

Research Paper :

Dielectric and thermal properties of 1, 1' azobis (cyclohexanecarbonitrile) initiated methacrylonitrile copolymers

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ABSTRACT

Copolymer of methacrylonitrile (MAN) with methylmethacrylate (MMA) was synthesized by free radical polymerization using 1,1' azobis (cyclohexanecarbonitrile) (VAZO) as initiator in dimethyl formamide at $60 \pm 1^\circ\text{C}$. The glass transition temperature (T_g) of the copolymers was determined by differential scanning calorimetry. Thermogravimetric analysis of the copolymer was also studied. The dielectrical properties such as dielectric constant and dielectric loss of the copolymers are also studied.

Key words : Methyl methacrylate, Methacrylonitrile, Solution properties, Thermal properties, Dielectrical properties

Introduction of methylmethacrylate (MMA) into various copolymers appears to modify and improve the properties of a number of copolymers (Mihailo *et al.*, 2007, Kadir *et al.*, 2006, Brar *et al.*, 2006, Hossein *et al.*, 2005). The $^1\text{H-NMR}$ spectroscopic analysis has been used as a powerful tool for the estimation of copolymer composition (Ismail *et al.*, 2003; Balaji *et al.*, 1999). In this article we reported the synthesis, characterization, thermal properties and dielectric properties of the copolymers of MAN with MMA.

MATERIALS AND METHODS

Methacrylonitrile (MAN) (Aldrich), methyl methacrylate (MMA) (Aldrich), 1,1' azobis (cyclohexanecarbonitrile) (VAZO) (Aldrich) and dimethylformamide (DMF) (Merck) were used in this study.

MAN and MMA were purified by washing with 5% solution of sodium hydroxide and distilled water, dried over calcium chloride before distilling under reduced pressure. The middle fraction of the distillate was collected and used for copolymerization. VAZO was recrystallized from methanol. The solvent used in copolymerization was DMF which was a reagent grade chemical. This was dried and purified by distillation before use. All experiments were performed in glass tubes with appropriate quantities of dry monomers, solvents and initiator. The tubes were sealed in an atmosphere of nitrogen and introduced into the thermostat at $60 \pm 1^\circ\text{C}$ and the polymerization was continued for 90 min. to get less than 10% conversion. The polymerization mixture was poured into a large amount of water to isolate the

copolymer, which was filtered, washed thoroughly with water followed by ether and hexane, and finally dried under vacuum. Different samples were prepared by changing the initial monomer feed. The initiator was used at 2.5 g/dm^3 of solvent. The total monomer concentration was maintained at 1.5 M, while the feed ratio was varied. The data of composition of feed and copolymers are presented in Table 1.

Table 1 : Copolymerization data of MAN with MMA

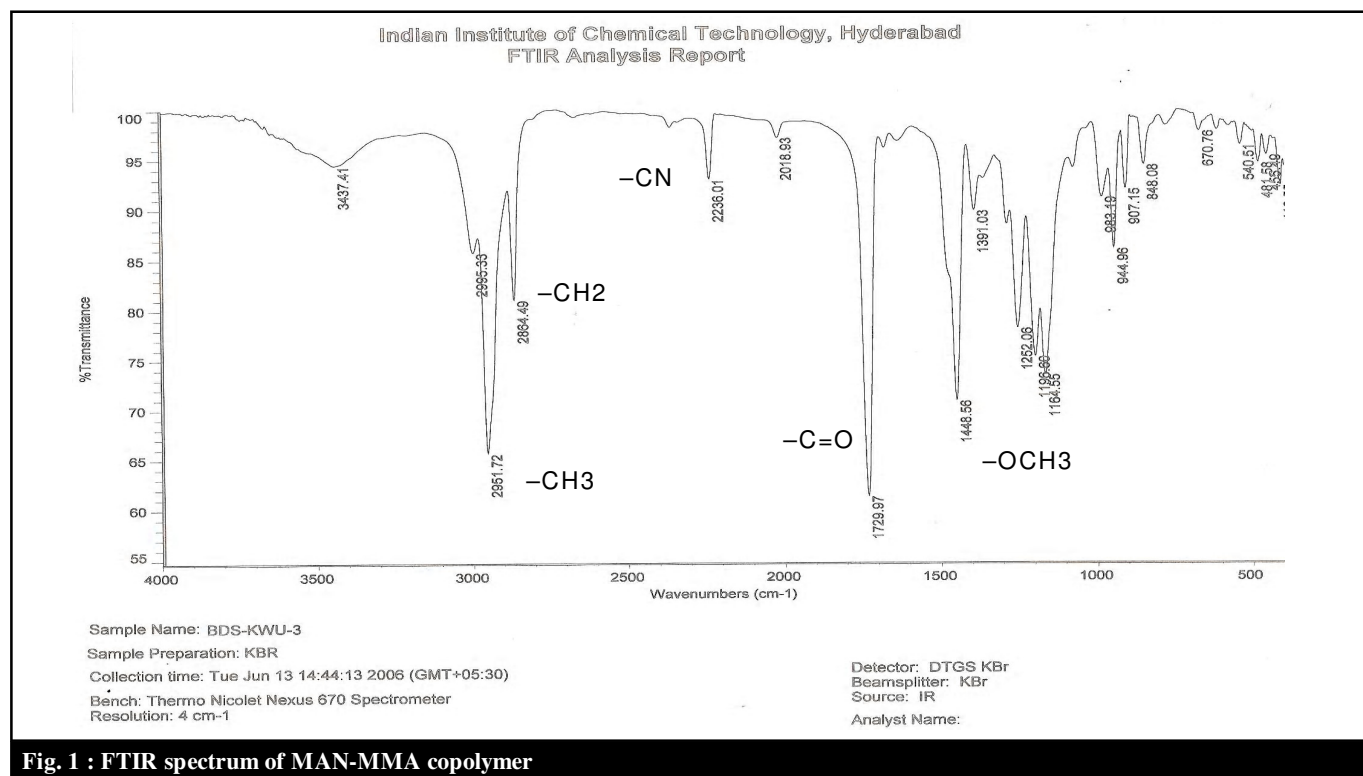
Monomer	Copolymer system	Mole fraction of MAN in the feed
Methyl methacrylate	MAN-MMA ₁	0.80
	MAN-MMA ₂	0.932
	MAN-MMA ₃	1.08
	MAN-MMA ₄	1.12
	MAN-MMA ₅	1.20

RESULTS AND DISCUSSION

The results obtained from the present investigation are below :

IR Spectroscopy:

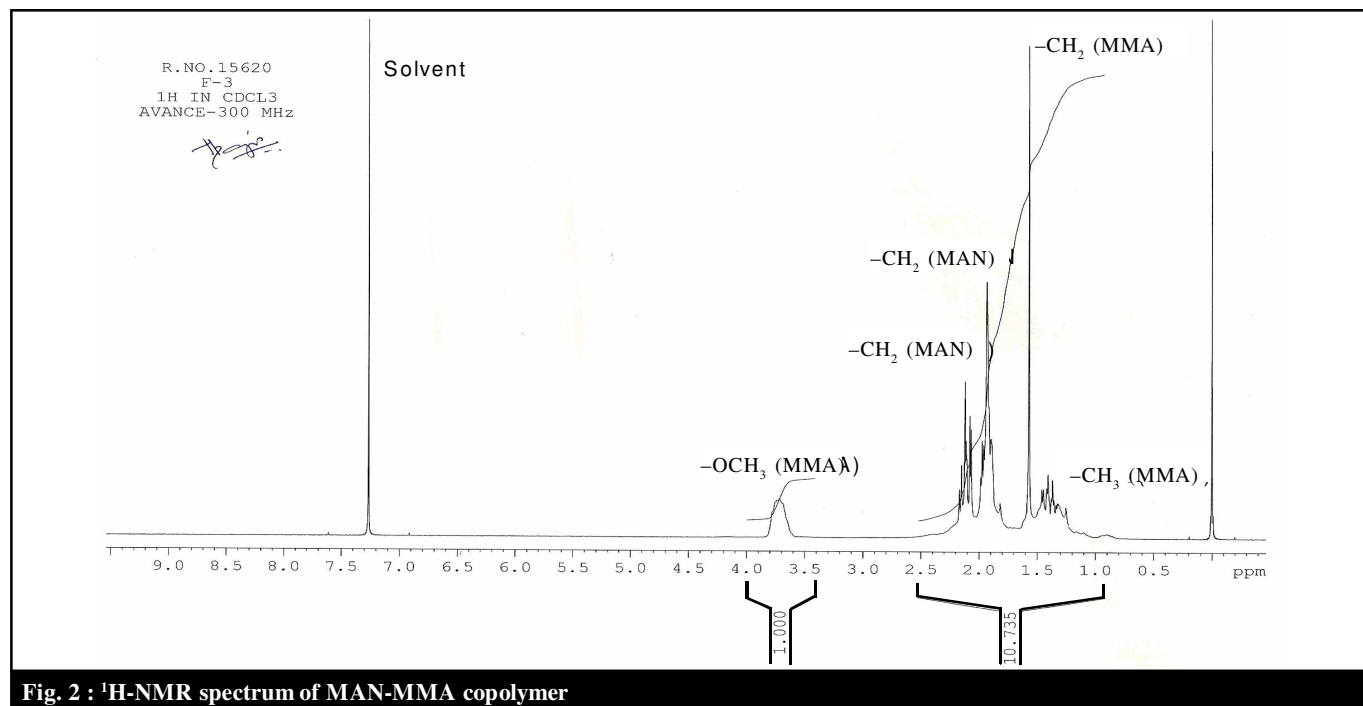
Infrared spectra of the samples were recorded on a Thermo Nicolet Nexus 670 IR spectrophotometer in 4000 to 400 cm^{-1} range with KBr pellets. The IR spectrum of the copolymer of MAN and MMA (MAN-co-MMA) is shown in (Fig. 1) showing the characteristic bands of both the monomer units. Appearance of strong absorption bands at 2864.49 , 1729.97 , 2236.01 , 1448.56 and 2951.72 cm^{-1} corresponds to methylene ($-\text{CH}_2$) stretching, $>\text{C}=\text{O}$ stretching in ester, cyano ($-\text{CN}$), methoxy group ($-\text{OCH}_3$)



and methyl (-CH₃) stretching vibrations, respectively. The appearance of absorption bands corresponding due to ester >C=O, -OCH₃ and -CN group and the disappearance of absorption bands corresponding to olefinic bond is the evidence for the formation of MAN-MMA copolymer.

¹H-NMR Spectroscopy:

¹H-NMR spectra of the samples were recorded using DMSO-d₆ as solvent for MAN copolymer on an advance 300 MHz NMR spectrometer with TMS as internal reference. The copolymer compositions were determined by ¹H-NMR spectra shown in (Fig. 2). The characteristic peaks due to methyl (-CH₃) protons of methyl



methacrylate unit appears at 1.36- 1.46 ppm, methylene ($-\text{CH}_2$) protons of MMA unit appears at 1.6 ppm, methylene ($-\text{CH}_2$) protons of MAN unit appears at 1.95 ppm, methoxy ($-\text{OCH}_3$) protons of MMA unit appears at 3.71 ppm, $-\text{CH}_3$ protons of MAN appears at 2.1-2.2 ppm. The appearance of absorption peaks corresponding due to $-\text{CH}_3$, $-\text{CH}_2$, and $-\text{OCH}_3$ of MMA unit and $-\text{CH}_2$, and $-\text{CH}_3$ of MAN unit are evidence for the formation of MAN-MMA copolymer.

Thermal studies:

The thermogravimetric analysis of the polymers was performed on a Perkin Elmer Diamond thermal analyzer at a heating rate of $15^\circ\text{C}/\text{min}$. Glass transition temperature (T_g) of the copolymers was determined using a Mettler Toledo 822E thermal analyzer at a heating rate of $15^\circ\text{C}/\text{min}$ and shown in Fig. 3. T_g values of the copolymers obtained from the DSC curves. T_g of the copolymer increases with increase in the MAN content.. When the MAN content increases intramolecular interaction increase and the polymer segments become less mobile and T_g occurs at higher temperature (Raghunath rao *et al.*, 2007, Ewing *et al.*, 2003, Julio San Roman *et al.*, 2003, Raghunath rao *et al.*, 1993, Salem *et al.*, 1988). The relative thermal stabilities are evaluated by the

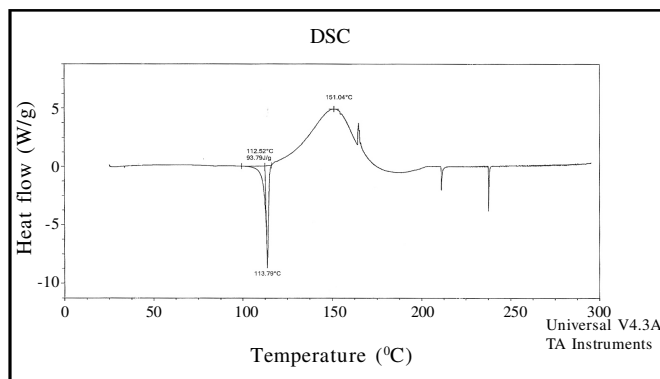


Fig. 3 : DSC curve of MAN-MMA copolymer

comparison of the initial decomposition temperature (IDT), the integral procedural decomposition temperature (IPDT) and decomposition temperature (DT) at 50% weight loss shown in Fig. 4. To obtain a comparative picture of relative thermal stability of the copolymer their IDT, IPDT and DT values are given in Table 2.

Dielectric properties:

A Capacitance bridge model GR 1620(WG) is used to measure the dielectric constant (ϵ) and dielectric loss (tand) of the MAN-MMA copolymers. All samples are annealed prior to use for the measurement. The results

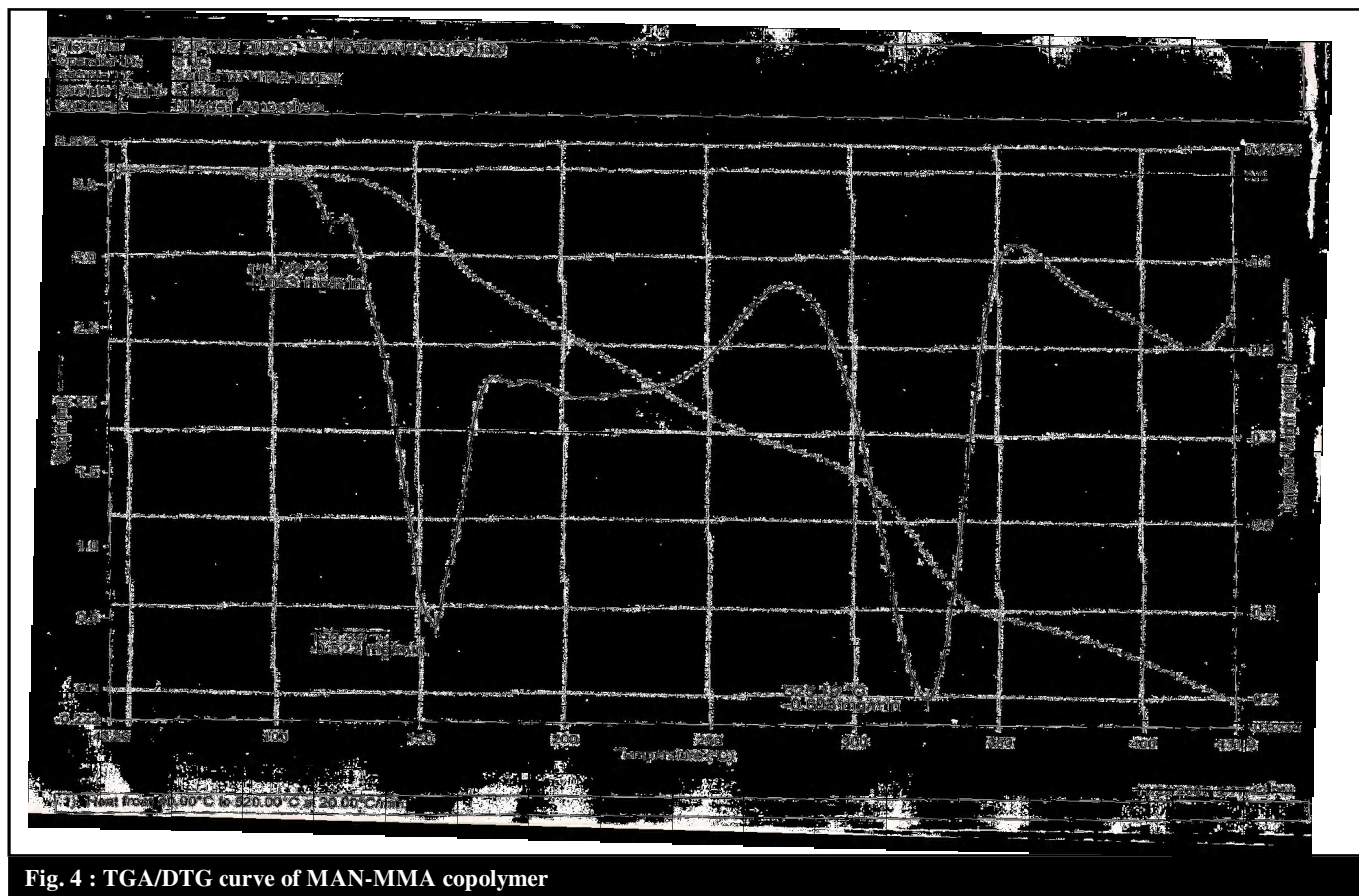


Fig. 4 : TGA/DTG curve of MAN-MMA copolymer

Table 2 : Thermal behavior of MAN-MMA copolymers

Copolymer	IDT (°C)	IPDT(°C)	Temperature (°C) at wt. loss			T _g (°C)
			10%	20%	50%	
MAN-MMA ₁	120.42	162.33	152.54	171.59	171.59	113.79
MAN-MMA ₂	121.55	163.13	153.65	172.66	172.66	115.21
MAN-MMA ₃	122.36	165.29	154.36	176.95	176.95	118.85
MAN-MMA ₄	125.24	166.85	155.74	183.47	183.47	--
MAN-MMA ₅	126.35	167.15	157.26	186.36	186.36	--

of variation of (ϵ) and $\tan\delta$ at constant frequency of 20 KHz against temperature for MAN-MMA Fig. 5 are given in Table 3. The results show that ϵ and $\tan\delta$ are unaffected by temperatures up to 125°C. Beyond that region, both ϵ and $\tan\delta$ increases. A peak due to relaxation is observed in $\tan\delta$, known as α relaxation, at about 120°C, in the rubbery state of the polymer (Anustella Mathews *et al.*, 2008, Tanaka *et al.*, 1960). This temperature is higher than T_g for the polymer obtained by a DSC method is 113.79°C. At lower temperature, molecular chains are not only immobile but also tightly bound at some points because of dipole-dipole interactions (Gupta *et al.*, 1981, Raghunath rao *et al.*, 2003). As the temperature is raised,

more and more dipole groups are released and the mobility of polymers segment increases.

Conclusions:

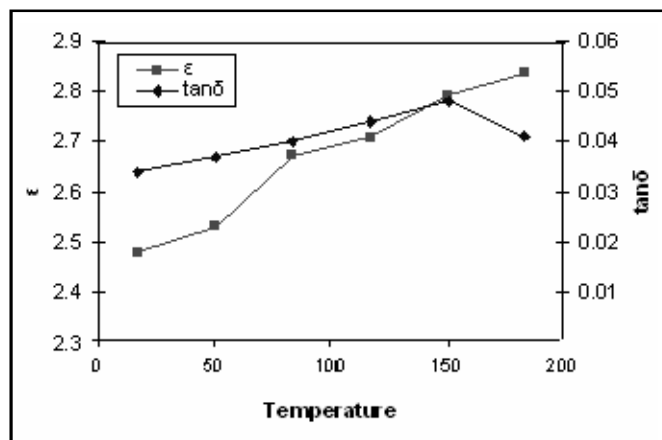
The copolymer of MAN with MMA has been synthesized using a VAZO as initiator in DMF. The copolymer is characterized by IR and ¹H-NMR. Thermal properties like T_g, IDT and IPDT have been evaluated to find the thermal stability of the polymer. Dielectric properties of copolymers are studied to find the electrical stability.

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Table 3 : Variation of dielectric constant and dielectric loss with temperature for MAN-MMA copolymer at 20 KHz

Temperature	MAN-MMA	
	ϵ	$\tan\delta$
25	2.48	0.034
50	2.532	0.037
75	2.672	0.04
100	2.707	0.044
125	2.792	0.048
150	2.837	0.041

**Fig. 5 : Typical plot of ϵ and $\tan\delta$ against temperature of MAN-MMA copolymer**

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