Asian Journal of Chemistry Vol. 15, No. 1 (2003), 241–249

Synthesis and Characterization of Isobornyl Acrylate and Methacrylate-N-Methyl Acrylamide Copolymers

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Free radical copolymerization of N-methyl acrylamide (NMA) with isobornyl acrylate (IBA) and isobornyl methacrylate (IBM) has been investigated in N,N′-dimethyl formamide (DMF) at 60 ± 1°C using 2,2′-azobisisobutyronitrile (AIBN) as an initiator by ^1H NMR analysis. The monomer reactivity ratios were computed by both Fineman-Ross (F-R) and Kelen-Tudos (K-T) methods. The molecular weights of the copolymers were determined by gel permeation chromatography. The solubility parameters were determined with viscometric method. The glass transition temperatures of the copolymers were determined by differential scanning calorimetry. Thermogravimetric analysis of the copolymers was performed and their thermal stabilities were studied. The dielectric properties of the copolymers were also studied. The reactivity of acrylate was found to be more than that of methacrylate towards NMA. The reactivity ratio values suggest the formation of random copolymers which has been supported by the azeotropic composition evaluation. The molecular weights of the copolymers increase with the increase of the amide content. The solubility parameter values of acrylate copolymer are more than the corresponding methacrylate copolymer. The T_g values of actylate copolymers are less than the corresponding methacrylate copolymers. Thermal stability of IBM coplymers is found to be more than that of IBA copolymers. The dielectric loss of the copolymers is found to be shifting to a higher temperature from acrylate to methacrylate copolymers.

Key Words: N-Methyl acrylamide, Isobornyl acrylate, Isobornyl methacrylate, Copolymerization.

INTRODUCTION

Acrylic copolymers have acquired prime importance in various avenues of industrial applications[1–3]. They serve as basic materials for the preparation of formulations which are used as base and top coats in leather industry.

The copolymers of isobornyl methacrylate and methylmethacrylate seem to show high tensile strength, elongation at break and upper service temperature[4]. Introduction of isobornyl acrylate and methacrylate into various copolymers seems to modify and improve the properties of a number of copolymers[5–9].

The present work was undertaken to study the properties of copolymers so formed with isobornylacrylate and methacrylate with amides. This work describes the synthesis, characterization, reactivity ratios, solution properties, thermal properties and dielectric properties of the copolymes of isobornyl acrylate and methacrylate with N-methyl acrylamide.

EXPERIMENTAL

Manomers: N-methyl acrylamide (Fluka) was recrystallised from chloroform before polymerization. Isobornyl acrylate (Aldrich) and isobornyl methacrylate (Lancaster) was purified by washing with 5% solution of sodium hydroxide twice and subsequently with distilled water for three to four times. Then they are dried over calcium chloride before distilling under reduced pressure. The middle fraction of the distillate is collected and used for copolymerization.

Initiator: 2-2′-Azobisisobutyronitrile (AIBN) (Fluka) was crystallized from methanol.

Solvent: The solvent used in copolymerization was DMF which is a reagent grade chemical. This is dried and purified by distillation before use.

Synthesis of Copolymers

Polymerization was carried out in DMF in the presence of AIBN in sealed glass tubes in an atmosphere of nitrogen at 60 ± 1°C. After a given time, the polymerization mixture was poured into a large amount of water to isolate the polymer, which was filtered and washed thoroughly with water followed by ether and hexane for purification. Then it was dried under vacuum.

Different samples were prepared by changing the initial monomer feed. The initiator is used at 2.5 g/L of solvent.

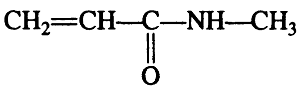
The total monomer concentration was maintained at 1.5 M, while the feed ratio is varied.

The data of composition of feed and copolymers are presented in Table-1.

TABLE-1
LOW CONVERSION COPOLYMERIZATION DATA OF NMA WITH IBA AND IBM

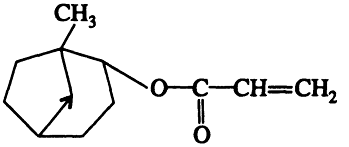
Copolymer system	Mole fraction in the feed		Intensity of N-methyl proton (3H)	Intensity of isobornyl methyl proton (9H)	Copolymer composition	
	NMA (M_1)	IBA/IMB (M_2)			NMA (m_1)	IBA/IBM (m_2)
NMA IBA_1	0.600	0.400	43.846	72.172	0.6457	0.3542
NMA IBA_2	0.666	0.333	63.140	85.382	0.6893	0.3107
NMA IBA_3	0.734	0.266	85.202	94.824	0.7294	0.2706
NMA IBA_4	0.800	0.200	121.551	101.404	0.7824	0.2175
NMA IBA_5	0.867	0.133	116.236	52.263	0.8696	0.1303
NMA IBM_1	0.600	0.400	76.38	130.420	0.6372	0.3627
NMA IBM_2	0.666	0.333	85.580	120.430	0.6800	0.3190
NMA IBM_3	0.734	0.266	93.480	170.020	0.7240	0.2760
NMA IBM_4	0.800	0.200	75.550	58.420	0.7950	0.2049
NMA IBM_5	0.867	0.133	114.030	56.380	0.8585	0.1414

The manomer units are represented as follows:

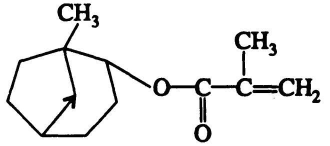


$$CH_2{=}CH{-}\underset{\underset{O}{\|}}{C}{-}NH{-}CH_3$$

N-methyl acrylamide (NMA).



Isobornyl acrylate (IBA)



Isobornyl methacrylate (IBM)

RESULTS AND DISCUSSION

IR spectroscopy

The IR spectrum of copolymer of N-methyl acrylamide and isobornyl acrylate (NMA-CO-IBA) shows the characteristic bands of both the monomer units. Appearance of strong absorption bands at 2950, 1750, 1680 and 1380 cm^{-1} correspond to methylene (—CH—) stretching, >C=O stretching in ester, >C=O stretching in amide and —CH_3 stretching vibration respectively and 3500–3300 cm^{-1} due to —NH— stretching vibrations. The appearance of absorption bands corresponding to ester and amide and the disappearance of absorption band corresponding to olefinic bond is the evidence for the formation of NMA-IBA copolymer.

The infrared spectra of copolymer of N-methyl acrylamide and isobornyl methacrylate (NMA-CO-IBM) show the characteristic absorption bands at 2940, 1740, 1670 and 1380 cm^{-1} correspond to methylene (—CH—) stretching, >C=O stretching in ester, >C=O stretching in amide and —CH_3 stretching vibration respectively and 3500–3350 cm^{-1} due to —NH— stretching vibrations. The appearance of absorption bands corresponding to ester and amide and the disappearance of absorption bands corresponding to olefinic bond is the evidence for the formation of NMA-IBM copolymer.

Determination of Copolymer Composition

The copolymer compositions were determined by ^1H NMR spectra. In ^1H NMR spectra, the distinct peaks due to the methyl groups (*ca.* 0.9 ppm, 9H) of IBA and IBM units and N-methyl group (*ca.* 2.5 ppm, 3H) of the NMA unit are considered for the composition analysis. Since the peak area corresponds to the total number of protons of a particular group, the composition of the copolymer was calculated[10] by % IBA or IBM.

$$\text{in NMA} = \frac{^1\text{H-methyl}/9}{^1\text{H-methyl}/9 + {^1\text{H-N-methyl}}/3} \qquad (1)$$

This equation is based on the fact that the methyl groups of isobornyl unit corresponds to nine protons and N-methyl group of NMA unit to three protons.

Reactivity Ratios

The copolymer composition data was used for the evaluation of reactivity ratios of the NMA-IBA and NMA-IBM copolymers by Fineman-Ross (F-R) and Kelen-Tudos (K-T) methods. The values of reactivity ratios were summarised in Table-2.

TABLE-2
REACTIVITY RATIOS OF NMA WITH IBA AND IBM BY F-R AND K-T METHODS

M_1	M_2	F-R		K-T	
		r_1	r_2	r_1	r_2
NMA	IBA	0.68 ± 0.05	0.20 ± 0.05	0.67 ± 0.01	0.19 ± 0.01
NMA	IBM	0.86 ± 0.05	0.50 ± 0.05	0.84 ± 0.01	0.50 ± 0.01

In the systems studied the reactivity ratio values of NMA are greater than those of IBA and IBM (acrylate and methacrylate) indicating that the copolymer formed will be richer in NMA. The r_1 and r_2 values (Table-2) which are less than 1 suggest that the monomers were arranged in a random sequence. This may be attributed to the steric factor which is enabling the molecule to participate in the reaction. This is unlike the case[11, 12] where the alkyl methacrylates are straight chain compounds whereas here the acrylate and methacrylate contain fused rings.

The rate of polymerizaton depends on the nature of the acrylate and methacrylate, this can be understood from the 1/r values that give a measure of the relative reactivity of the acrylate and methacrylate towards NMA radical. The higher the value of $1/r_1$, the greater the chance that the acrylate and methacrylate will add to NMA radical. The value of $1/r_1$, for NMA-IBA copolymer is 1.4925 and that of NMA-IBM copolymer is 1.1905 which clearly shows that acrylate is more reactive than methacrylate towards NMA; it may be due to the hindrance caused by $—CH_3$ group present at the double bond in the methacrylate.

To ascertain normal copolymer kinetic behaviour the plots of m_1 *vs.* M_1 were drawn, in which m_1 is the mole fraction of NMA in NMA-IBA and NMA-IBM systems. M_1 is that in the feed which is given in Table-1. The shapes of the curves indicate that the azeotropic compositions of the copolymer systems and the distribution of monomeric units are random and in no case a homopolymer formation is expected. The azeotropic compositions for the two systems are also determined by the following equation[13]:

$$N_1 = \frac{(1 - r_2)}{(2 - r_1 - r_2)} \qquad (2)$$

These values of NMA-IBA and NMA-IBM are 0.73 and 0.71 respectively. For the system NMA-IBA the value is 0.73 indicating that the copolymer is richer in NMA below this point and richer is IBA above this point. Similarly, for the system NMA-IBM the value is 0.71 below which the copolymer is richer in NMA and above which it is richer is IBM. This behaviour also suggests the random distribution of manomers in the copolymer.

Table-3 summarises the $\overline{M}_w$ and $\overline{M}_n$ values of the copolymers. These values increase with the increase in the NMA content of the copolymer. This trend is in consonance with variation in intrinsic viscosity. The ratios of $\overline{M}_w$ to $\overline{M}_n$ of all the copolymers are nearly equal to unity. This indicates that the copolymer samples prepared were almost manodispersed in nature.

The concept of solubility parameter helps in explaining the viscosity behaviour of solution, polymer-polymer compatibility, dispersion and tolerance for dilution with non-solvents. Proper solvents can be selected to control the viscosity of polymer solution by using these values. The evaporation of solvent can be adjusted by selecting proper solvents using this solubility parameter concept to get good film with no defects.

Plots of η_{sp}/c against concentration are found to be linear and the intrinsic viscosity values are obtained by extrapolating it to zero concentration. In all the copolymers intrinsic viscosity increases with increase in the NMA content (Table-3). This may be attributed to the greater reactivity of amide radical which facilitates propagation in preference to termination. Thus it can be inferred that with increase in the content of NMA the molecular weight of the copolymer is increasing.

TABLE-3
INTRINSIC VISCOSITIES AND MOLECULAR WEIGHTS OF NMA-IBA AND NMA-IBM COPOLYMERS

Copolytmer	[η] d/g	$\overline{M}_w \times 10^{-5}$	$\overline{M}_n \times 10^{-5}$	$\overline{M}_w/\overline{M}_n$
NMA-IBA$_1$	0.5753	3.890	3.110	1.2
NMA-IBA$_2$	0.6294	4.365	3.571	1.2
NMA-IBA$_3$	0.6834	5.088	4.142	1.2
NMA-IBA$_4$	0.7121	5.870	4.730	1.2
NMA-IBA$_5$	0.7682	6.694	5.107	1.3
NMA-IBM$_1$	0.5291	3.910	3.259	1.2
NMA-IBM$_2$	0.5824	4.423	3.538	1.3
NMA-IBM$_3$	0.6283	4.982	4.058	1.2
NMA-IBM$_4$	0.6473	5.742	4.683	1.2
NMA-IBM$_5$	0.6914	6.481	5.239	1.2

Intrinsic viscosities of the copolymers in different solvents have been determned by using extrapolation method. Solubility parameter values are determined from the plot of intrinsic viscosity against solubility parameter of solvents. Solubility parameter values of NMA-IBA and NMA-IBM have been determined. Solvents which cover a range of solubility parameter from 8.9 to 12.1 $(\text{cal/mL})^{0.5}$ have been selected. The solubility parameter values of NMA-IBA and NMA-IBM are 10.6 and 10.1 $(\text{cal/c})^{0.5}$ respectively (Fig. 1 and 2). From these values it is evident that the solubility parameter value of the acrylate copolymer is more than that of the corresponding methacrylate copolymer.

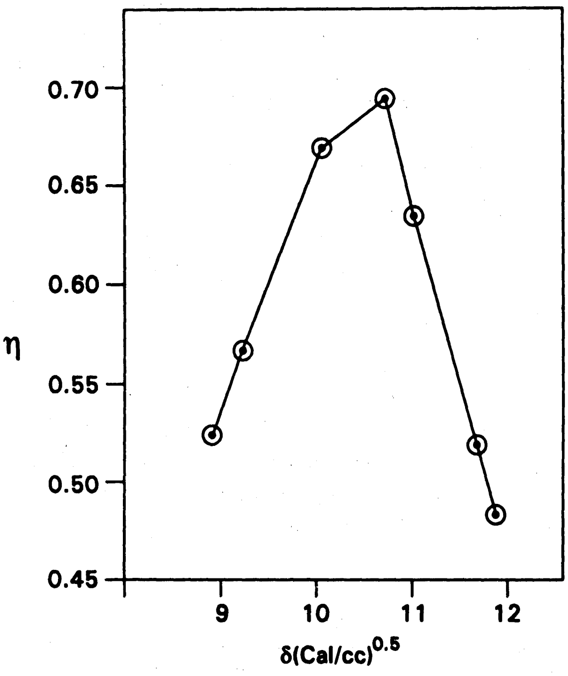


Fig. 1. Plot of intrinsic viscosity of NMA-IBA copolymer 0.66 : 0.33 *vs* .δ of the solvent

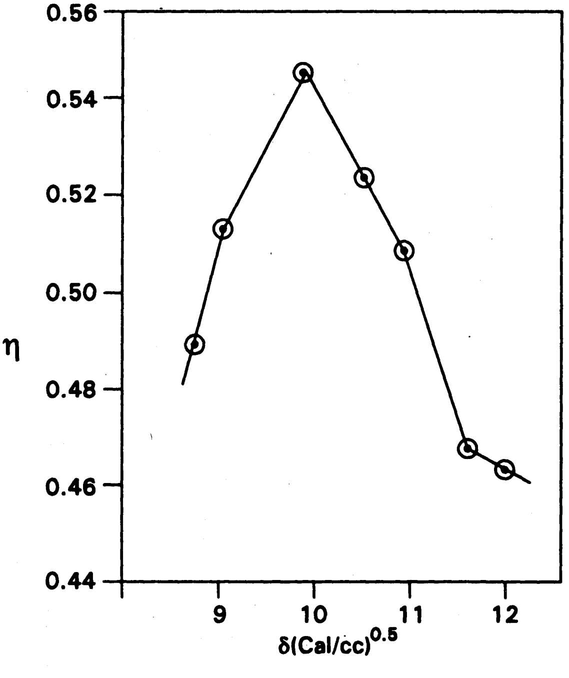


Fig. 2. Plot of intrinsic viscosity of NMA-IBM copolymer (0.80 : 0.20) *vs.* δ of the solvent

The glass transition temperaturees of the copolymers are summarised in Table-4. These values show that the acrylate copolymers posses low T_g values than the methacrylate copolymers. This increasing trend of T_g values from acrylate to methacrylate may be due to α-methyl group in the methacrylate which increases the steric hindrance. Effect of composition of copolymer on T_g was summarised in Table-4. T_g of the copolymer is increasing with increase in the NMA content. Inter- and intramolecular interaction influence T_g. When amide content increases intra and intermolecular interaction increase and the polymer segments become less mobile and T_g occurs at high temperature[14]; chain regidity is increasing with increase in the amide content of the copolymer and thus T_g is increasing.

TABLE-4
VARIATION OF T_g WITH COMPOSITION OF NMA-IBA AND NMA-IBM COPOLYMERS

Copolymer	T_g (°C)	Copolymer	T_g (°C)
NMA-IBA$_2$	87.21	NMA-IBM$_1$	92.41
NMA-IBA$_3$	89.38	NMA-IBM$_2$	104.43
NMA-IBA$_4$	92.00	NMA-IBM$_3$	105.39
—	—	NMA-IBM$_4$	118.35

Thermal stability of the copolymers NMA-IBA and NMA-IBM are determined. The relative thermal stabilities are evaluated by the comparison of the initial decomposition temperature (IDT), the integral procedural decomposition temperature (IPDT) and decomposition temperature at 50% weight loss. In these copolymers, the factors that can influence thermal stability are (a) backbone structure (b) nature of the acrylate and methacrylate and (c) amide content.

To obtain a comparative picture of relative thermal stability, initial decomposition temperature, integral procedural decomposition temperature and decomposition temperature for 50% weight loss are summarised in Table-5.

TABLE-5
THERMAL BEHAVIOUR OF NMA-IBA AND NMA-IBM COPOLYMERS

Copolymers	IDT (°C)	IPDT (°C)	Temperature (°C) at 50% wt. loss
NMA-IBA$_2$	50.48	290.01	333.30
NMA-IBA$_3$	65.77	335.91	358.20
NMA-IBA$_4$	82.61	369.82	374.30
NMA-IBM$_2$	53.85	300.00	319.98
NMA-IBM$_3$	65.62	291.00	323.31
NMA-IBM$_4$	92.55	131.32	329.97

The thermal stabilities of NMA-IBM copolymers are found to be more than those of NMA-IBA copolymers. This is evident from IDT and IPDT values of these copolymers. This may be attributed to the stability of the radicals formed by the decomposition process.

The typical plot of ε^1 and tan δ against temperature for NMA-IBA$_3$ (Fig. 3) shows that ε^1 and tan δ are unaffected by temperatures up to 80°C. Beyond that

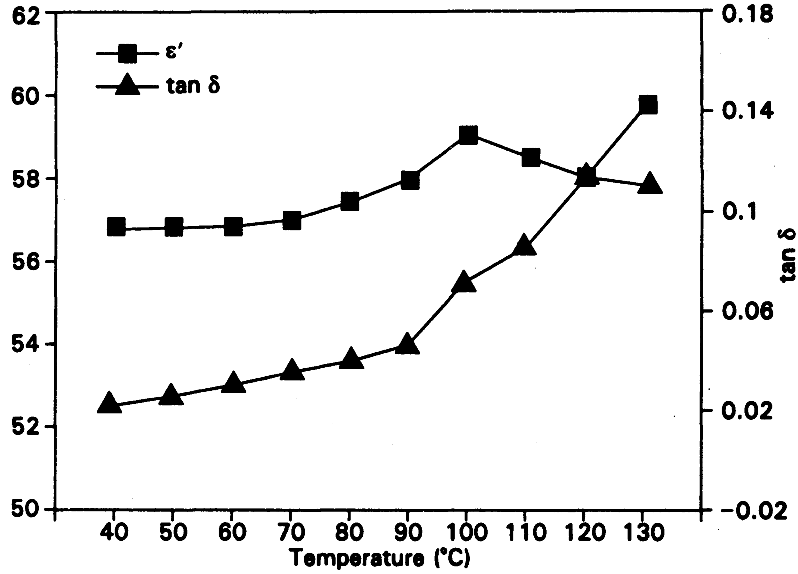


Fig. 3. Typical plot of ε' and tan δ against temperature for NMA-IBA$_3$ copolymer

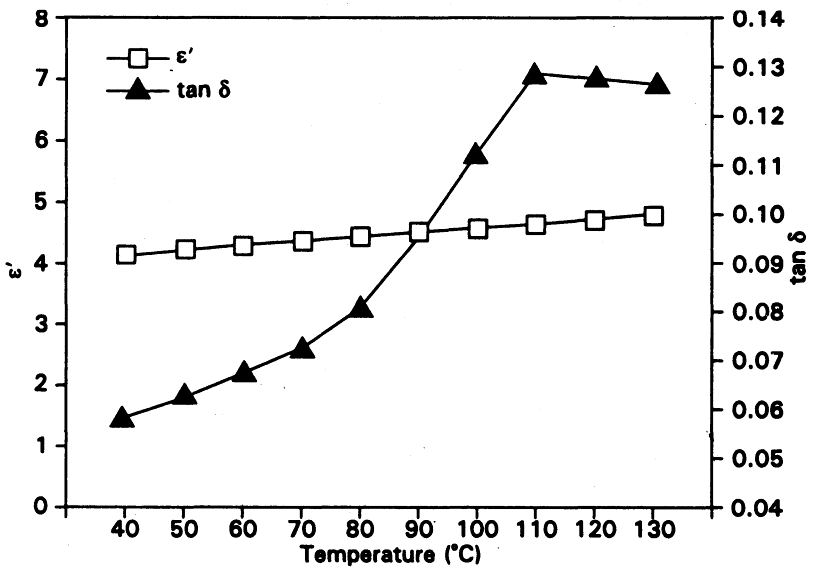


Fig. 4. Typical plot of ε' and tan δ against temperature for NMA-IBM$_3$ copolymers

region, both ε^1 and tan δ are increased. A peak due to relaxation is observed in tan δ, known as α relaxation, at about 100°C, in the rubbery state of the polymer[15, 16]. This temperature is higher than T_g for the polymer obtained by a static method. At lower temperature, molecular chains are not only immobile but also tightly bound at some points because of dipole-dipole interactions[17]. As the temperature is raised, more and more dipole groups are released and the mobility of polymer segments increases.

A similar plot for NMA-IBM$_3$ (Fig. 4) shows a similar behaviour but the α relaxation is at about 110°C. This might be due to the presence of relatively bulkier group present in the IBM unit than in IBA unit.

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(*Received*: 17 June 2002; *Accepted*: 19 August 2002) AJC-2825