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Research Paper :

Reactivity ratios determination of methacrylonitrile with isobornyl methacrylate by ^{1}H NMR spectroscopy

S. SRIDEVI AND P. RAGHUNATH RAO

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See end of the article for authors' affiliations

Correspondence to:

P. RAGHUNATH RAO
Department of Chemistry,
Kakatiya University,
WARANGAL (A.P.) INDIA

ABSTRACT

Copolymer of Methacrylonitrile (MAN) with Isobornyl methacrylate (IBM) has been studied by free radical polymerization using 1,1' azo bis (cyclohexanecarbonitrile) (VAZO) as initiator in Dimethyl formamide (DMF) at 60±1^0 C. The monomer reactivity ratio was computed by both Fineman–Ross (F-R) and Kelen–Tudos (K-T) methods. The reactivity ratio values suggested the formation of random copolymers which has been supported by the azeotropic composition evaluation. The mean sequence length ($\bar{n}$) and probabilities (p) in the formation of various structurally units were evaluated. The molecular weights of the polymers were determined by gel permeation chromatography and they increase with increasing MAN content. The solubility parameters were determined with viscometric method. The glass transition temperature (T_g) of the copolymers were determined by differential scanning calorimetry (DSC). Thermo gravimetric analysis (TGA) of the copolymer was studied. The dielectric properties of the copolymer like the dielectric constant and dielectric loss were studied. The results have been compared with methacrylonitrile and isobornyl acrylate (MAN-IBA) system.

Key words : Methacrylonitrile, Isobornyl methacrylate, Copolymerization, Reactivity ratios, Thermal and Dielectric properties

Introduction of IBM into various copolymers seem to modify and improve the properties of a number of copolymers[1, 2]. The estimation of copolymer composition and determination of the reactivity ratios are important for making copolymer with required-physico chemical properties.The H NMR spectroscopic analysis has been used as a powerful tool for the estimation of copolymer composition[3-6]. In this paper, the synthesis, characterization, reactivity ratios, solution properties, thermal and dielectric properties of the copolymers of IBM with MAN have been described.

MATERIALS AND METHODS

MAN (Aldrich) and IBM (Lancaster) were purified by washing with 5% solution of sodium hydroxide and distilled water. Then they were dried over calcium chloride before distilling under reduced pressure. The middle fraction of the distillate was collected and used for copolymerization. VAZO was crystallized from methanol. The solvent used in copolymerization was DMF (reagent grade) 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 then sealed in an atmosphere of nitrogen and then they were introduced into the thermostat at 60 $\pm$ 1^{0}C for 90 minutes to get less than 10% conversion. After that the polymerization mixture was poured into a large amount of water to isolate the copolymer, which was filtered and washed thoroughly with water followed by ether and hexane. Pure sample was then dried under vacuum. Different samples were prepared by changing the initial monomer feed. The initiator was used at 2.5 gr/ lit 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 given in Table 1.

Table 1 : Copolymerization data of MAN with IBM

Copolymer system	Mole fraction in the feed		Intensity of Methyl protons (3H)(M_1)	Intensity of isobornyl methyl protons (9H) (M_2)	Copolymer composition	
	MAN (M_1)	IBM (M_2)			MAN (m_1)	IBM (m_2)
MAN-IBM$_1$	0.600	0.400	35.84	62.63	0.636	0.364
MAN-IBM$_2$	0.666	0.333	37.45	79.23	0.679	0.321
MAN-IBM$_3$	0.734	0.266	33.88	81.50	0.723	0.277
MAN-IBM$_4$	0.800	0.200	26.14	96.60	0.787	0.215
MANIBM$_5$	0.867	0.133	17.02	98.78	0.853	0.147