

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 ($-\text{OCH}_3$)