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ELECTRICAL STUDIES OF N-METHYL ACRYLAMIDE COPOLYMERS INITIATED BY BIS (1-OXODODECYL) PEROXIDE

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ABSTRACT

Copolymer of N-methyl acrylamide (NMA) with methyl methacrylate (MMA) was synthesized by free radical polymerization using bis (1-oxododecyl) peroxide as initiator in dimethyl formamide (DMF) at 60±1°C. The chemical structure is determined by Fourier transform infrared spectroscopy and ^{1}H-NMR spectroscopy. The polymer was characterized by thermogravimetric analysis (TGA) and dielectrical properties like dielectric constant and dielectric loss of the copolymer were studied.

KEY WORDS: N-methyl acrylamide / Bis (1-oxododecyl) peroxide / Thermogravimetric analysis and Dielectrical property.

1.INTRODUCTION

Introduction of N-methyl acrylamide (NMA) into various copolymers appears to modify and improve the properties of a number of copolymers (Mihailo and Danica,2007; Kadir,2006; Brar and Tripta,2006; Hossein,2005). The ^{1}H-NMR spectroscopic analysis has been used as a powerful tool for the estimation of structure of copolymer (Jayasimha Reddy,2006; Feroz,2009; 2010; Alvaro,2003). In this article we reported the synthesis, characterization, thermal properties and dielectric properties of the copolymers of NMA with MMA.

2.MATERIAL AND METHODS

NMA (Aldrich) and MMA (Aldrich), bis (1-oxododecyl) peroxide were used. 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°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 vaccum. 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 Table1.

3.RESULTS AND DISCUSSION

FTIR Spectroscopy: The Fourier transform infrared (FTIR) spectra were recorded on a Thermo Nicolet Nexus 670 IR spectrophotometer using KBr pellets in the range 4000 to 400 cm^{-1}. The IR spectrum of the copolymer of NMA and EMA (NMA-co-EMA) is shown in Figure-1. The characteristic adsorption bands related to –C=O of ester (1731.50cm^{-1}), –C=O of amide (1648.35cm^{-1}), -OCH_2 (1460.23cm^{-1}), -NH (3462.12cm^{-1}), -N-CH_3 (1070.08cm^{-1}) and C-N (1162.38cm^{-1}) confirms the formation of MA-MMA copolymer.

^{1}H-NMR: ^{1}H-NMR spectra of the samples were recorded using DMSO-d_6 as solvent for NMA copolymer on a Avance 300 MHz NMR spectrometer with TMS as internal reference. The copolymer compositions were determined by ^{1}H-NMR spectra shown in Figure-2. In the spectrum, methoxy (-OCH_3) protons of MMA unit appears at 3.5 ppm, methylene (-CH_2) protons of MMA unit appears at 1.22 ppm, methylene (-CH_2) protons of NMA unit appears at 2.5 ppm, α-methyl (-CH_3) protons of MMA unit appears at 0.8-1.0 ppm, N-methyl (-N-CH_3) protons of NMA unit appears at 2.79 ppm and –NH protons appears at 6.9-7.3 ppm.

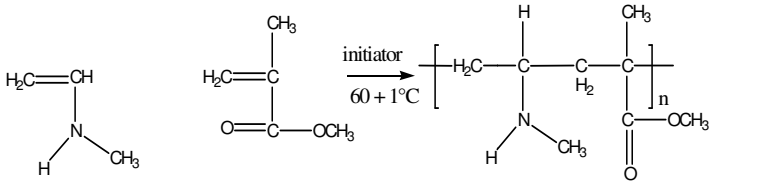
Thermal studies*:* The thermogravimetric analysis of the polymers was performed on a Perkin Elmer Diamond thermal analyzer at a heating rate of 15°C/min. Glass transition temperature (T_g) of the copolymers was determined using a Mettler Toledo 822E thermal analyzer at a heating rate of 15°C/min and shown in Figure-3. T_g values of the copolymers obtained from the DSC curves. T_g of the copolymer increases with increase in the AN content. When the NMA content increases intramolecular interaction increase and the polymer segments become less mobile and T_g occurs at higher temperature [9-13]. The relative thermal stabilities are evaluated by the comparison of the initial decomposition temperature (IDT), the integral procedural decomposition temperature (IPDT) and decomposition temperature (DT) at 50% weight loss shown in Figure-4.To obtain a comparative picture of relative thermal stability of the copolymer their IDT, IPDT and DT values are given in Table 6.

Di-electric properties: A Capacitance bridge model GR 1620(WG) is used to measure the dielectric constant (ε) and dielectric loss (tanδ) of the NMA-MMA copolymers. All samples are annealed prior to use for the measurement. The results of variation of (ε) and tanδ at constant frequency of 20 KHz against temperature for NMA-MMA Figure-5 are given in Table-3. The results shows that the ε and tanδ are unaffected NMA by temperatures up to 175°C. Beyond that region, both ε and tanδ increases. A peak due to relaxation is observed in tanδ, known as α relaxation, at about 175°C, in the rubbery state of the polymer [14-15]. This temperature is higher than T_g for the polymer obtained by a DSC method is 164.64°C At lower temperature, molecular chains are not only immobile but also tightly bound at some points because of dipole-dipole interactions [16-17]. As the temperature is raised, more and more dipole groups are released and the mobility of polymers segment increases.

4.CONCLUSION

The copolymer of NMA with MMA has been synthesized using bis (1-oxododecyl) peroxide as initiator in DMF. The copolymer is characterized by FTIR and ^{1}H-NMR. Thermal properties like T_g, IDT and IPDT have been evaluated to find the thermal stability of the polymer. Di-electric property of copolymer is also studied to find the electrical stability.

Copolymer system	Mole fraction in the feed	
	NMA	MMA
NMA-MMA$_1$	0.80	0.70
NMA-MMA$_2$	0.85	0.65
NMA-MMA$_3$	0.90	0.60
NMA-MMA$_4$	0.95	0.55
NMA-MMA$_5$	1.00	0.50



N- methyl acrylamide Methyl methacrylate Poly(N-methyl acrylamide-co- methyl methacrylate)

Table - 1 Copolymerization data of NMA with MMA

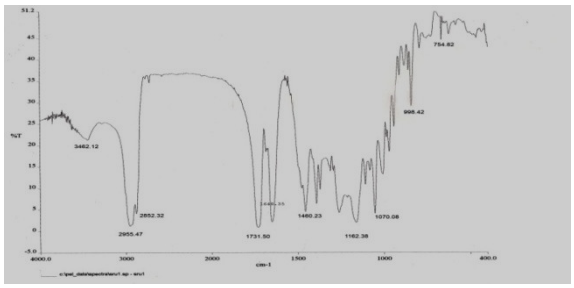


Fig-1 FTIR Spectrum of NMA-MMA

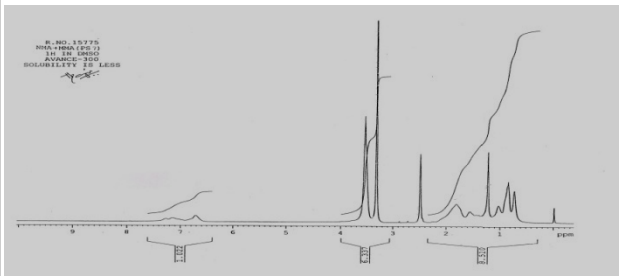


Fig-2 ^{1}H-NMR Spectrum of NMA-MMA

Copolymer	IDT(^{0}C)	IPDT(^{0}C)	Temperature(^{0}C) at wt.loss			Tg(^{0}C)
			10%	20%	50%	
NMA-MMA$_1$	102.22	158.95	140.11	160.58	290.57	164.64
NMA-MMA$_2$	103.41	160.48	142.25	162.13	294.28	165.76
NMA-MMA$_3$	104.74	161.65	142.91	163.55	297.25	168.25
NMA-MMA$_4$	105.52	163.71	143.51	164.91	298.66	169.43
NMA-MMA$_5$	105.95	165.36	144.18	165.51	299.14	169.43

Table– 2 Thermal behavior of NMA-MMA copolymers

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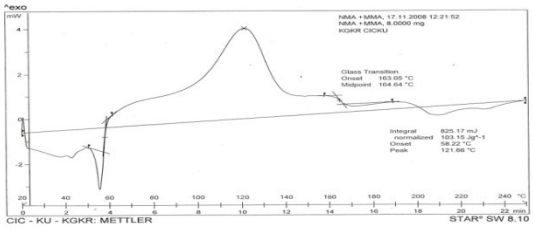

Figure-3 DSC curve of NMA-MMA

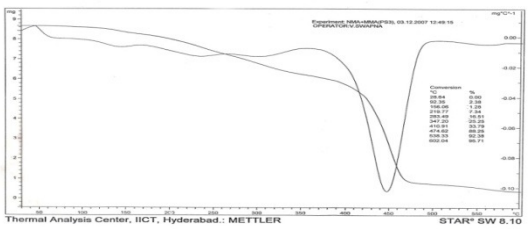

Figure- 4 TGA/DTG curve of NMA-MMA

Temperature (^{0}C)	NMA-MMA	
	ε	tanδ
25	4.401	0.032
50	4.445	0.035
75	4.498	0.036
100	4.537	0.042
125	4.617	0.045
150	4.683	0.048
175	4.711	0.052
200	4.729	0.044

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

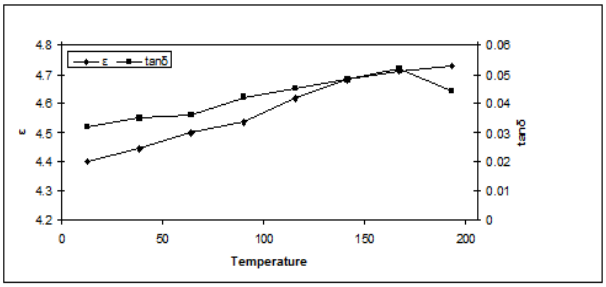

Fig-9 Typical plot of ε and tanδ against temperature for NMA-MMA

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