Studies on the Grafting of Methyl Methacrylate onto Polyacrylonitrile

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SYNOPSIS

Grafting of methyl methacrylate onto polyacrylonitrile was carried out using benzoyl peroxide as initiator and dimethylformamide as solvent. The occurrence of grafting was confirmed by IR spectroscopy and SEM analysis. Effects of various parameters such as reaction time, reaction temperature, initiator concentration, and monomer concentration on rate of polymerization, percentage grafting, and grafting efficiency were studied. The graft copolymers were found to have the similar thermal and structural properties like virgin polyacrylonitrile. Decreasing extent of swelling was observed for the polymers of higher percentage graft in polar solvents. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Acrylonitrile-based copolymers have a variety of applications in the textile industry, housewares, and custom molding products.[1,2] Acrylonitrile homopolymers, because of their combination of high melting point, high melt viscosity, and poor thermal stability, have few applications. By copolymerizing acrylonitrile with other monomers like acrylates, the deficiencies of polyacrylonitrile have been tempered, and desirable properties have been achieved.[3] Copolymers of acrylonitrile (> 90%) and methyl methacrylate represent a good fiber-forming material, and the methods of production of such copolymers on an industrial scale have already been introduced.[4] Even though random and block copolymers of acrylonitrile (AN) and methyl methacrylate (MMA) have been studied extensively, very few attempts have been made to study grafting of MMA onto PAN. Sengupta and Palit[5] carried out grafting of MMA onto PAN through the formation of a thioamido group, treating PAN with hydrogen sulfide (H₂S) and using halogen as initiator. Bamford et al.[6] synthesized graft copolymer of MMA onto PAN using triethylamine initiator. Novoselova et al.[7] synthesized graft copolymers of MMA and AN

by a two-stage process involving initial formation of living polyacrylonitrile and subsequent addition of poly(methyl methacrylate). They used BuLi as catalyst. Beevers et al.[8] studied X-ray scattering from a powder sample of PAN-g-MMA and found that X-ray scattering from the acrylonitrile block remains unaltered in the graft copolymers.

In this paper the method of synthesis of PAN-g-MMA using benzoyl peroxide initiator and its characterisation is discussed. The effects of various factors like reaction temperature, time, initiator concentration, and monomer concentration on rate of polymerization, percentage grafting, and grafting efficiency are discussed.

EXPERIMENTAL

Materials

PAN with $\bar{M}_v = 3.61 \times 10^4$, used in this work was synthesised in our laboratory.[9] Methyl methacrylate (Fluka) was purified prior to use. The inhibitor from MMA was removed by washing it first with sodium hydroxide solution and then with distilled water to remove traces of alkali, and was dried over anhydrous calcium chloride and distilled under reduced pressure. The purity of monomer was checked by gas chromatographic analysis and by refractive index assessment. Benzoyl peroxide (BDH) was pu-

rified by dissolving it in chloroform at room temperature and precipitating by methanol.

Graft Copolymerization

The grafting reactions were carried out in a reaction vessel equipped with stirrer, cooling facility, and thermometer. The temperature in the flask was maintained with an accuracy of ±0.5°C. A precise amount of PAN (2 g) was dissolved at 75°C in 70 cm^3 DMF in the reaction vessel. Benzoyl peroxide (0.2072 g in 5 cm^3 DMF) was added to the reaction mixture. After 10 min of stirring, 10.65 cm^3 (10 g) of MMA was added to the reaction mixture. The reaction was continued for 6 h, and the reaction mixture was poured into fourfold excess of chloroform under vigorous stirring. The isolated precipitate was washed several times with small portions of chloroform to remove the traces of unreacted MMA and homopolymer of MMA. The precipitates were again extracted with boiling chloroform in the Soxhlet for 48 h to remove the traces of any impurity and homopolymer. The precipitate was dried under reduced pressure in an oven at 50°C to constant weight. The homopolymer of MMA was recovered from chloroform by using methanol as nonsolvent. PMMA was dried under reduced pressure at 60°C to constant weight. For the confirmation of the effectiveness of the product separation technique, the graft copolymer was additionally purified by dissolving it in DMF and then precipitating in methanol. The results of the elemental analysis of both products were similar, indicating a negligible amount of impurities such as unreacted monomer or homopolymer. Blank experiments, conducted with PAN without addition of monomer, did not show any loss of weight due to degradation during the synthesis. The percentage total conversion, the percentage grafting (PG), grafting efficiency (GE), rate of polymerization (R_p), rate of graft copolymerization (R_g), and rate of homopolymerization (R_h) were calculated gravimetrically following the procedure of Vijaykumar et al.[10]

Infrared Spectra

IR spectroscopic information of the graft copolymers in KBr pellets was obtained using a Shimadzu IR 408 spectrophotometer.

Wide Angle X-Ray Study

X-ray crystallography was done with a Siemens Crystalloflux 4 Model coupled to a Hiltonbrooks/

Phillips diffractometer. The X-rays generated were Cu$_\alpha$ rays at 40 kV and 20 mA.

Swelling Study

Swelling study of the graft copolymers was done with a powdered sample (ca. uniform particle size) in water, methanol, and absolute alcohol. 1-Propanol, cyclohexane, and n-heptane. Percent swelling was calculated from the equation:

$$\text{percent swelling} = \frac{W_s - W_d}{W_d} \times 100$$

where W_s is the weight of the swollen polymer and W_d is the weight of the dry polymer.

Thermal Analysis

DSC analysis was carried out on a DuPont 2000 thermal analyzer equipped with a DSC cell at a heating rate of 10°C/min under nitrogen atmosphere. Thermogravimetric analysis was carried out on the DuPont 2000 TGA Model 951 at a heating rate of 10°C/min. All measurements were made under nitrogen atmosphere at a flow rate of 50 cm^3/min.

SEM Analysis

The scanning electron microscopic study of the graft copolymers was done with a JEOL-15 scanning electron microscope operated at 15–25 kV. The samples were mounted on a SEM stub using a double-sided tape. The samples were then coated using a Polaroin S-500 diode sputtering coater with 200 Å gold coating. The samples were then scanned at magnification of 250 times.

RESULTS AND DISCUSSION

In order to optimize the conditions for grafting, the concentrations of initiator and monomer, as well as temperature and time, were varied.

Effect of Monomer Concentration

The effect of monomer concentration on the grafting reaction is shown in Figure 1. Percentage grafting is found to increase continuously with increase in monomer concentration. With increasing MMA concentration in reaction mixture, the rate of all the reactions, i.e., grafting, homopolymerization, etc.,
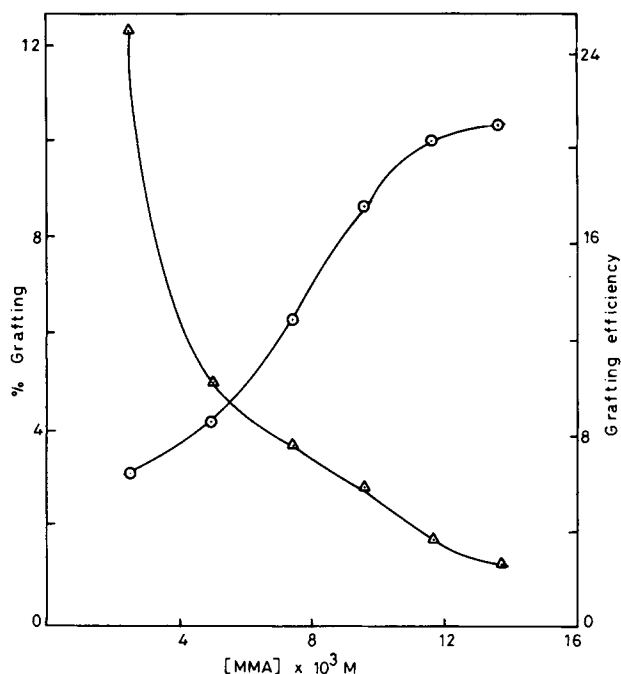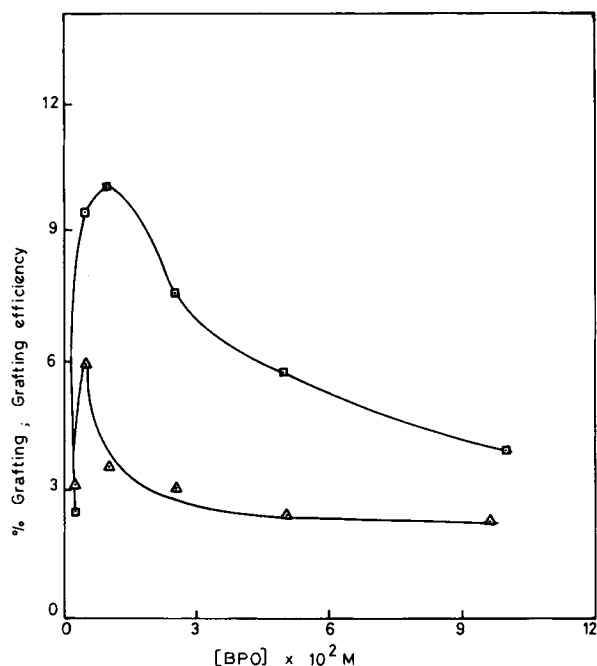
Figure 1 Effect of monomer concentration on percentage grafting ($\odot$) and grafting efficiency ($\triangle$): PAN, 2 g; BPO 10^{-2} M; temp = 75°; time = 6 h; total volume = 85 cm^3.

Figure 2 Effect of initiator concentration on percentage grafting ($\square$) and grafting efficiency ($\triangle$): PAN, 2 g; [MMA] = 1.168M; time = 6 h; temp = 75°C; total volume = 85 cm^3.

increases, leading to increase in percentage grafting but decreasing grafting efficiency. This is due to the fact that, within the monomer concentration range studied, with increasing MMA concentration the rate of homopolymerization increases to a greater extent than the rate of grafting, leading to a decrease in percentage grafting efficiency. This is clearly indicated by the steady growth in rate of homopolymerization (Table I).

Effect of Initiator Concentration

Figure 2 shows the effect of initiator concentration on the grafting reaction. The observed trend is a typical character of grafting reactions occurring via chain transfer. The initial increase in the percentage grafting and grafting efficiency is caused due to an increase in the concentration of free radicals formed through the decomposition of the initiator. Thus, the higher the concentration of initiator, the higher the chain transfer to the polymer and the higher the percentage grafting and grafting efficiency. But further increase in the initiator concentration (beyond $10^{-2}M$) decreases the molecular weight of the side chains due to the increased consumption of monomer in the process of homopolymerization. This results in a decrease in percentage grafting. These two

Table I   Effect of Monomer Concentration on the Graft Copolymerization of MMA Onto PAN[a]

[MMA] $\times$ 10 (M)	Total Conversion (%)	$R_p \times 10^6$ (mol L^{-1} s^{-1})	$R_g \times 10^6$ (mol L^{-1} s^{-1})	$R_h \times 10^6$ (mol L^{-1} s^{-1})
2.57	12.67	1.37	0.34	1.03
5.06	21.08	4.59	0.46	4.13
7.44	30.87	15.56	0.69	14.87
9.60	37.79	16.47	0.95	15.52
11.68	56.46	30.75	1.09	29.66
13.66	66.39	43.39	1.14	42.25

[a] PAN, 2 g; [BPO] = $10^{-2}M$; temperature = 75°C; reaction time = 6 h; total volume = 0.085 L.

Table II Effect of Initiator Concentration on the Graft Copolymerization of MMA Onto PAN[a]

Initiator Concentration $\times 10^2$ (M)	Total Conversion (%)	$R_p \times 10^6$ (mol L^{-1} s^{-1})	$R_g \times 10^6$ (mol L^{-1} s^{-1})	$R_h \times 10^6$ (mol L^{-1} s^{-1})
0.25	16.37	8.90	0.27	8.63
0.50	31.74	17.29	1.03	16.26
		3		
1.00	56.46	0.75	1.09	29.66
2.50	42.63	23.22	0.83	22.39
5.00	40.07	20.09	0.63	20.46
10.00	33.78	18.40	0.45	17.95

[a] PAN, 2 g; [MMA] = 1.168M; temperature = 75°C; reaction time = 6 h; total volume = 0.085 L.

opposite tendencies give rise to the appearance of maxima.

Effect of initiator concentration on R_p, R_g, and R_h is given in Table II. It is observed that R_p, R_g, and R_h initially increase and then decrease with increasing concentration of initiator. As mentioned earlier, with an initial increase of initiator concentration, the number of radical sites for polymerization increase, thereby increasing the rate of reaction (i.e., R_p, R_g, and R_h). Further increase in the initiator concentration increases the mutual termination reaction, thereby decreasing R_p, R_g, and R_h. In addition, at these conditions, concentration of monomer added must have been quantitatively exhausted during polymerization reaction due to excess of free radical concentration. The extent of homopolymerization was brought down considerably by delaying the addition of monomer after addition of initiator. Similar results were observed by Hebeish and Mehta.[11] This is expected due to the elimination of direct contact of free radicals with the monomer.

Effect of Temperature

The influence of temperature on grafting reaction is shown in Figure 3. On increasing temperature, both percentage grafting and grafting efficiency pass through a maxima. R_p, R_g, and R_h are also observed to give a similar trend (Table III). With increasing temperature decomposition of initiator increases, resulting in an increased number of free radicals. Hence initially the rates of polymerization and grafting increase. But further increase in temperature increases mobility of these free radicals, and hence mutual termination takes place, resulting in decreased availability of the free radicals for polymerization. Hence R_p, R_h, and R_g are observed to decrease.

Effect of Reaction Time

The effect of reaction time on the grafting of MMA onto PAN is shown in Figure 4. With increase in reaction time, both percentage grafting and grafting efficiency initially increase and then decrease. Because, with increase in reaction time, the radicals have more time for reaction, as a result, increases in percentage grafting and grafting efficiency were observed. Further increase in reaction time causes the deplation of initiator and monomer due to homopolymerization, hence lowering the percentage
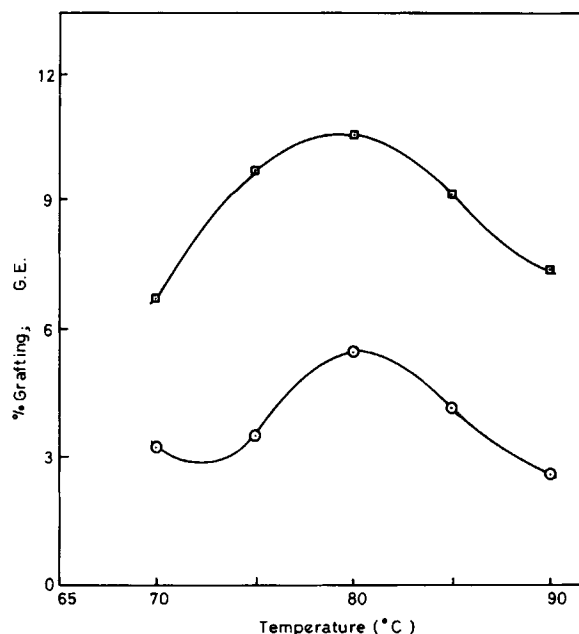
Figure 3 Effect of temperature on percentage grafting (□) and grafting efficiency (○): PAN, 2 g; [MMA] = 1.168M;; [BPO] = $10^{-2}M$; time = 6 h; total volume = 85 cm^3.

Table III   Effect of Temperature on the Graft Copolymerization of MMA Onto PAN[a]

Temperature (°C)	Total Conversion (%)	$R_p \times 10^6$ (mol L^{-1} s^{-1})	$R_g \times 10^6$ (mol L^{-1} s^{-1})	$R_h \times 10^6$ (mol L^{-1} s^{-1})
70	41.35	22.52	0.73	21.79
75	56.46	30.75	1.09	29.66
80	58.00	20.70	1.16	19.54
85	42.93	17.38	1.01	16.38
90	40.61	15.20	0.82	14.38

[a] PAN, 2 g; [MMA] = 1.168M; [BPO] = 10^{-2}M; reaction time = 6 h; total volume = 0.085 L.

grafting and grafting efficiency. The rate of polymerization decreases with increasing reaction time. This effect can be attributed to the fact that the relative increment in the total yield is comparatively less when compared to that of time: in the expression for R_p, the numerator becomes almost constant, and when the time for the reaction is raised, the denominator becomes larger, reducing R_p accordingly. Since R_g and R_h are related to R_p, the relative decrease of R_g and R_h with time can be explained (Table IV).
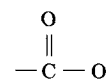
Evidence of Grafting

IR Spectroscopy

Figure 5 shows the IR spectra of PAN and PAN-g-MMA. The appearance of new peaks in grafted
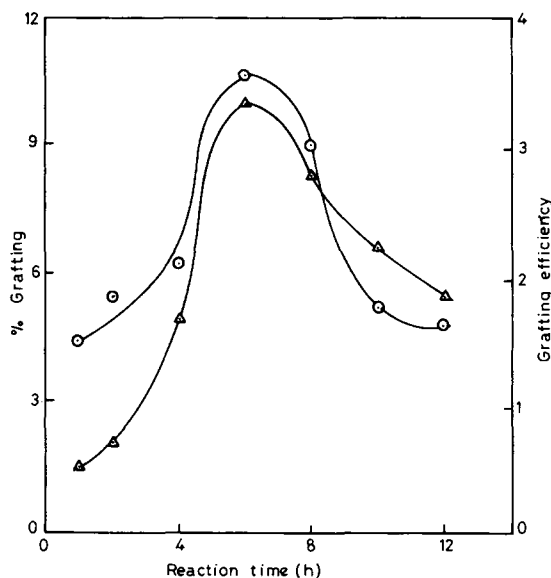
Figure 4   Effect of reaction time on percentage grafting (◯) and grafting efficiency (△): PAN, 2 g; [MMA] = 1.168M; [BPO] = 10^{-2}M; temp = 75°C; total volume = 85 cm^3.

sample at 1735 and 1148 cm^{-1} indicates the introduction of

$$\overset{\overset{\textstyle O}{\|}}{-C} - O$$

group of methyl methacrylate onto PAN. This confirms the occurrence of grafting.

SEM Analysis

Figure 6 shows the scanning electron micrographs of purified PAN and a grafted sample. The rough surface of the grafted polymer with respect to ungrafted one, due to the grafted branches of PMMA on PAN, confirms the occurrence of grafting.

Wide Angle X-Ray Scattering Study

In Figure 7 the X-ray scattering patterns for PAN and the graft copolymer are shown. PAN shows a peak at d = 5.15 Å with additional unresolved peak arising from spacing 3–4 Å, suggesting orthorhombic unit cell structure. The X-ray scattering curve for graft copolymer shows the similar scattering pattern as that of PAN. This suggests that the X-ray scattering from the acrylonitrile block appears to be unaffected by the presence of PMMA side chains in the graft copolymer. A similar observation was made by Beevers et al.[8]

Thermal Properties

Differential scanning calorimetric data for the various graft copolymers and homopolymers are given in Table V. No remarkable change in the melting temperature of PAN was observed due to lower percentage of grafting. However, the heat of crystallization is observed to decrease with increase in the percentage grafting due to the decreased crystalline

**Table IV** **Effect of Reaction Time on the Graft Copolymerization of MMA Onto PAN[a]**

Reaction Time (h)	Total Conversion (%)	$R_p \times 10^6$ (mol L^{-1} s^{-1})	$R_g \times 10^6$ (mol L^{-1} s^{-1})	$R_h \times 10^6$ (mol L^{-1} s^{-1})
1	18.84	61.56	0.91	60.65
2	25.35	41.42	0.65	40.77
4	48.16	39.35	0.83	38.52
6	56.46	30.75	1.09	29.66
8	58.34	22.61	0.69	21.92
10	65.52	20.68	0.44	20.44
12	67.60	18.40	0.30	18.10

[a] PAN, 2 g; [BPO] = $10^{-2}M$; [MMA] = $1.168M$; temperature = 75°C; total volume = 0.085 L.

character of the graft copolymers. Graft copolymers are observed to give the single glass transition values, indicating the compatibility of the graft chains with the main chain polymers. Figure 8 represents the DSC curves of a representative graft copolymer. Figure 9 represents the representative TG and DTG
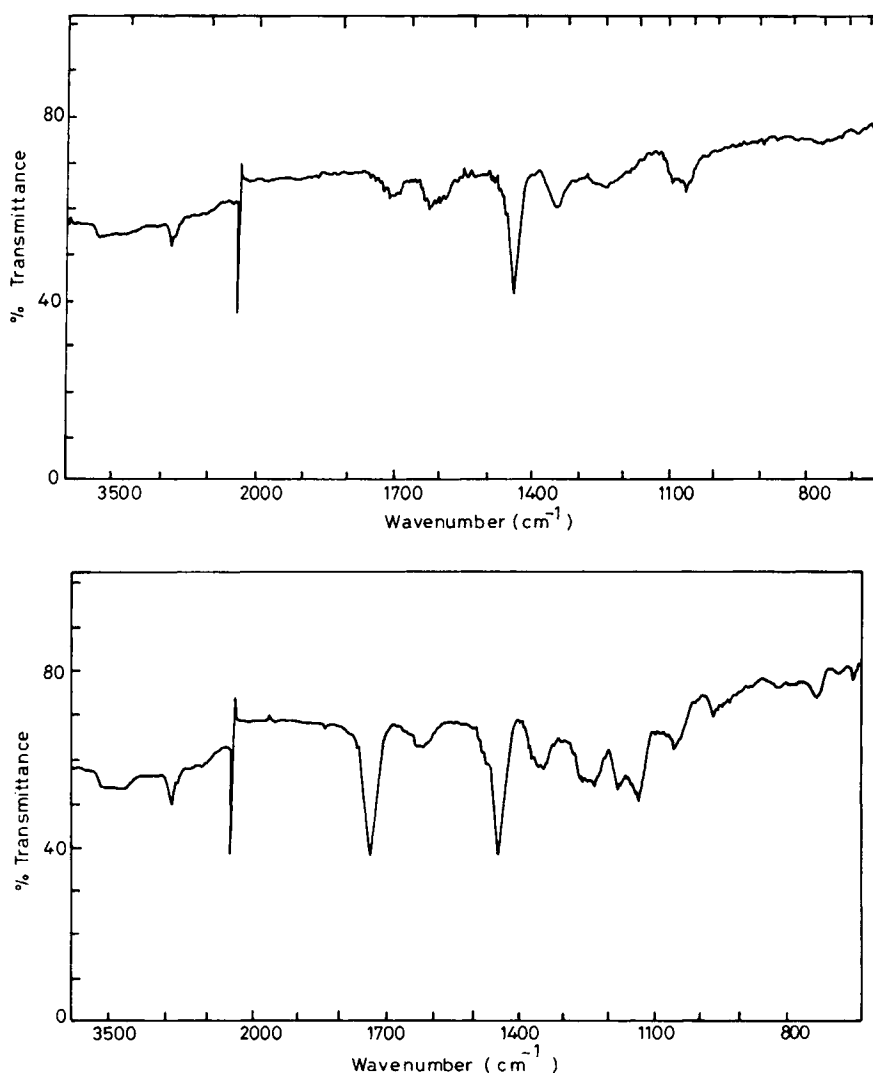
Figure 5 IR spectra of (a) PAN and (b) graft copolymer.
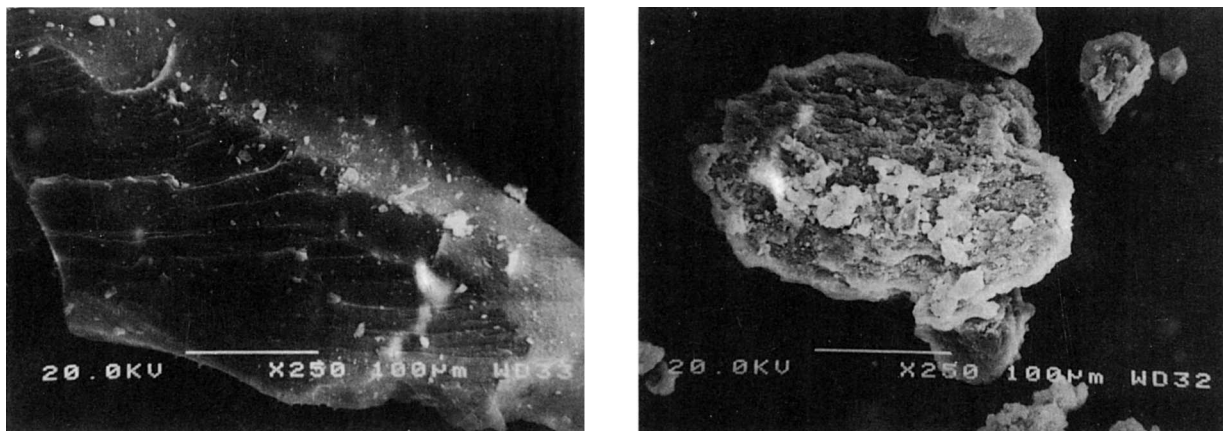
Figure 6 Scanning electron micrographs (SEMs) of (a) purified PAN and (b) graft copolymer (6.3% grafting).
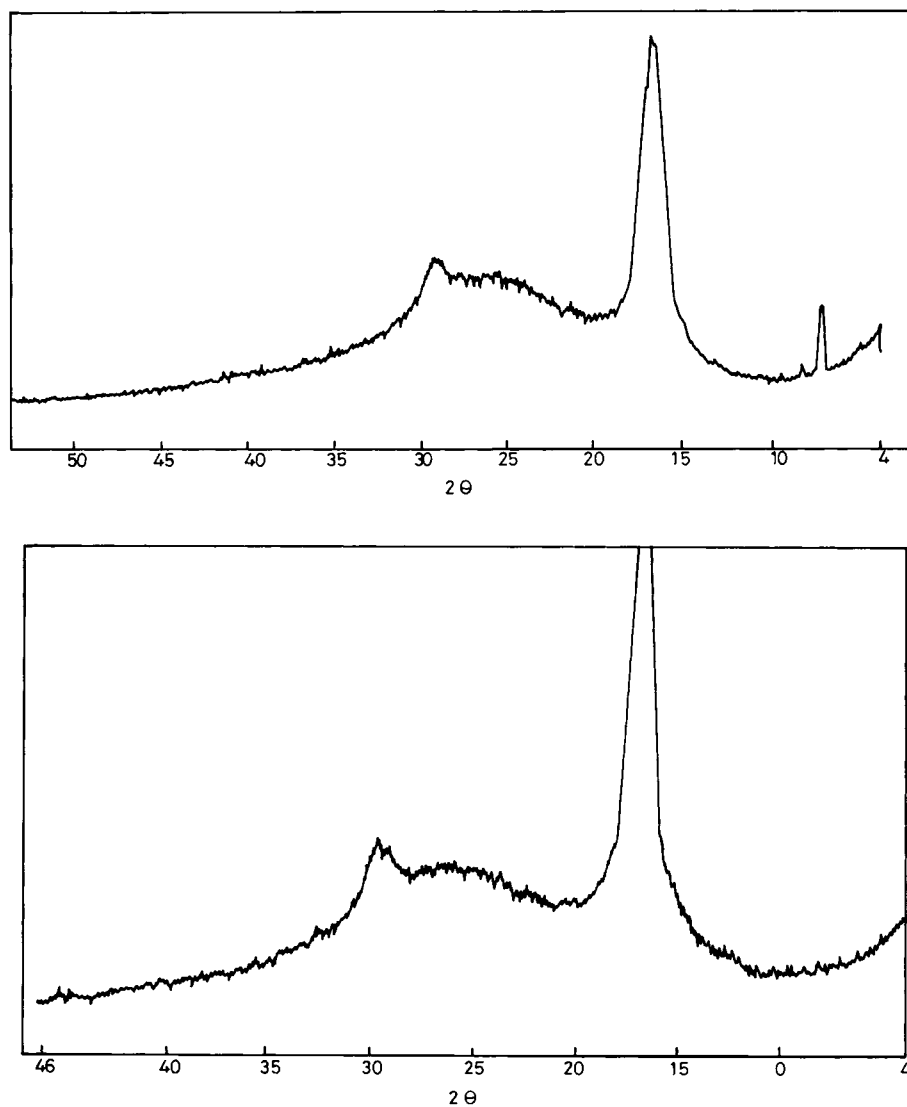
Figure 7 Wide angle X-ray scattering patterns for (a) PAN and (b) graft copolymer.

Table V   DSC Analysis Data for Poly(AN-*g*-MMA) Polymer

Sample	Percentage Grafting	Melting Temperature (°C)	Heat of Crystallization (J/g)	Glass Transition Temperature (°C)
PAN	—	268.0	390.0	98.0
G_1	3.10	262.5	—	96.63
G_2	4.20	265.2	370.8	97.93
G_3	6.33	266.6	322.8	—
G_4	8.66	268.1	283.2	94.61
G_5	10.05	266.2	265.7	—
G_6	10.47	271.0	—	85.67
PMMA	—	178.1	81.4	89.74

thermograms for PAN and PAN-*g*-MMA sample. The initial decomposition temperature for graft co-polymer was observed to be 273.26°C and that for PAN 278.7°C. The weight loss in the first stage of degradation of graft copolymer could be associated with nitrile oligomerization, which produces volatile products (NH_3, HCN, CH_3CN, etc.) and subsequent chain scission. The second stage degradation of graft copolymers occurs at 417.25°C. The activation energy associated with thermal break down of the graft copolymers was calculated following the Broido[12] method and was found to be 25.67 and 44.73 kJ mol^{-1} for first and second transitions.

Swelling Behavior

Swelling of the graft copolymers was studied in various solvents. Figure 10 represents the results obtained. It was observed that extent of swelling of the graft copolymers in a given solvent decreases with the increase in percentage grafting. This may be due to the increased concentration of bulky hydrophobic methyl methacrylate groups in PAN backbone. When the extent of swelling is compared in different solvents for the same sample, it was observed that swelling is higher in more polar solvents. The increase of percent swelling of a particular graft
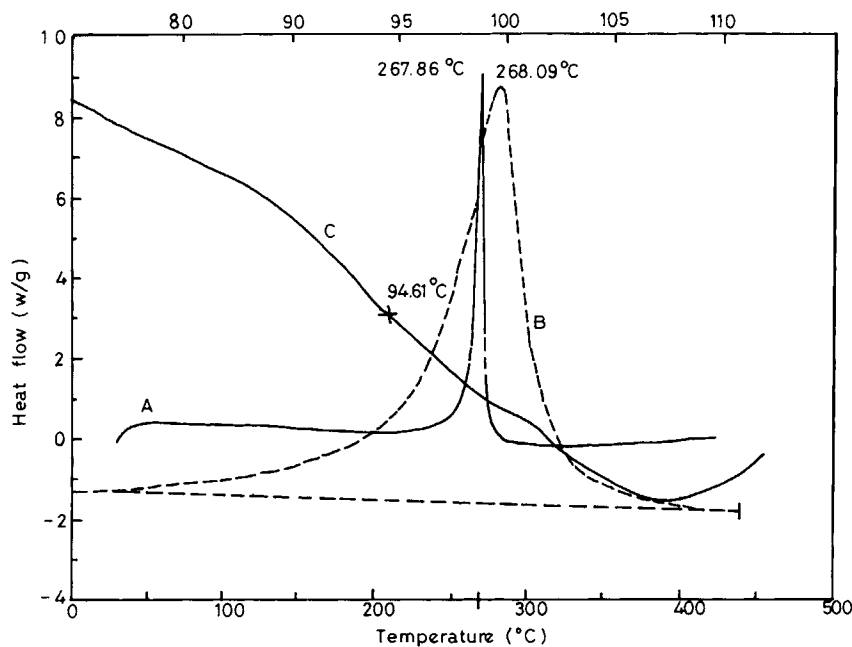
Figure 8   DSC curves for G4 sample: (a, b) lower *X*-axis scale; (c) upper *X*-axis scale (for T_g).
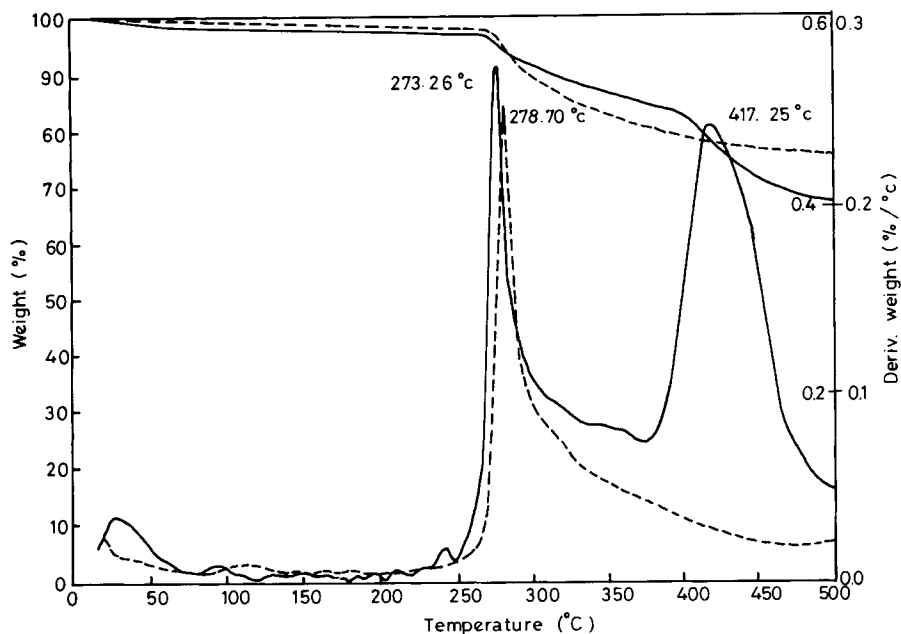
Figure 9 TGA analysis: (———) G2 sample; (– – –) PAN.

copolymer with the increase of polarity of the solvent may be due to the hydrophillic nature of the PAN backbone of the graft copolymer.
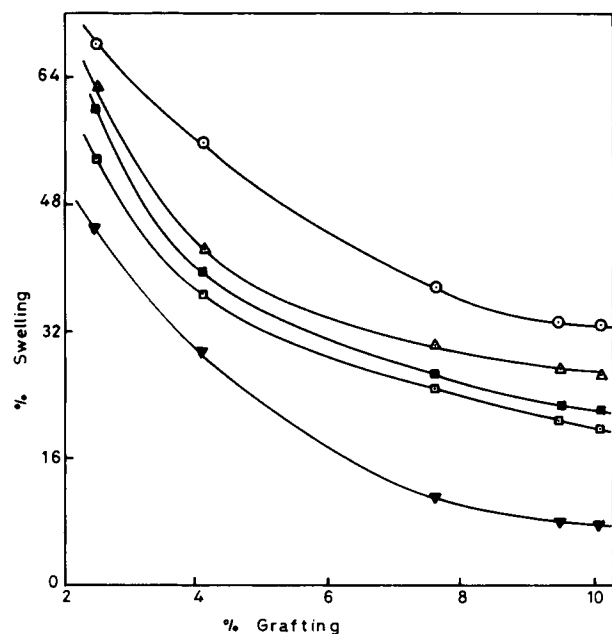

Figure 10 Swelling of graft copolymer: (○) methanol; (△) absolute alcohol; (■) 1-propanol; (□) cyclohexane; (▲) water.

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