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Charge Transfer Copolymerisation and Sequence-Length Distribution of Methylmethacrylate with Acrylonitrile and Methacrylonitrile

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CHARGE TRANSFER COPOLYMERISATION AND SEQUENCE-LENGTH
DISTRIBUTION OF METHYLMETHACRYLATE WITH ACRYLONITRILE
AND METHACRYLONITRILE

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ABSTRACT

Copolymers of methacrylate (MMA) with acrylonitrile (AN) and methacrylonitrile (MAN) were synthesized by a charge-transfer mechanism using a mixture of n-Butylamine (nBA) and carbon tetrachloride (CCl_4) as the initiator in dimethyl sulfoxide at 60°C and 80°C respectively. The percentage composition of the copolymer was established by elemental analysis. The reactivity ratios of AN-MMA and MAN-MMA copolymers were determined by both Fineman-Ross (F-R) and Kelen-Tudos (K-T) methods. For AN-MMA system, the values are $r_1 = 0.35 \pm 0.03$ (AN), $r_2 = 1.49 \pm 0.02$ (MMA) by F-R method while $r_1 = 0.34 \pm 0.04$ and $r_2 = 1.49 \pm 0.02$ by K-T method. Similarly, for MAN-MMA system, $r_1 = 1.10 \pm 0.01$ (MAN) and $r_2 = 0.25 \pm 0.05$ (MMA) by F-R method and $r_1 = 1.10 \pm 0.02$ and $r_2 = 0.27 \pm 0.03$ by K-T method. These values indicate that the system follows random distribution of the monomeric units. The copolymers were characterized by IR, $^1\text{H-NMR}$, $^{13}\text{C-NMR}$ spectroscopy and viscosity. The mean sequence lengths (\bar{n}) and probabilities (P) in the formation of various structural units and solubility parameter (δ) values were evaluated for these copolymers. The thermal behaviour of the AN-MMA copolymers was studied by thermogravimetry (TG) in air. The thermal stability increases with increasing AN content in the copolymer.

INTRODUCTION

It has been reported by several workers that charge-transfer complexes can initiate the polymerization of many vinyl monomers like methylmethacrylate¹, methylacrylate² and vinylpyridine³ etc. Only a few reports have appeared on charge-transfer (C-T) initiated copolymerization of MMA and AN⁴ in DMSO using Ferrocene and carbon tetrachloride (CCl₄), MMA and acrylic acid (AA) in DMSO using trimethyl amine and CCl₄ as C-T initiators, and charge transfer copolymerization of 2-vinylpyridine⁶ with methylmethacrylate and ethylmethacrylate and EMA, IPMA⁷, with acrylonitrile and methacrylonitrile were reported^{7,8}. However, no work has been done on the copolymerization of MMA with AN and MAN using nBA-CCl₄ as a C-T initiator. We report in this paper the reactivity ratios, sequence length distribution, viscosity, solubility parameter and thermal properties of MMA with AN and MAN copolymers prepared by C-T initiation.

EXPERIMENTAL

MMA, AN and MAN [Fluka] was freed from inhibitor by washing with 5% sodium hydroxide and water and dried over calcium chloride and distilled twice under reduced pressure. DMSO, nBA¹⁰ and CCl₄¹¹ all are Analar grade, were purified as stated in the literature.

Polymerizations were carried out in vacuum with nBA [0.7588 mol.l⁻¹] and CCl₄ [1.55 mol.l⁻¹] at varying feed ratios of [AN] and [MMA], [MAN] and [MMA] in DMSO at 60°C and 80°C respectively. The total monomer concentration was maintained at 1.50 mol.l⁻¹, while the ratio [AN]/[MMA] and [MAN]/[MMA] were varied. The experiments were performed in a three-limbed vessels. The first limb was filled with a mixture of two monomers (ie., AN-MMA and/or MAN-MMA) varying ratios in DMSO and the second with nBA and CCl₄ in DMSO. The vessel was completely evacuated, and then the contents of the two limbs were thoroughly mixed and transferred to the third limb. The sealed vessel was then immediately introduced into the thermostat at desired temperature. When the reaction time attains less than 10% conversion, the reactions were stopped by adding excess volume of distilled water as non-solvent and the copolymers were precipitated. Then the residue was filtered, washed and dried. Reprecipitation was done from acetone solution.

The copolymers were characterized by IR, $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectroscopy, viscosity and thermogravimetric analysis. The IR absorptions were obtained in KBr disk using a Perkin-Elmer model spectrophotometer ($4000-400\text{ cm}^{-1}$).

$^1\text{H-NMR}$ spectras were recorded from CDCl_3 solution using a 60 MHz varian spectrometer.

$^{13}\text{C-NMR}$ spectra of the copolymer (AN-MMA) in CDCl_3 solution at ambient temperature was obtained using a JEOL-FX-60 MHz spectrophotometer.

Thermogravimetric analysis (TGA) was carried out using a Dupont 9900 thermal analyzer in air at a heating rate of $10^\circ\text{C}/\text{min}$.

The AN and MAN content of the copolymer samples were determined by Carlo-Erba 1106 elemental analyzer to obtain data on the copolymer compositions. The copolymer compositions were ascertained from the AN and MAN content in the copolymers. The r -values for the AN-MMA and MAN-MMA systems in DMSO were estimated by Fineman-Ross¹² (F-R) equation (1) and Kelen-Tudos¹³ (K-T) equation (2).

$$F(f-1)/f = r_1 F^2/f - r_2 \quad (1)$$

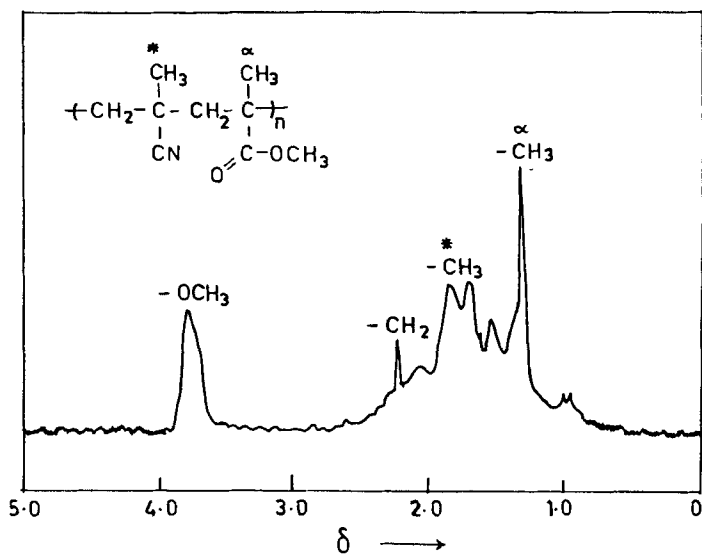
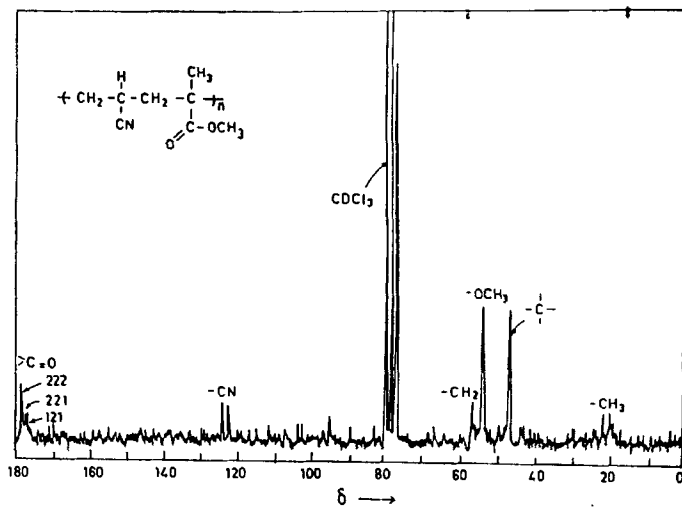
$$\eta = (r_1 + r_2/\alpha)\xi - r_2/\alpha \quad (2)$$

where terms and symbols have usual significance¹⁴.

The mean sequence lengths (\bar{n}_1 and \bar{n}_2) and distribution probabilities (P_1) were calculated using equations suggested by Ekpenyong¹⁵.

Intrinsic Viscosity Determination: For determination of solubility parameter, the viscosities were measured using a suspended level dilution viscometer of Ubbelohde type. The intrinsic viscosity $[\eta]$ was evaluated at a single concentration (1%) from the flow time of pure solvent (t_0) and the solution (t) by the relationship^{16,17,18}.

$$[\eta] = [2 \{t/t_0 - \ln(t/t_0) - 1\}]^{1/2} / C \quad (3)$$

Fig. 1 ¹H-NMR OF MAN-MMA COPOLYMERFig. 2 ¹³C-NMR OF AN-MMA COPOLYMER

RESULTS AND DISCUSSION

The IR spectrum of the copolymers shows a sharp peak at 2220 cm^{-1} indicating the presence of the nitrile group and hence confirms the incorporation of AN or MAN into the polymer chain. The peak at 1720 cm^{-1} indicating the presence of ester carbonyl group from MMA.

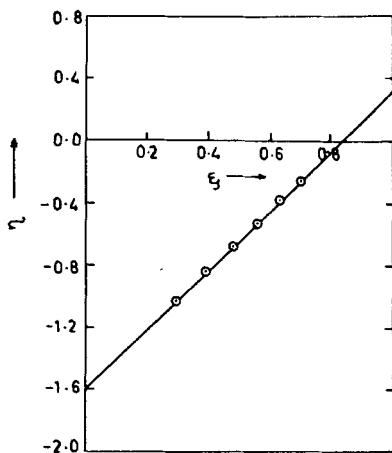
Characterization of the copolymers was done by $^1\text{H-NMR}$ spectroscopy. The $^1\text{H-NMR}$ spectral assignments are given in figure-1 and $^{13}\text{C-NMR}$ spectra comparing the signals arising from carbonyl carbon of MMA units at (176-178 ppm) and the nitrile carbons of AN units at (120-124 ppm) confirmed the incorporation of MMA and AN in the copolymer. The other signal peaks are indicated in the figure-2. Similarly, for MAN and MMA system $^{13}\text{C-NMR}$ confirms the formation of copolymer.

Assignments of various $^{13}\text{C-NMR}$ signals are evident that the change in monomer concentration in the copolymer does not affect the chemical shift of major resonance frequencies of carbonyl group. The intensities of various other resonance peaks change with the monomer concentration. We have chosen $>\text{C}=\text{O}$ frequency for sequence determination. Since carbonyl group is present in only MMA monomer unit in the copolymer, the $>\text{C}=\text{O}$ frequency is sensitive in only those triads in which the central place is occupied by MMA unit. Carbonyl resonance shows three major peaks having chemical shifts of $\delta 178.2$, $\delta 177.1$, and $\delta 176.4$ ppm are due to 222, 221/122 and 121 triads respectively, where 1 represents [AN] and 2 represents [MMA]. The addition of AN (1) to MMA (2) in the copolymer renders the carbonyl carbon to shift upfield. The chemical shift of 121 triad is observed at 176.4 ppm. The polarity of the environment also increases with increase in MMA concentration and hence 222 triad appears most downfield.

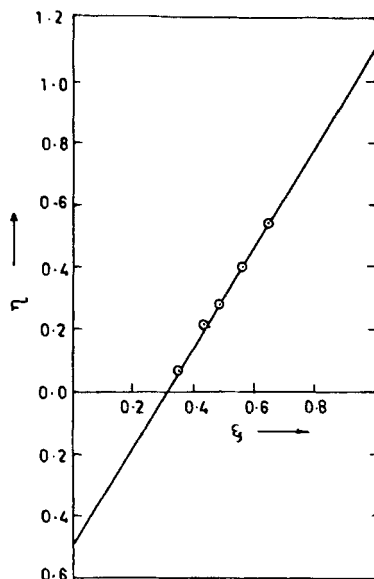
The composition of the copolymers formed with varying feed composition was determined by nitrogen estimation (Table-1). These data were used for the evaluation of reactivity ratios of AN-MMA and MAN-MMA systems by F-R and K-T methods. The values of r_1 and r_2 so obtained were 0.35 ± 0.03 and 1.49 ± 0.02 by F-R; 0.34 ± 0.04 & 1.49 ± 0.02 by K-T methods, and the corresponding plot was shown in Fig-3 for AN and MMA copolymer

Table-1: Monomer Feeds and Copolymer Composition for AN-MMA and MAN-MMA Copolymer Systems in Mole Fractions.

S.No.	<u>AN - MMA System</u>		<u>MAN-MMA System</u>							
	<u>Feed Composition</u>	<u>%</u>	<u>Copolymer Composition</u>	<u>%</u>						
	$AN[m_1]$	$MMA[m_2]$	$AN(m_1)$	$MMA(m_2)$						
			$MAN[m_1]$	$MMA[m_2]$						
			<u>Feed Composition</u>	<u>Copolymer Composition</u>						
				$MAN(m_1)$						
				$MMA(m_2)$						
1	0.200	0.800	2.01	0.135	0.865	0.599	0.401	12.53	0.692	0.308
2	0.267	0.733	2.78	0.182	0.818	0.534	0.466	11.45	0.645	0.355
3	0.333	0.667	3.56	0.230	0.770	0.467	0.533	10.55	0.600	0.400
4	0.400	0.600	4.40	0.274	0.726	0.433	0.567	10.06	0.582	0.418
5	0.467	0.533	5.35	0.324	0.676	0.366	0.634	8.89	0.526	0.474
6	0.534	0.466	6.40	0.377	0.623	--	--	--	--	--

Fig. 3 PLOT OF r_1 Vs ξ

K-T plot of AN-MMA
Copolymer.

Fig. 4 PLOT OF r_1 Vs ξ

K-T plot of MAN-MMA
Copolymer.

system. These values are in good agreement with the literature data using Ferrocene and CCl_4 as C-T initiator and using benzoyl peroxide as initiator. U. Johnsen et.al.²⁰ have reported the r -values, $r_1(\text{AN}) = 0.46 \pm 0.08$, $r_2(\text{MMA}) = 1.14 \pm 0.02$ using free radical initiator in DMSO, which are in reasonable agreement with our values. The product of r_1 and r_2 is less than one, which shows deviation from the ideal copolymerisation. The value of $r_2 = 1.49 \pm 0.02$ shows that addition of MMA in the copolymer is preferred.

For MAN and MMA system the values of r_1 and r_2 are 1.10 ± 0.01 and 0.25 ± 0.05 by F-R and 1.10 ± 0.02 and 0.27 ± 0.03 by K-T (Fig.4) methods. The product of r_1 and r_2 remains less than unity indicating that the copolymers are weakly ordered, with a predominantly random distribution of the monomeric units in the polymer chain.

TABLE-2
Mean Sequence-Length Distribution of AN-MMA
Copolymerization

Sl. No.	$[M_1]$ Mol%	\bar{n}_1	\bar{n}_2	\bar{n}_1/\bar{n}_2	$\bar{n}_1:\bar{n}_2$	Distribution*
1	20.0	1.085	6.96	0.156	1:7	122222221
2	26.7	1.124	5.09	0.221	1:5	--
3	33.3	1.170	3.98	0.294	1:4	--
4	40.0	1.226	3.23	0.379	1:3	12221
5	46.7	1.297	2.70	0.480	1:3	--
6	53.4	1.388	2.30	0.603	1:2	--

* Only a few cases are illustrated.

TABLE-3
Mean Sequence-Length Distribution of MAN-MMA
Copolymerization

Sl. No.	$[M_1]$ Mol%	\bar{n}_1	\bar{n}_2	\bar{n}_1/\bar{n}_2	$\bar{n}_1:\bar{n}_2$	Distribution*
1	59.9	2.65	1.18	2.247	3:1	21112
2	53.4	2.26	1.24	1.828	2:1	2112
3	46.7	1.96	1.31	1.498	2:1	--
4	43.3	1.84	1.35	1.363	2:1	--
5	36.6	1.63	1.47	1.109	2:1	--

* Only a few cases are illustrated.

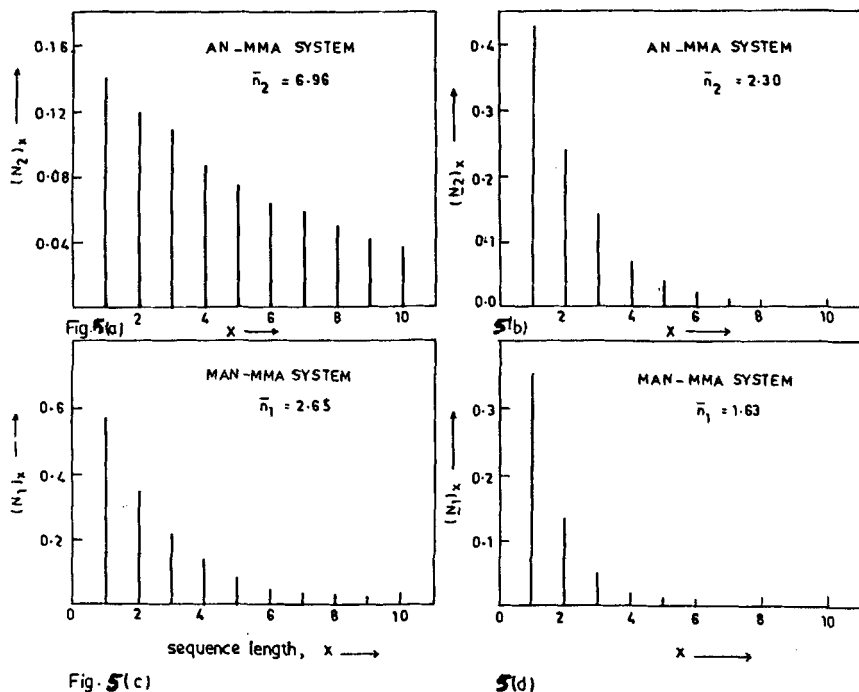


Fig-5a & b Sequence length distribution of AN-MMA copolymer. Fig-5c & d Sequence length distribution of MAN-MMA copolymer.

Sequence-Length Distribution: Table 2 and 3 shows that the mean sequence lengths \bar{n}_1 and \bar{n}_2 for the formation of M_1 and M_2 units were calculated using equations suggested by Ekpenyong¹⁵. In table-2 significant differences exist between the \bar{n}_1 and \bar{n}_2 values for each monomer mixture in the AN-MMA copolymerization. Thus, for example, at 20% M_1 (80% M_2) in the monomer mixture each copolymer segment with M_2 units was approximately seven times longer than its adjoining segment with M_1 units. The sequence may be expressed as $\sim 122222221 \sim$. Similarly, for MAN-MMA copolymerization, in table-3 not much difference exist between the \bar{n}_1 and \bar{n}_2 values for each monomer mixture. In AN-MMA system \bar{n}_2 increases approximately from 2 to 7, when $[AN]/[MMA]$ is changed from 1.143 to 0.25. The number of MMA units in copolymer increases with increase in $[MMA]$ in the feed, but this is not so for AN. Thus AN acts as retarder in

the copolymerization. The ratios of the mean sequence lengths \bar{n}_1/\bar{n}_2 which theoretically correspond to the ratio dm_1/dm_2 ; dm_1 and dm_2 are the corresponding compositions of M_1 and M_2 in the copolymer for each monomer mixture defined.

The microstructure of a copolymer is defined by the distributions of the various lengths of the M_1 and M_2 sequences, that is, the sequence-length distributions. The probabilities or mole fractions $(N_1)_x$ and $(N_2)_x$ of forming M_1 and M_2 sequences of length 'x' are given by

$$(N_1)_x = P_{11}^{x-1} P_{12} \quad (4)$$

$$(N_2)_x = P_{22}^{x-1} P_{21} \quad (5)$$

where terms $(P_{11}, P_{12}, P_{22}, P_{21})$ have usual significance²¹. Equation (4) and (5) allow one to calculate the mole fractions of different lengths of M_1 and M_2 sequences. Figure-5a and 5b shows the sequence-length distribution for AN-MMA copolymerization with $r_1 = 0.34$, $r_2 = 1.49$, for 0.3/1.2 (A) and 0.8/0.7 (B) feed compositions respectively and figure-5c and 5d shows the sequence length distribution for MAN-MMA copolymerization with $r_1 = 1.10$, $r_2 = 0.27$ for 0.90/0.60 (C) and 0.55/0.95 (D) feed compositions respectively.

From the figure-5a the sequence is M_2 at 14.4% with 12.3%, 10.5%, 9%, 7.7%, 6.6%, 5.7%, 4.8%, 4.1% and 3.5% respectively of diad, triad, tetrad, pentad, hexad heptad, octad, nonad and decad and smaller amounts of longer M_2 sequences for A composition. For other feed composition (B) (Fig-5b) the most plentiful sequence is M_2 at 43.4% with 24.6%, 13.9%, 7.8% and 4.4% respectively of diad, triad, tetrad and pentad, M_2 sequences. There are smaller amounts of longer sequences 2.5% and 1.4% of hexad and heptad M_2 sequences.

In the MAN-MMA copolymer system, from the figures-5c and 5d, there are the most plentiful sequence is M_1 at 56.6% and 35.4% for (C) and (D) compositions respectively. There are considerable amounts of diad, triad, tetrad, pentad and hexad M_1 sequences and also smaller amounts of heptad and octad M_1 sequences are possible for (C) feed composition. For (D) feed composition there are only diad, triad, and a small amounts of tetrad M_1 sequences are possible.

TABLE-4
 Intrinsic Viscosity $[\eta]$ and Their Dependence on
 Solubility Parameter δ of Solvents.

Sl. No.	Solvent	Solubility Parameter δ (cal/cc) ^{1/2}	AN-MMA System $[\eta]$ dl/g	MAN-MMA System $[\eta]$ dl/g
1	Toluene	8.9	0.1163	--
2	Benzene	9.2	0.1678	--
3	Chloroform	9.3	--	0.1148
4	Chlorobenzene	9.5	0.1823	--
5	Dichloromethane	9.7	0.2051	0.1347
6	1,4-Dioxane	10.7	0.1798	0.1535
7	Acetic anhydride	10.3	0.1474	0.1262
8	Diethylformamide	10.6	0.1282	0.1152

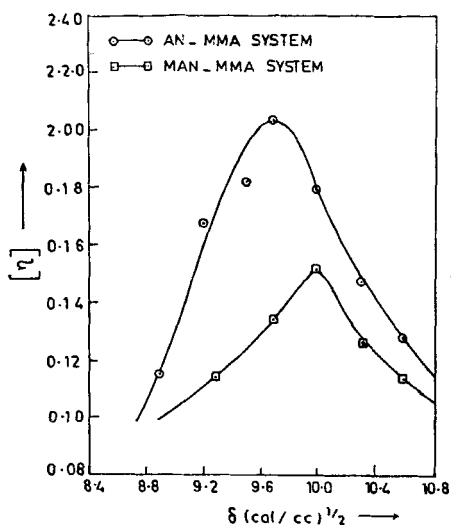


Fig. 6

TABLE - 5

Intrinsic Viscosities and Molecular Weights of Copolymer Systems

Mole ratio in feed [AN]/[MMA]	AN - MMA System		Mole ratio in feed [MAN]/[MMA]	MAN - MMA System	
	$[\eta]$ dl/g	$\bar{M}_w \times 10^{-4}$		$[\eta]$ dl/g	$\bar{M}_w \times 10^{-4}$
0.250	0.3017	11.06	0.578	0.2208	7.87
0.364	0.2842	8.44	0.764	0.2113	7.31
0.500	0.2751	7.42	0.875	0.2089	6.92
0.666	0.2678	6.30	1.145	0.1956	6.31
0.875	0.2586	5.53	1.500	0.1874	5.59
1.145	0.2392	5.12			

TABLE - 6

Thermal Properties of AN-MMA Copolymers

Sl. No.	Mole ratio in feed [AN]/[MMA]	DT at Different Wt. Losses			IPDT $^{\circ}$ C
		10%	40%	60%	
a	0.250	265.91	288.64	302.27	284.37
b	0.364	254.54	293.18	315.91	291.68
c	0.500	250.00	295.45	320.45	295.05

Solubility Parameter of Copolymers: Analytical reagent grade solvents with solubility parameters in the range of 8.9 to 10.6 (cal/cc)² were selected for viscosity measurements. The composition of the copolymer used was 0.80/0.70 [AN] or [MAN]/[MMA]. The intrinsic viscosity $[\eta]$ and their dependence on solubility parameter δ of solvents are given in table-4. The solubility parameter ^{22,23,24} of polymer was determined by measuring the intrinsic viscosity of the polymer in different solvents. Then, the intrinsic viscosity is plotted against the solubility parameter of the several

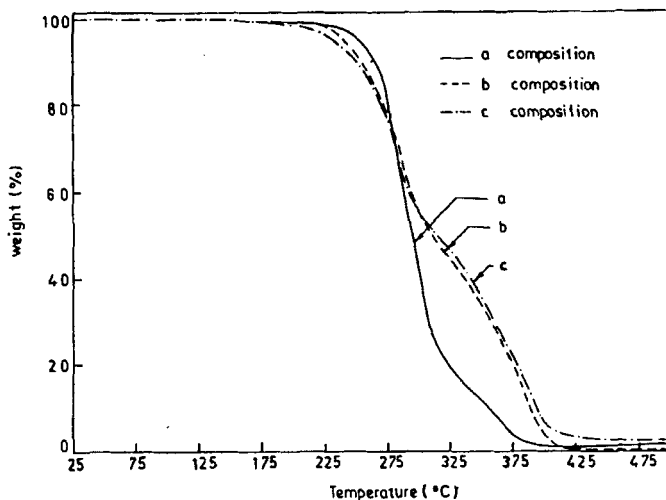


Fig-7. Thermograms of AN-MMA copolymer.

solvents, since the chain conformation is most expanded in the best solvent, the intrinsic viscosity will be highest for the best match in solubility parameter.

In the present study, the dependence of intrinsic viscosity on the solubility parameter of solvents has been used for estimating solubility parameter of the copolymer. The intrinsic viscosity of the copolymer solutions attains optimum value when solubility parameter of the copolymer falls in the vicinity of that of the solvents δ_p , the solubility parameter of the copolymer has been estimated by equating it to that of the solvent at which $[\eta]$ has the maximum value in the plot $[\eta]$ Vs δ (fig.6).

The estimated values for AN-MMA and MAN-MMA copolymer systems were 9.7 (cal/cc)^2 and 10.0 (cal/cc)^2 respectively.

The results of intrinsic viscosities $[\eta]$ and molecular weights of the copolymer compositions were summarised in Table-5. An increase in content of MMA is associated with an increase in viscosity. The results of integral procedural decomposition temperature (IPDT)²⁵ and the decomposition temperature (DT) at different weight losses for the AN-MMA copolymer are summarised in Table-6.

Figure-7 shows TGA curves in air for copolymers of AN-MMA with feed ratios 0.250, 0.364 and 0.500 (a, b and c composition). The IPDT value is a measure of thermal stability of a polymer. It is evident from the data (Table-6) that the IPDT values increases with an increasing content of AN. This is due to cross linking of tertiary carbons or polymerization of nitrile groups²⁶. Thus the higher rate of oligomerisation of nitrile groups in the copolymers lead to a polyene and cyclised ring structures containing carbon nitrogen double bonds²⁷.

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