

# Synthesis and Characterization of Homopolymers and Copolymers of Various Acrylates and Acrylonitrile

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## SYNOPSIS

Various homopolymers and copolymers of methyl acrylate, ethyl acrylate, butyl acrylate, and acrylonitrile in different feed ratios were synthesized. These were characterized by IR,  $^{13}\text{C}$ -NMR, DSC, DTA, and TGA. Spectroscopic characterization helped in differentiating copolymers of different mol ratios. Thermal analysis revealed different degradation patterns for homopolymers and copolymers. The temperature and energy changes associated with various phase transitions were dependent on the chemical composition of homo- and copolymers, as expected. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

Adsorption of polymers at the solid–liquid interface is very important in coatings, adhesives, laminates, etc.<sup>1,2</sup> To understand the adsorption of polymers at the interface, one needs to have well-characterized polymers. Hence, in continuation of our interest in polymer adsorption,<sup>3</sup> we synthesized various homopolymers and copolymers of acrylonitrile and methyl, ethyl, and butyl acrylates. These were then characterized and their adsorption at the solid/liquid interface was studied. The characterization was done by elemental analysis, IR,  $^{13}\text{C}$ -NMR, DSC, DTA, and TGA as was done earlier.<sup>4</sup> The results are presented and discussed here.

## EXPERIMENTAL

The monomers acrylonitrile, methyl acrylate (Fluka), and ethyl acrylate and butyl acrylate (National Chemicals, Baroda, India) were purified as described in an earlier paper.<sup>5</sup> The solution polymerization technique was used for synthesizing the copolymers and homopolymers. To synthesize copolymers of various compositions, the acrylonitrile–acrylate feed ratios were varied. They were 1 : 1,

1 : 2, and 1 : 3 (w/w), symbolized as ANXA<sub>11</sub>, ANXA<sub>12</sub>, and ANXA<sub>13</sub>, respectively, where XA stands for acrylates, in which X may be methyl (M), ethyl (E), or butyl (B) and AN is for acrylonitrile. The copolymers were synthesized and purified as reported earlier.<sup>5</sup> The corresponding homopolymers were also synthesized and purified under similar experimental conditions. Nitrogen estimation was done by the Dumas' method.

Infrared spectra (IR) were recorded on a Shimadzu IR 408 spectrophotometer. The films were prepared by dissolving the polymers in acetone and pouring the solutions over a pool of mercury. The films were obtained by vacuum evaporation of the solvent. In case of PAN, a transparent pellet of KBr with the polymer sample was prepared for the IR.

$^{13}\text{C}$ -NMR spectra of the polymers were recorded on a Varian XL-300 NMR spectrometer at the Regional Sophisticated Instrumentation Centre (RSIC), IIT, Bombay, India. The spectra of acrylate homopolymers were recorded using  $\text{CDCl}_3$  as the solvent. For PAN and copolymers, DMSO was used. The internal standard used was TMS.

DSC was recorded on a DuPont 2000 thermal analyzer, in a nitrogen atmosphere at a heating rate of  $10^\circ\text{C}/\text{min}$ , at the Department of Colour Chemistry, Leeds University, Leeds, U.K., and on a Mettler TA 4000 system at the Applied Chemistry Department, M.S. University, Baroda, India.

TGA and DTA were recorded on a Shimadzu thermal analyzer DT-30B. The heating rate maintained was  $10^\circ\text{C}/\text{min}$  in presence of air.

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**Table I** Some Experimentally Determined Parameters for the Homopolymers and Copolymers

Polymer	Percentage Nitrogen Content (N %)	Expt Mol Ratio AN : XA	Viscosity Average Mol. Wt. ( $M_v^a \times 10^{-3}$ )	$T_g$ ( $^{\circ}\text{C}$ )
ANMA <sub>11</sub>	11.49	1 : 0.86	15.7	58
ANMA <sub>12</sub>	8.05	1 : 1.40	13.2	53
ANMA <sub>13</sub>	5.65	1 : 2.27	12.6	37
ANEA <sub>11</sub>	12.63	1 : 0.58	22.6	57
ANEA <sub>12</sub>	9.25	1 : 0.98	18.8	48
ANEA <sub>13</sub>	7.41	1 : 1.36	21.0	—
ANBA <sub>11</sub>	11.71	1 : 0.52	15.8	55
ANBA <sub>12</sub>	8.51	1 : 0.82	15.3	—
ANBA <sub>13</sub>	7.95	1 : 0.96	13.8	—
PMA	—	—	20.5	—
PEA	—	—	21.0	—
PBA	—	—	22.1	—
PAN	25.2 <sup>b</sup>	—	52.0	—

<sup>a</sup>  $K$  and  $\alpha$  values were taken from Ref. 29.

<sup>b</sup> Theoretical value 26.4.

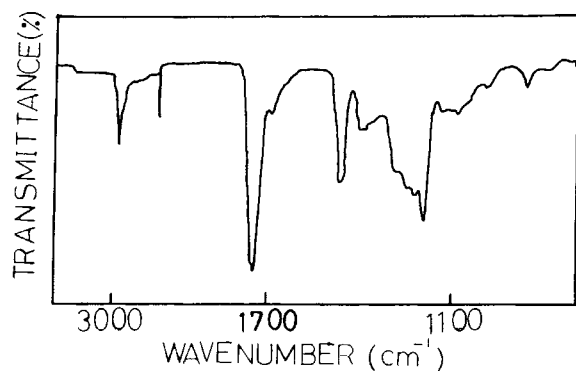
## RESULTS AND DISCUSSION

### (a) Elemental Analysis

From the results obtained by nitrogen estimation, the experimental mol ratios were calculated. The results are compiled in Table I. These results show that the amount of acrylate moiety is less in the copolymer samples than is expected from the feed ratios. Viscosity-average molecular weights are also given in Table I.

### (b) Infrared Spectra

A representative copolymer spectrum is shown in Figure 1. The spectrum shows characteristic bands



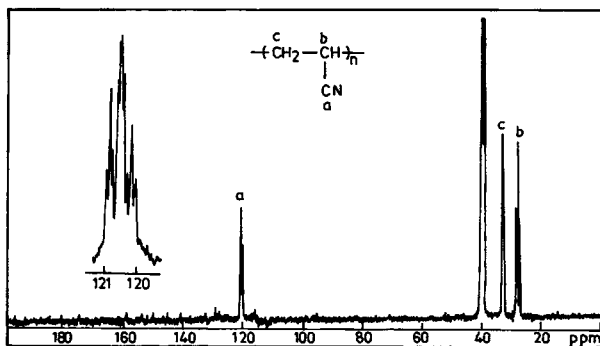
**Figure 1** IR spectrum of ANMA<sub>11</sub>. Peak height ratio (acrylonitrile/acrylate) for ANMA<sub>11</sub> = 0.23; ANMA<sub>12</sub> = 0.17, and ANMA<sub>13</sub> = 0.15. This qualitative trend was also observed for other series of copolymers.

at 2241 and 1741  $\text{cm}^{-1}$  for  $-\text{CN}$  and  $-\text{COOR}$  groups, respectively. A comparison of various spectra (not shown) indicates a qualitative trend when the peak heights corresponding to acrylonitrile and acrylate are compared to the experimental mol ratios of the copolymers as mentioned in Figure 1.

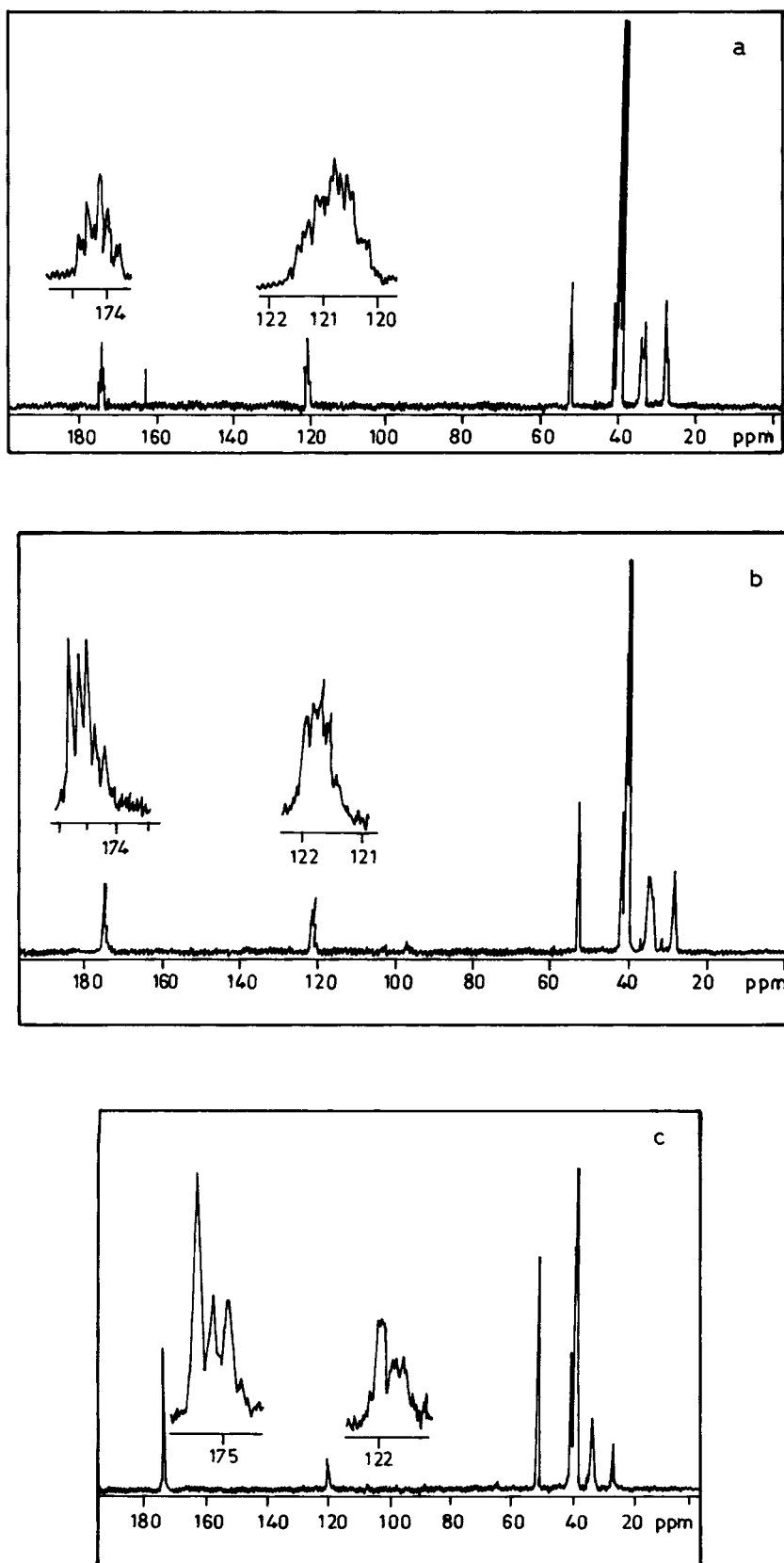
### (c) $^{13}\text{C}$ -NMR Spectra

#### Homopolymers

The  $^{13}\text{C}$ -NMR spectra of PAN, poly(methyl acrylate) (PMA), poly(ethyl acrylate) (PEA), and poly(butyl acrylate) (PBA) were obtained. The assignments of various resonance peaks due to different carbon atoms were made by comparison with the reported spectra of analogous groups from the literature.<sup>6-9</sup> The spectrum of PAN (Fig. 2) matches well with that reported in the literature.<sup>9</sup> The rel-



**Figure 2**  $^{13}\text{C}$ -NMR spectra of PAN.



**Figure 3**  $^{13}\text{C}$ -NMR spectra of (a) ANMA<sub>11</sub>, (b) ANMA<sub>12</sub>, and (c) ANMA<sub>13</sub>.

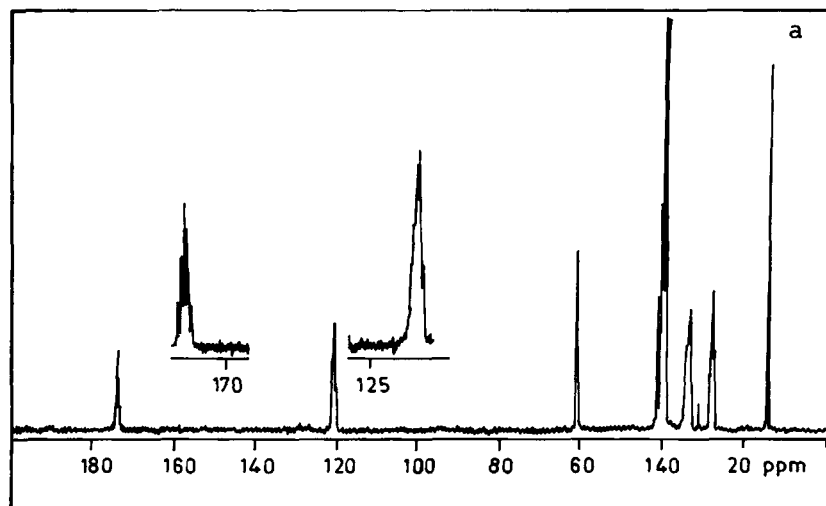


Figure 4  $^{13}\text{C}$ -NMR spectra of ANEA<sub>11</sub>.

ative intensities observed for the triads of nitrile carbon resonance are about 3 : 4 : 2.5 and are consistent with increased stereoregularity, the atactic fraction being dominant. The three lines have been assigned to iso-, hetero-, and syndiotactic triads in order of increasing field from left to right. The spectra of PMA, PEA, and PBA are in agreement with those in the literature<sup>6,9</sup> and, hence, are not discussed here. However, it should be emphasized that in these polyacrylates, unlike carbonyl carbons, peaks due to methylene carbons show splitting because of configurational effects.

### Copolymers

The  $^{13}\text{C}$ -NMR spectra of various copolymers were obtained. A few representative spectra are shown in Figures 3-5. Unlike homopolymers, the peaks due to carbonyl carbons of these copolymers show splitting. Various splitting patterns were observed in resonance of backbone methylene, nitrile, and quaternary carbons. This splitting is influenced by the composition, configurational, and sequence distribution effects. Quantitative determination could not be done due to unavailability of a standard. It can

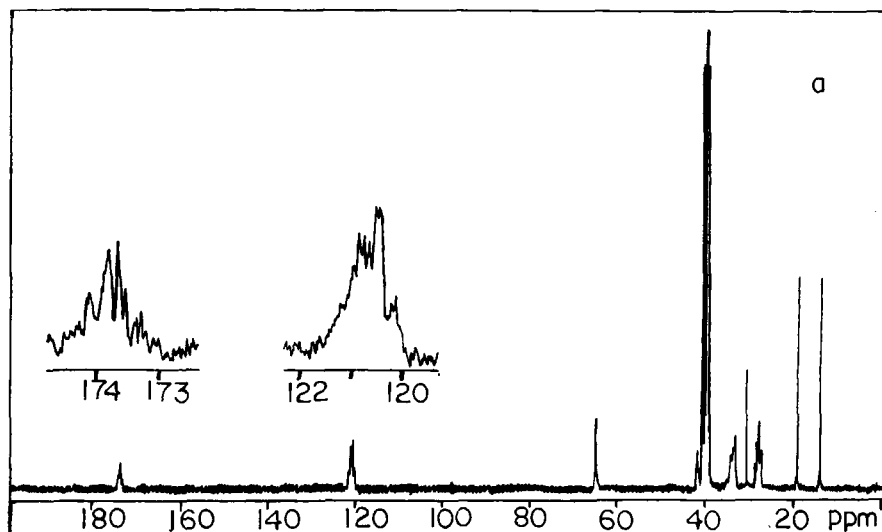
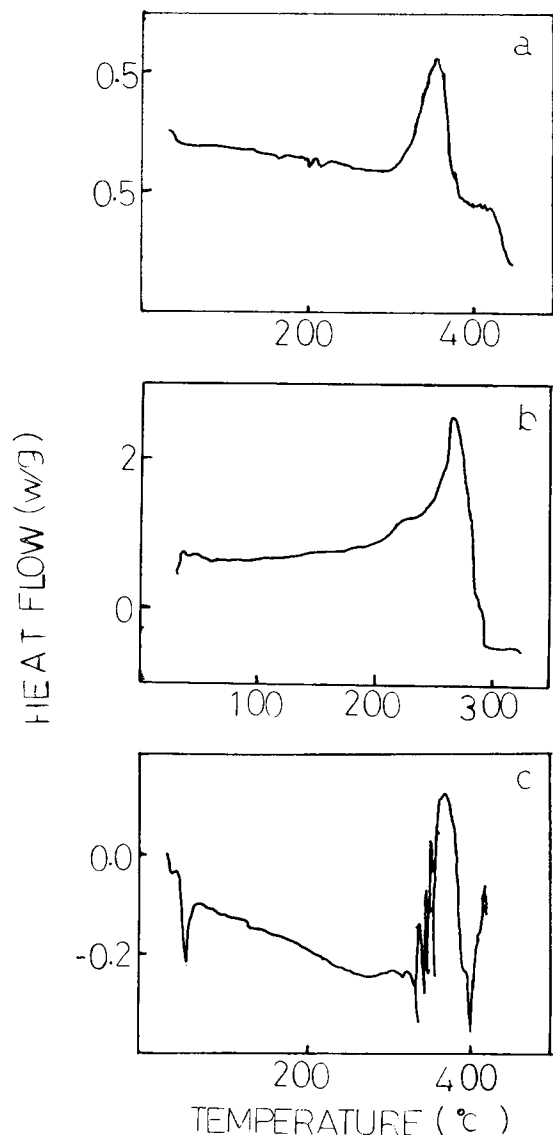


Figure 5  $^{13}\text{C}$ -NMR spectra of ANBA<sub>11</sub>.



**Figure 6** DSC curves of (a) ANMA<sub>11</sub>, (b) ANEA<sub>11</sub>, and (c) ANBA<sub>11</sub>.

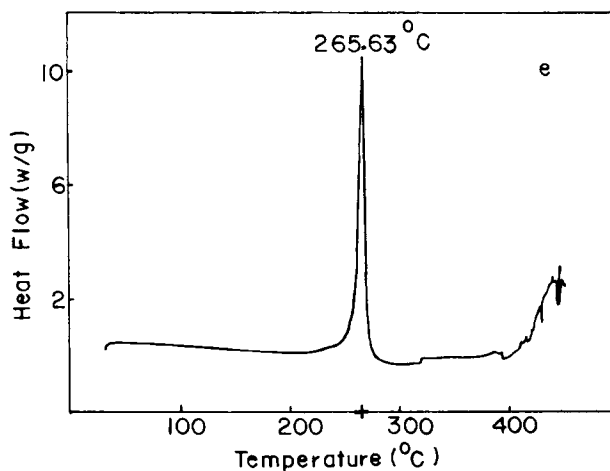
be observed [Fig. 3(a)–(c)] that with increasing content of MA (acrylate fraction) in the copolymers there was greater tendency toward ordered arrangement, with the isotactic fraction predominant. The intensities of the carbonyl resonance peaks also increase. This diminishes the intensity and resolution of nitrile carbons. However, the tendency for a more ordered arrangement is relatively less in ANBA copolymers with increasing content of BA (though spectra are not shown). Similar phenomena were observed in the copolymers of glycidyl methacrylate–alkyl acrylate, where the resolution of the carbonyl carbon diminished with increasing alkyl acrylate content.<sup>6</sup>

Thus, these results indicate that with the incorporation of lower alkyl acrylates, as in ANMA and ANEA, the tendency for ordered arrangement is relatively more where the isotactic fractions predominate. The tendency is less when higher alkyl acrylates are used, as in ANBA copolymers.

#### (d) Thermal Analyses

##### *Differential Scanning Calorimetry (DSC)*

Representative DSC thermograms of copolymers of the acrylate–acrylonitrile series (1 : 1) are shown in Figure 6. The heating rate was maintained at 10°C/min. The observed glass transition values are given in Table I. The  $T_g$  values were found to decrease with increasing acrylate content. A similar effect was observed for higher homologs of acrylates. The  $T_g$  values of PAN and polyacrylates have been reported by many workers.<sup>10–13</sup> The values of copolymers were found to be in between those of the corresponding homopolymers. The DSC thermograms of PAN in N<sub>2</sub> atmosphere (Fig. 7) showed a sharp exothermic peak, centered at 265.6°C, followed by decomposition at higher temperatures. This was also observed earlier.<sup>14,15</sup> The exothermic peaks were prominent only in the ANXA<sub>11</sub> copolymer samples (Fig. 6). At higher acrylate concentration, the exotherms were deemed to have been masked by the endothermic degradation process, though that is somewhat surprising. However, similar observations have been reported earlier<sup>14,16</sup> for the copolymers of acrylonitrile and methyl methacrylate, where the increasing concentration of methyl methacrylate masked the exothermic reaction. This could be attributed to the effect of the bulkier comonomer acrylates, dimin-



**Figure 7** DSC curve of PAN.

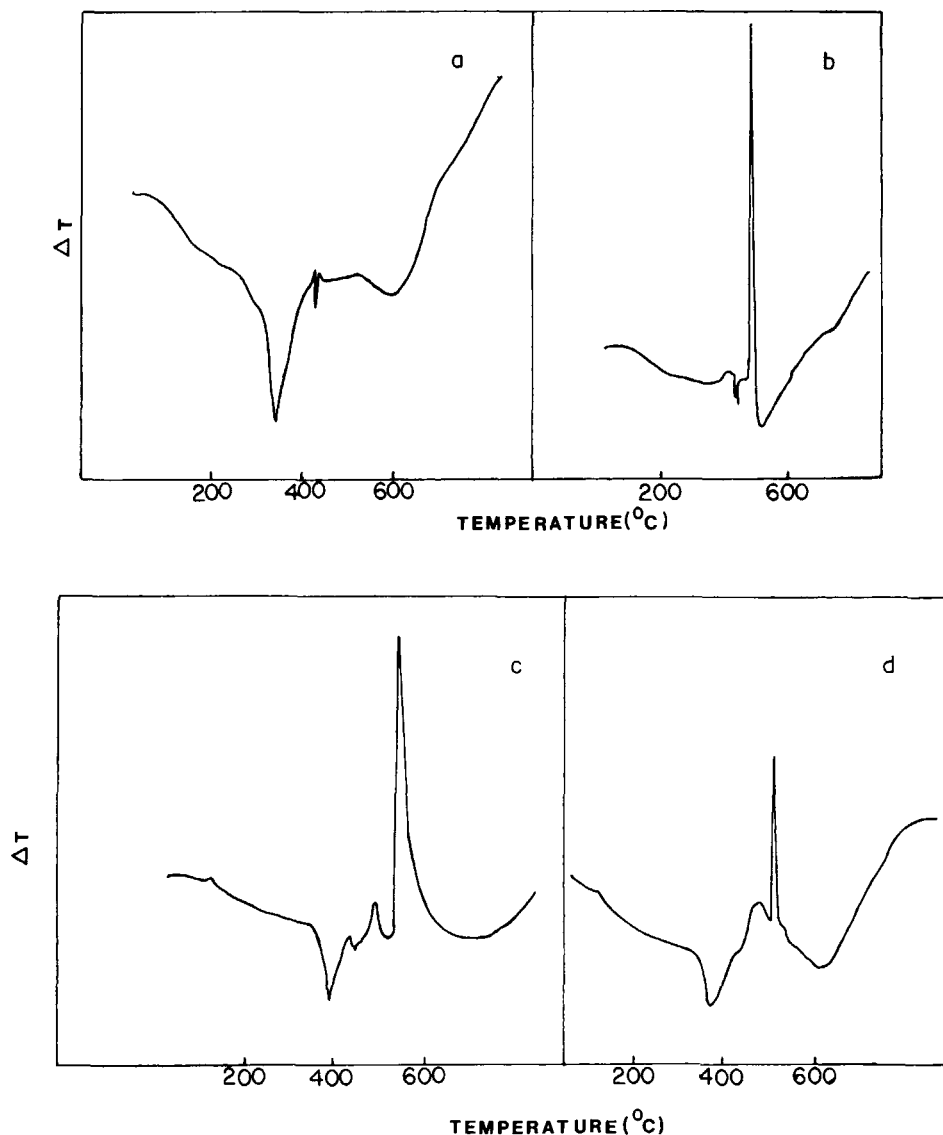


Figure 8 DTA thermograms of (a) PAN, (b) PBA, (c) ANBA<sub>II</sub>, and (d) ANMA<sub>II</sub>.

ishing the crystallization considerably by restricting the chain length that allows cocrystallization.<sup>16</sup> The decomposition endotherm sets in at a lower temperature with higher alkyl acrylate concentration. Moreover, as the molecular weights of the copolymers were not high (Table I), the large number of chain ends do not permit close packing, conferring more flexibility by occupying a large free volume.

#### Differential Thermal Analysis (DTA)

Representative DTA thermograms are shown in Figure 8. Pronounced heat changes were observed in the degradation reactions of the polymers. The

exotherm started at a higher temperature (above 400°C) in all systems, indicating that the oxidative resistance of the polymers was high. This was also earlier found to be true for PAN.<sup>17</sup> As the thermal characteristics depend on the conditions under which the polymers were tested, care was taken to maintain identical experimental conditions for all the samples. The thermograms obtained show broad shoulders. This was because the runs were performed in air. A prominent exothermic peak (very sharp) at the higher temperature region was observed for all the copolymers and homopolymers of acrylates. This was due to the cross-linking reactions taking place in the acrylate chains at higher temperatures.

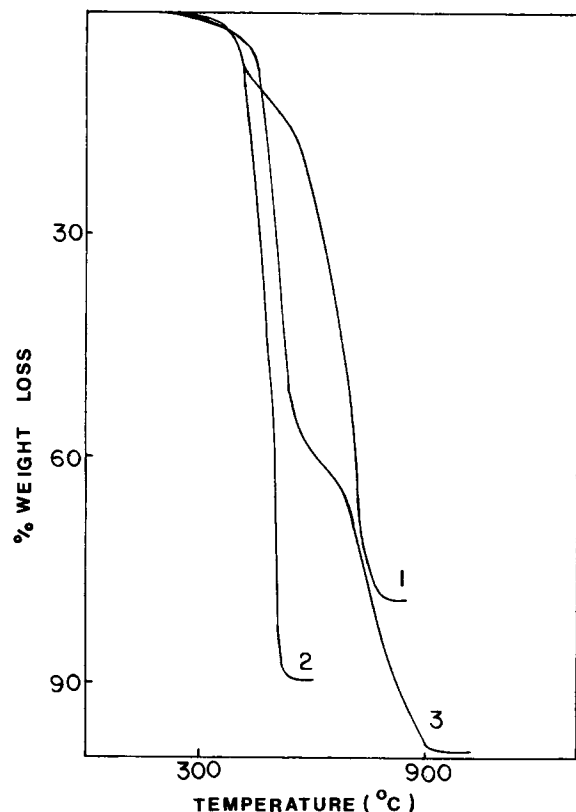


Figure 9 TGA curves of (1) PAN, (2) PBA, and (3) ANEA<sub>11</sub>.

### Thermogravimetric Analysis (TGA)

Representative thermograms for the homopolymers and copolymers are shown in Figures 9 and 10. A different degradation mechanism for the copolymers was evident from the two-stage thermograms obtained. For homopolymers, the thermograms show

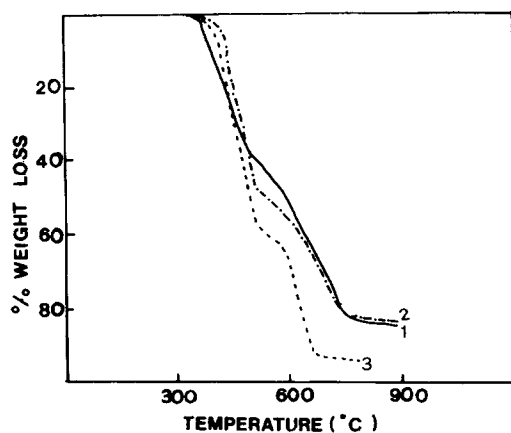


Figure 10 TGA curves of (a) ANBA<sub>11</sub>, (b) ANBA<sub>12</sub>, and (c) ANBA<sub>13</sub>.

Table II Activation Energy of Decomposition for Homopolymers and Copolymers by Thermogravimetric Analysis

Polymer	Decomposition Temp (°C) Range	Weight Loss (%)	$E_a$ (kJ mol <sup>-1</sup> )
ANMA <sub>11</sub>	360-500	51	82.8
	510-800	97	29.7
ANMA <sub>12</sub>	360-500	62	102.0
	540-750	98	41.8
ANMA <sub>13</sub>	420-620	70	150.5
	700-850	94	41.4
ANEA <sub>11</sub>	440-570	58	120.4
	680-920	99	54.8
ANEA <sub>12</sub>	375-530	64	132.1
	560-810	93	28.8
ANEA <sub>13</sub>	450-580	54	160.1
	630-815	83	38.9
ANBA <sub>11</sub>	380-520	44	120.8
	570-760	82	53.9
ANBA <sub>12</sub>	410-520	51	143.8
	610-770	82	35.1
ANBA <sub>13</sub>	390-510	60	130.4
	560-665	93	47.2
PMA	320-500	89	92.0
PEA	380-510	87	136.3
PBA	360-530	90	141.3
PAN	550-790	79	71.5

a single-step degradation pattern. In this study, the Broido method<sup>18</sup> was used to calculate the activation energy of degradation for all systems. The linearity of the Broido plots was good with correlation coefficients greater than .99. The slopes of those lines were related to activation energy of degradation. The temperature range used is indicated in Table II.

The calculated activation energies of decomposition ( $E_a$ ) are compiled in Table II. It can be seen that there is no clear correlation between  $E_A$  and the size of the acrylate moiety as well as the concentration of the acrylates in the copolymers. The range in activation energy indicates that major decomposition occurs in the first step.

DiEdwardo<sup>19</sup> reported four main categories of degradation reaction, namely, chain scission, cross-linking, hydrogenation, and cyclization in PAN and the main degradation products have been identified

as ammonia and hydrogen cyanide.<sup>20</sup> The PAN thermogram shows extensive weight loss (Fig. 9). This indicates that chain scission reactions are also evident, though the predominant reaction is formation of fused heterocyclic rings.<sup>20</sup> The  $E_a$  value of PAN in the presence of air is much less (71.1 kJ mol<sup>-1</sup>) than the reported value of 129.6 kJ mol<sup>-1</sup> in N<sub>2</sub>.<sup>21</sup> This was calculated for the 550–790°C decomposition range. The lower temperature range was neglected. In the case of PMA, a similar decrease was also observed, the reported value being 154.7 kJ mol<sup>-1</sup> in N<sub>2</sub>.<sup>22</sup> This is also because the decomposition reactions were faster in the presence of air than in nitrogen. The sample characteristics also contribute to this effect. Moreover, the Broido method yielded lower values<sup>23</sup> when compared to the methods of Flynn and Wall<sup>24</sup> and Anderson and Freeman.<sup>25</sup>

A recent study<sup>26</sup> on the thermal characteristics of the polyacrylates showed that PMA exhibited lower thermal stability than did PEA, whereas other polymers beginning from PBA exhibited higher and approximately the same thermal stability at a heating rate of 2°C/min. The same polyacrylates considered in the present study also followed a similar pattern (Table II). It was suggested that, at higher heating rates, cross-links cannot be formed as the temperature range in which cross-linking was possible is limited. In other words, though the cross-linking process at the initial stage of thermal degradation in PMA was thermodynamically favorable, it did not occur at a high heating rate due to kinetic reasons. Hence, the observed  $E_a$  values were lower.<sup>26</sup> The decomposition process was sharp, indicating that the process was essentially a chain reaction.<sup>27</sup>

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## REFERENCES

1. R. P. Hopkins, E. W. Lewandowski, and T. E. Purcell, *J. Paint Technol.*, **44**, 85 (1972).
2. D. W. Zunker, *J. Coat. Technol.*, **48**, 37 (1976).
3. V. Vangani, R. Joseph, S. Devi, and A. K. Rakshit, *Coll. Polym. Sci.*, **269**, 242 (1991).
4. V. Vangani and A. K. Rakshit, *J. Appl. Polym. Sci.*, **45**, 1165 (1992).
5. R. Joseph, S. Devi, and A. K. Rakshit, *Polym. Int.*, **26**, 89 (1991).
6. P. K. Dhal, G. N. Babu, and R. K. Nanda, *Macromolecules*, **17**, 1131 (1984).
7. J. Schaefer, *Macromolecules*, **4**, 105 (1971).
8. L. P. Johnson, F. Heatley, and F. A. Bovey, *Macromolecules*, **3**, 175 (1970).
9. K. Matsuzaki, T. Kanai, T. Kawamura, S. Matsumoto, and T. Uryu, *J. Polym. Sci., Polym. Chem. Ed.*, **11**, 961 (1973).
10. F. P. Reading, J. A. Faucher, and R. D. Whitman, *J. Polym. Sci.*, **55**, 483 (1962).
11. J. A. Shelter, *J. Polym. Sci.*, **B1**, 209 (1963).
12. J. J. Keavney and E. G. Eberlin, *J. Appl. Polym. Sci.*, **3**, 47 (1960).
13. R. H. Wiley and G. M. Brauer, *J. Polym. Sci.*, **3**, 455 (1948).
14. J. N. Hay, *J. Polym. Sci.*, **6**, 2127 (1968).
15. J. Shurz, H. Bayzer, and W. Stubehen, *Makromol. Chem.*, **23**, 152 (1957).
16. L. S. Bark and S. Allen, *Analysis of Polymer Systems*, Applied Science, London, 1982.
17. N. Grassie and R. McGuchan, *Eur. Polym. J.*, **6**, 1277 (1970).
18. A. Broido, *J. Polym. Sci.*, **7**, 1762 (1969).
19. A. H. DiEdwardo, *Am. Chem. Soc. Div. Org. Coat. Plast. Chem. Prepr.*, **38**, 692 (1978).
20. J. P. Kennedy and C. M. Fontana, *J. Polym. Sci.*, **39**, 501 (1959).
21. S. Strauss and S. L. Madorsky, *J. Res. Nat. Bur. Std.*, **61**, 77 (1958).
22. S. Strauss and S. L. Madorsky, *J. Res. Nat. Bur. Std.*, **50**, 165 (1953).
23. R. Patel, K. C. Patel, B. N. Mankad, and R. D. Patel, *Proc. Ind. Acad. Sci. (Chem. Sci.)*, **89**, 561 (1980).
24. J. H. Flynn and R. A. Wall, *J. Res. Nat. Bur. Stand.*, **70**, 487 (1966).
25. D. A. Anderson and E. S. Freeman, *J. Polym. Sci.*, **54**, 253 (1961).
26. Yu. N. Sazanov, L. A. Shibaev, N. G. Stepanov, and N. A. Sokolovskaya, *Int. J. Polym. Mater.*, **14**, 85 (1990).
27. E. V. Thompson, *J. Polym. Sci. B*, **4**, 361 (1966).

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