due to monomer (up to six monomer units) and oligomer were also observed. The data obtained at 339.1°C suggested random chain cleavage in the polymer backbone. The intensity of the peak due to monomer was found to be higher than that of the dimmer at 339.1°C whereas it was other way round at 201.6°C. A detailed analysis of the thermal degradation products indicates that the polymer backbone consisted of unsaturated bonds at elevated temperatures [24]. Thus it can be concluded that unsaturation increases along the polymer backbone with the increase in temperature. It has also been known that AN homopolymer form conjugated polyene structure at higher temperatures, which are used to make fiber [24, 25]. The relevant mass-spectral data is summarized in Table 3.

The DIP-MS analysis of GMA-AN copolymers (II, III and IV) produced similar spectra as shown in Fig. 11 for the copolymer IV. The data of the copolymer IV is summarized in Table 3. By comparing the TIC curves of I, IV and V it was found that the TIC curve of the copolymer IV shifted to higher temperatures indicating an enhanced thermal stability of this polymer. The MS scan recorded at the maximum of the TIC curve showed resemblance to that of GMA and AN peaks indicating the presence of both the components in the copolymer. However, the relative intensities were different and the abundance of lower mass fragments increased significantly. The base peak at $m/z=41$ was found to be due to C_3H_5 .



Scheme 2 Copolymerization of GMA and AN

The TG/DTG, DTA activation energy and order of reaction data for copolymers under investigation are very consistent in showing an increase of the overall thermal stability with an increase of AN moiety in the copolymer. The presence of AN in copolymer may have disproportionate stabilizing effect on GMA polymer chain due to the fact that the copolymer has fewer unsaturated chain ends than GMA homopolymer because of favored cross-termination step in the copolymerization. The presence of both the monomers in the degradation products of GMA-AN copolymers indicates that the depolymerization does occur. The MS study by DIP allowed detailed mechanisms to be worked out for degradation of the polymer systems under investigation. The most reasonable mechanism would involve random chain scission of the copolymer as the first step. Degradation behavior of GMA-AN copolymers suggests that the mechanism of monomer formation at lower temperature is similar to that of GMA homopolymer possibly due to the presence of some unsaturated chain ends. On the basis of TG/DTG, DTA and MS analyses the degradation behavior of GMA-AN copolymers can be explained by comparing it with the known breakdown pattern of related materials. The information obtained

through the present study suggests a mechanism for copolymerization of GMA and AN as shown in Scheme 2. The copolymer containing more than 25% AN appears to be stable in the temperature range where decomposition of homopolymers occurs and the stability further increases with an increase in AN concentration. The thermal studies (TG and DTA) show that GMA homopolymer degrades thermally and gives volatile products such as carbon dioxide, dimethyl ketone, propane, acrolein, allyl alcohol and glycidol in addition to GMA monomer. These results are in line with those already reported [7]. The degradation products of AN homopolymer are NH₃, HCN, H₂ and N₂ which is also in line with the reported results [15]. All the copolymers of GMA-AN under study showed more or less similar degradation patterns with the presence of some kind of stable product decomposing very slowly at higher temperatures as observed previously [22]. The stable product is formed possibly due to linking of nitrile groups in conjugated carbon-nitrogen sequence. With the increase in AN concentration the polymer itself serves as an initiator by virtue of the presence of tertiary hydrogen atoms and the reaction may move on from chain to chain resulting in cross-linking and thus en-

hancing the stability as shown in Scheme 2. In the MS analysis of AN homopolymer V the decomposition product of AN is mainly HCN, a highly toxic substance, along with sixteen nitrile compounds. At higher temperatures the quantities of HCN, acetonitrile, acrylonitrile and aromatic nitriles increase, whereas those of aliphatic dicyanides decrease. Ammonia was found to be another decomposition product which is relatively less toxic than HCN.

Conclusions

In this work GMA-AN copolymers were prepared, characterized and their thermal stability was studied. The DIP-MS data of the copolymers indicated the presence of mixed dimers which confirmed the formation of copolymers. The results of this study clearly indicate that thermal stability of GMA-AN copolymers depends upon the AN content in the copolymer; it is enhanced with the increase in AN concentration. In the process of preparation of these copolymers a kind of chain reaction has been indicated to take place in the side groups of acrylonitrile which results in their linkage together to form a sequence of fused heterocyclic rings. The copolymers with an increased AN content are thermally more stable due to such linking of nitrile groups in conjugated carbon-nitrogen (unsaturated cyclic imine segments) sequence.

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