Charge Transfer Copolymerization and Properties of Isopropyl Methacrylate with Acrylonitrile and Methacrylonitrile

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SYNOPSIS

Isopropyl methacrylate (IPMA) with Acrylonitrile (AN) and Methacrylonitrile (MAN) copolymers of different compositions were prepared at 60°C and 80°C, respectively, using a mixture of n-Butylamine (nBA) and carbon tetrachloride (CCl_4) in dimethyl sulphoxide (DMSO) as a charge transfer (CT) initiator. The percentage composition of the copolymers was established by elemental analysis. The copolymerization reactivity ratios were computed by the Kelen–Tudos method. In both the systems, IPMA was found to be more reactive; the copolymers sequence was random in nature. The copolymers were characterized by IR, ^{1}H-NMR, ^{13}C-NMR spectroscopy and intrinsic viscosity measurements in dimethyl formamide (DMF) at 30 ± 0.1°C. The thermal behavior of the AN–IPMA copolymers was studied by thermogravimetry (TG) in air. The thermal stability increased with increasing AN content in the copolymer chain. The solubility parameter of AN–IPMA copolymer was evaluated by studying the intrinsic viscosity in different solvents. The solubility parameter of the copolymer was found to be 9.7 $(cal/cc)^{1/2}$.

INTRODUCTION

Homopolymerization of many vinyl monomers, such as methyl methacrylate (MMA),[1] methyl acrylate,[2] and 2-vinyl pyridine,[3] etc., by charge transfer mechanism were reported by several workers. Only a few reports, however, have appeared on charge transfer (CT) initiated copolymerization.[4-6] In our earlier publication, we reported CT copolymerization of 2-vinyl pyridine with methyl methacrylate and ethyl methacrylate.[7] No work has been reported on the CT copolymerization of IPMA with AN and MAN. This article deals with the synthesis and characterization of AN–IPMA and MAN–IPMA copolymers prepared by using nBA–CCl_4 in DMSO as a CT initiator. Thermal properties and the solubility parameter of an AN–IPMA copolymer are also reported.

EXPERIMENTAL

IPMA, AN, and MAN [Fluka] were freed from inhibitors by washing with 5% sodium hydroxide and water and drying over calcium chloride and distilling twice under reduced pressure. DMSO,[8] nBA,[9] and CCl_4,[10] all of Analar grade, were purified as stated in the literature. Polymerizations were carried out in vacuum with nBA [0.7598 mol l^{-1}] and CCl_4 [1.55 mol l^{-1}] at varying feed ratios of monomers AN–IPMA and MAN–IPMA in DMSO at 60°C and 80°C, respectively. The total monomer concentration was maintained at 1.50 mol l^{-1}, while the ratio of the two monomers was varied. The initial monomer concentrations of AN, MAN, and IPMA were 0.4, 0.4, and 1.10 mol/L, respectively, and the amount of the solution used was 40 mL in each case. The experiments were performed in a three-limbed glass vessel. The first limb was filled with a mixture of two monomers (i.e., AN/IPMA or MAN/IPMA) with varying ratios in DMSO; the second was filled with nBA and CCl_4 in DMSO. The vessels were
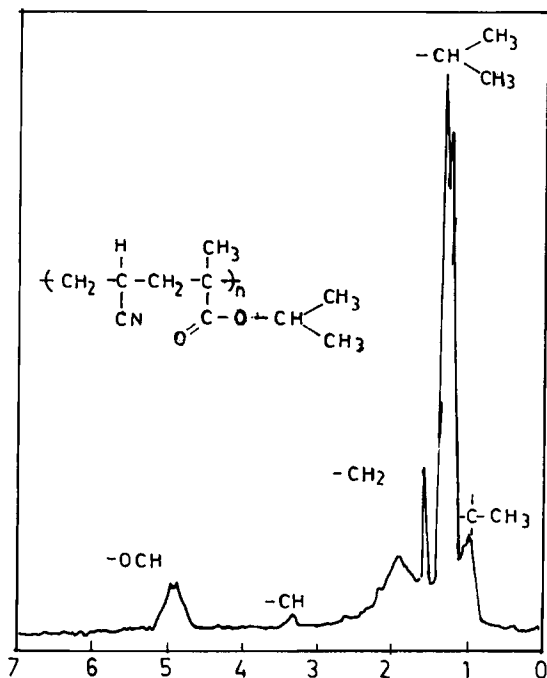
Figure 1 ^{1}H-NMR Spectrum of AN-IPMA Copolymer

evacuated and the reaction mixtures in the two limbs were mixed thoroughly and transferred into the third limb. The glass vessel was then immediately introduced into a thermostat at the desired temperature

(60 or 80°C). Next, the copolymers were precipitated by adding water. The percentage conversion was kept low (<10%) by limiting the time of polymerization.

The copolymers were characterized by IR, ^{1}H-NMR spectroscopy, viscosity, and thermogravimetric analysis (TGA). The IR absorptions were obtained in KBr disk using a Perkin-Elmer model spectrophotometer.

The ^{1}H-NMR spectra were obtained in CDCl$_3$ solution, using a 60 MHz varian spectrometer. ^{13}C-NMR spectra were recorded in CDCl$_3$ solution at ambient temperature using a JEOL-FX-60 MHz spectrometer.

The AN and MAN content of the copolymer samples were determined by Carlo-Erba model 1106 elemental analyzer to obtain data on the copolymer compositions. The values of reactivity ratios were determined using the Kelen-Tudos (K-T) method.[11] The mean sequence lengths ($\bar{l}_1$ and $\bar{l}_2$) were calculated using equations suggested by Ekpenyong.[12] The intrinsic viscosity [η] measurements were performed in a Ubbelohde viscometer at 30 ± 0.1°C with DMF as solvent. Thermogravimetric analyses (TGA) was carried out using a Dupont 1090 thermal analyzer in air at a heating rate of 10°C/min. Copolymers with three different feed ratios were analysed thermally.
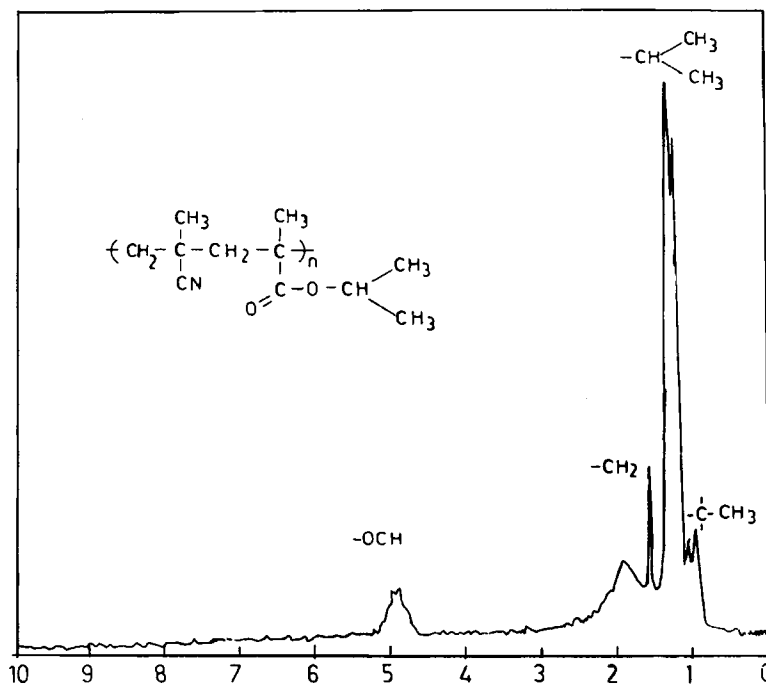

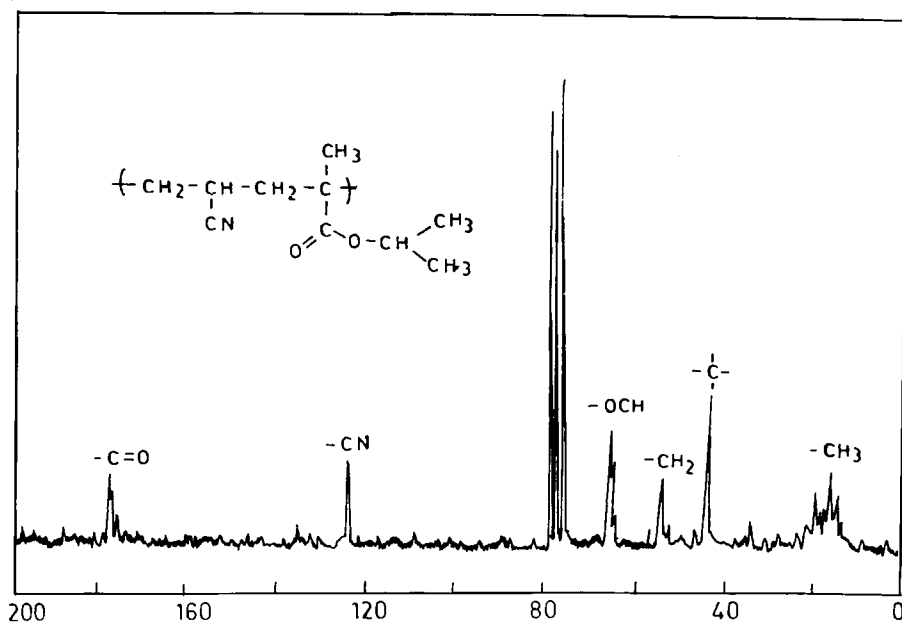**Figure 2** ^{1}H-NMR Spectrum of MAN-IPMA Copolymer

Figure 3 ^{13}C–NMR Spectrum of AN–IPMA Copolymer

Solubility Parameter

For the determination of the solubility parameters of the copolymers, the intrinsic viscosity [η] was evaluated at a single concentration (1%) from the flow time of pure solvent (t_0) and the solution (t) by the relationship[13-15]:

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

where C is the concentration in g/dL at $30 \pm 0.1°C$.

RESULTS AND DISCUSSION

The IR spectra of the copolymers showed a sharp peak at 2220 cm^{-1}, indicating the presence of the nitrile group, and hence confirmed the incorporation of AN or MAN into the polymer chain. Also, the peak at 1720 cm^{-1} indicated the presence of ester carbonyl group from IPMA. Characterization of the copolymers was done by ^{1}H–NMR and ^{13}C–NMR spectroscopy. The ^{1}H–NMR spectral assignments are given in Figure 1 (for AN–IPMA) and Figure 2 (for MAN–IPMA). From Figures 1 and 2, signals characteristic of IPMA and AN, IPMA and MAN, clearly showed their presence in the copolymer.

Figure 3 shows a typical ^{13}C–NMR spectrum of AN–IPMA copolymer. The signals arising from carbonyl carbon of IPMA units at (176–178 ppm) and the nitrile carbon of AN units at (120–124 ppm) confirmed the incorporation of IPMA and AN in the copolymer. The other signals are indicated in

Table I Copolymer Composition Data of AN–IPMA Copolymer System

| Sample	Mole Ratio in Feed [AN]/[IPMA]	N%	Copolymer Composition (mol %)		[η] [dl/g]	$\bar{M}_n \times 10^{-4}$	$\bar{M}_n \times 10^{-4}$	Mean Sequence Lengths		
			[AN]	[IPMA]				$\bar{l}_1$	$\bar{l}_2$	$\bar{l}_1/\bar{l}_2$
A	0.364	2.15	17.65	82.35	0.2013	4.08	2.99	1.08	4.97	0.217
B	0.666	3.51	27.10	72.90	0.1903	3.72	2.22	1.14	3.16	0.361
C	1.143	4.80	34.94	65.06	0.1823	3.25	2.01	1.25	2.26	0.553
D	2.000	6.81	45.66	54.34	0.1782	2.92	1.79	1.43	1.72	0.831
E	4.000	9.60	58.01	41.99	0.1734	2.69	1.57	1.86	1.36	1.367

Table II   Copolymer Composition Data of MAN–IPMA Copolymer System

Sample	Mole Ratio in Feed [MAN]/[IPMA]	N%	Copolymer Composition (mol %) [MAN]	Copolymer Composition (mol %) [IPMA]	$[\eta]$ [dl/g]	$\bar{M}_w \times 10^{-4}$	$\bar{M}_n \times 10^{-4}$	Mean Sequence Lengths $\bar{l}_1$	Mean Sequence Lengths $\bar{l}_2$	Mean Sequence Lengths $\bar{l}_1/\bar{l}_2$
A	0.364	4.97	37.40	62.60	0.1857	3.48	2.94	1.07	1.79	0.597
B	0.666	6.13	44.30	55.70	0.1802	3.11	2.37	1.13	1.43	0.790
C	1.143	7.18	50.05	49.95	0.1765	2.68	1.98	1.23	1.25	0.984
D	2.000	8.20	55.27	44.73	0.1721	2.42	1.74	1.40	1.14	1.228
E	4.000	9.65	62.17	37.83	0.1674	2.12	1.64	1.80	1.07	1.682

Figure 3. Similarly, for the MAN–IPMA system, ^{13}C–NMR confirmed the formation of copolymer.

AN–IPMA and MAN–IPMA copolymers (A to E) of different mole fractions were prepared. The percentage of AN or MAN in the copolymer was determined from nitrogen analysis. The percentage of AN, IPMA and MAN, IPMA in feed and in co-polymer are given in Tables I and II, respectively. These data were used for the evaluation of reactivity ratios. The values of r_1 and r_2 obtained were r_1 (AN) $= 0.21 \pm 0.03$, r_2 (IPMA) $= 1.44 \pm 0.06$ for AN–IPMA system and for MAN–IPMA system, r_1 (MAN) $= 0.19 \pm 0.03$, r_2 (IPMA) $= 0.29 \pm 0.04$ according to the K–T method and the corresponding
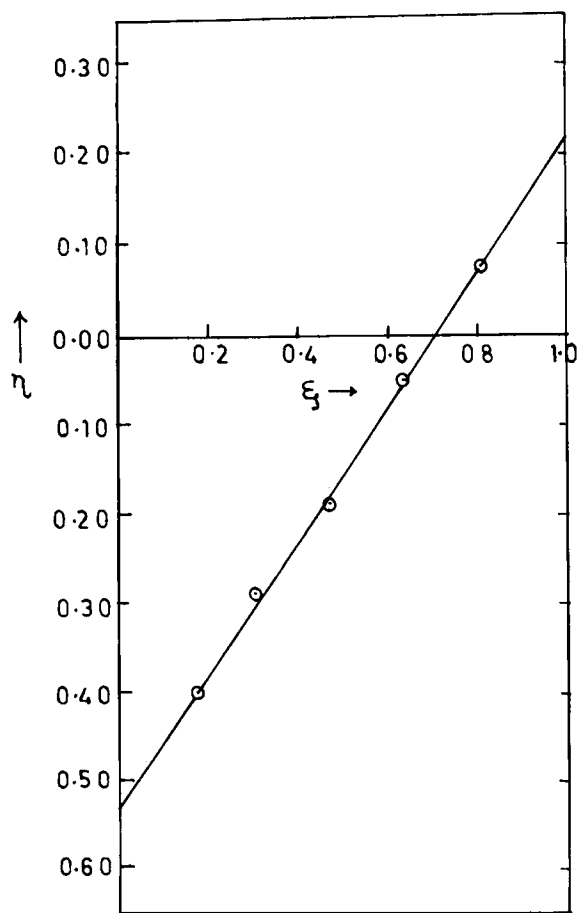
Figure 4   Kelen–Tudos plot of AN–IPMA Copolymer
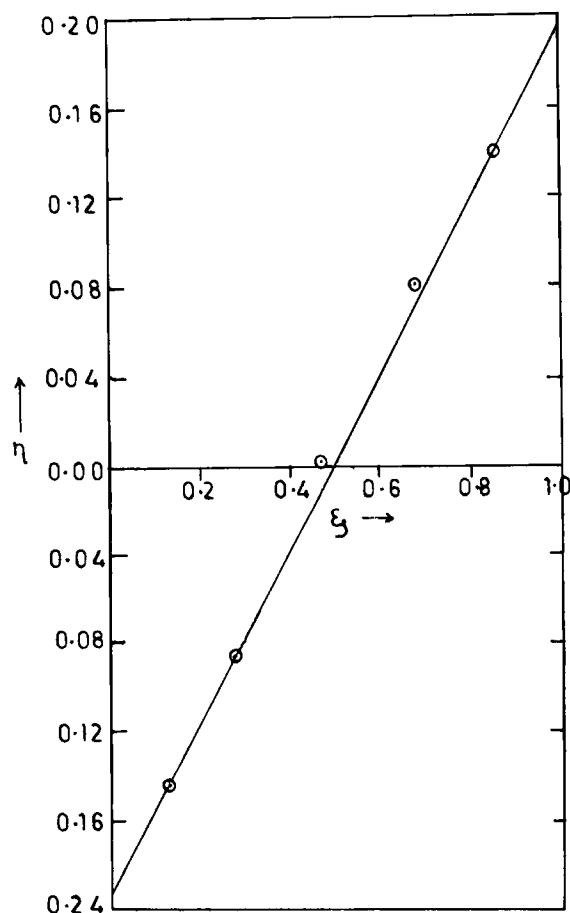
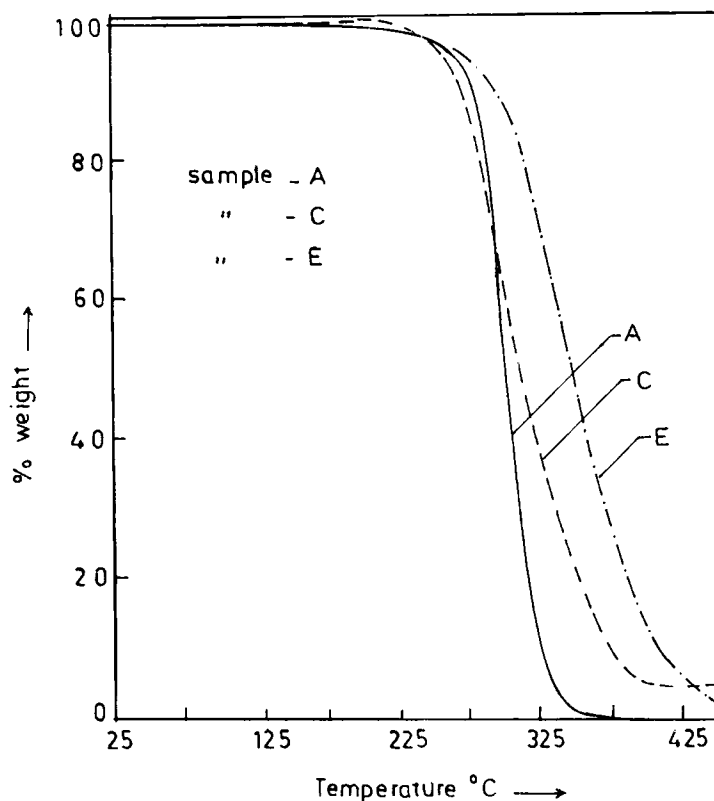**Figure 5**   Kelen–Tudos plot of MAN–IPMA Copolymer

Figure 6 Thermogravimetric curves of AN–IPMA Copolymer

plots are shown in Figures 4 and 5, respectively. Cameron et al.[22] studied the MAN–IPMA copolymers, using benzoylperoxide as an initiator, and obtained reactivity ratios of 0.43 ± 0.08 (MAN), 0.92 ± 0.08 (IPMA) at 80°C. However, AN–IPMA system is not available in the literature. The values obtained by CT initiation are different from that of free radical initiation.

For both the systems, $r_1 < 1$ and the product of r_1 and r_2 remains less than unity, indicating that the copolymers were predominantly, in random distribution in the monomeric units of the polymer chain. Value $\bar{l}_2$ increased from approximately 1 to 5 when [AN]/[IPMA] was changed from 4.00 to 0.364. A

slight increase in $\bar{l}_1$ and $\bar{l}_2$ was observed with increased concentration of MAN or IPMA in the feed. The number of IPMA units in AN–IPMA copolymer rapidly increased with an increase in [IPMA] in the feed, but this was not so for AN. Thus AN acted as retarder in the copolymerization. The data indicated the higher reactivity of IPMA in both the systems. The order of reactivity of IPMA towards macro radical ($\sim M_1^\cdot$) was found to be: AN > MAN. The higher reactivity of IPMA as compared to its comonomers may be attributed to the greater polarity of IPMA over the AN or MAN.

The results of intrinsic viscosities [η] and molecular weights $\bar{M}_w$ and $\bar{M}_n$ (by GPC) of the copol-

Table III Thermal Properties of AN–IPMA Copolymers

Sl. No.	Mole Ratio in Feed [AN]/[IPMA]	DT at Different Wt. Losses				IPDT °C
		10%	20%	40%	60%	
1	0.364	278.0	290.0	295.0	303.5	289.18
2	1.143	267.5	285.0	300.0	317.5	309.39
3	4.000	291.0	312.5	340.0	355.5	326.27

Table IV   Intrinsic Viscosity [η] and their Dependence on Solubility Parameter (δ) of Solvents for AN–IPMA Copolymer

Sl. No.	Solvents	Solubility Parameter δ (cal/cc)$^{1/2}$	[η] (dl/g)
1	Toluene	8.9	0.1544
2	Benzene	9.2	0.2330
3	Chlorobenzene	9.5	0.2578
4	Dichlormethane	9.7	0.2830
5	Nitrobenzene	10.0	0.2323
6	Acetic anhydride	10.3	0.1621
7	Isobutyl alcohol	10.5	0.1100

ymer compositions were summarized in Tables I and II. An increase in content of IPMA was associated with an increase in viscosity.

Further, intrinsic viscosities of AN–IPMA copolymers were higher as compared to MAN–IPMA copolymers.

Figure 6 shows TGA curves in air for copolymers of AN–IPMA with feed ratios (A, C, and E). The results of integral procedural decomposition temperature (IPDT)[16] and the decomposition temperature (DT) at different weight losses for the copolymers of three varying feed ratios are summarized

in Table III. The IPDT value is a measure of thermal stability of a polymer. It is evident from the data (Table III) that the IPDT values increase with an increasing content of AN. This is due to crosslinking of tertiary carbons or polymerization of nitrile groups.[17] Thus the higher rate of oligomerization of nitrile groups in the copolymers lead to a polyene and cyclized ring structures containing carbon–nitrogen double bonds.[18]

Solubility Parameters of Copolymers

Analytical reagent grade solvents, which cover a range of solubility parameters from 8.9 to 10.5 (cal/cc)$^{1/2}$, were selected for viscosity measurements. The solubility parameter of solvents, along with intrinsic viscosity values of copolymer, are summarized in Table IV. The solubility parameter was determined by measuring the intrinsic viscosity in different solvents.[19-21] The solubility parameter of the solvent in which the polymer exhibited the highest intrinsic viscosity was taken as the solubility parameter of a polymer. The solubility parameter values were estimated from the plot of intrinsic viscosities [η] against solubility parameters of solvents.

Figure 7 shows the plot of intrinsic viscosity values of copolymers against solubility parameters of different solvents. The intrinsic viscosity of the co-
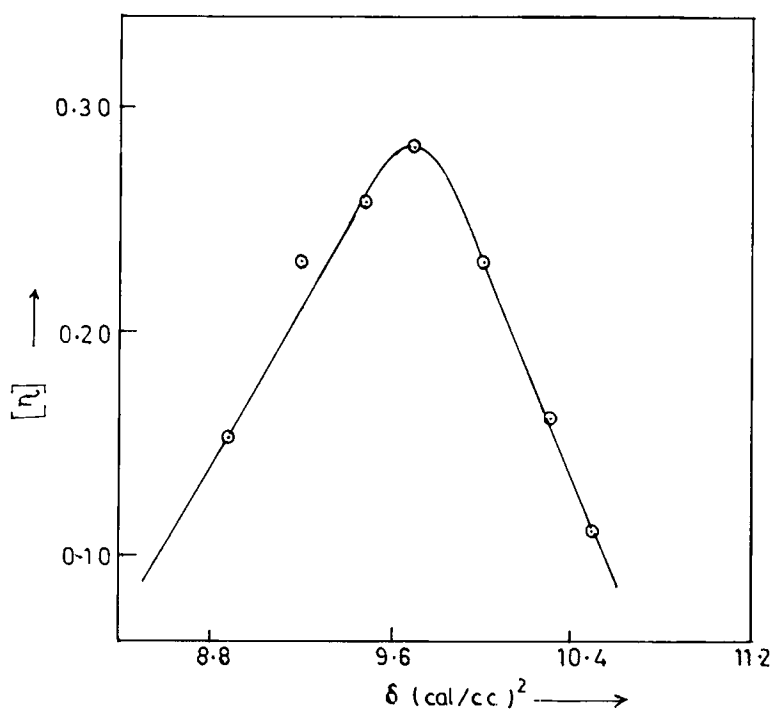
Figure 7   A plot of [η] vs. δ.

polymer solution attains optimum value when the solubility parameter of the copolymer falls in the vicinity of that of the solvent. The solubility parameter of the copolymer was estimated by equating it to that of the solvent at which $[\eta]$ has the maximum value in the plot of $[\eta]$ vs. δ. The peak value was taken as the solubility parameter of the AN–IPMA copolymer. From Figure 7, the solubility parameter of the copolymer was found to be 9.7 $(cal/cc)^{1/2}$.

In conclusion, we can state that the CT initiator used here gives random copolymers for both the systems studied. The copolymers obtained by the CT mechanism were less hygroscopic, were easily soluble in a number of organic solvents, and possessed easy processability in comparison to copolymers obtained by free radical initiation. An increase of AN content increased the thermal stability of the copolymers.

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