Asian Journal of Chemistry Vol. 18, No. 4 (2006), 2799–2808

Synthesis and Characterization of Copolymers of Acrylonitrile with Isobornyl Acrylate and Methacrylate

S. SRIDEVI, T. SREELATHA and P. RAGHUNATH RAO*
Department of Chemistry
Kakatiya University, Warangal-506 009, India

Free radical copolymerization of acrylonitrile with isobornyl-acrylate (IBA) and isobornyl methacrylate (IBM) has been investigated in N,N-dimethyl formamide at 60 ± 1°C using 2,2-azobisisobutyronitrile (AIBN) as an initiator by ^{1}H NMR analysis. The monomer reactivity ratios were computed by both Fineman-Ross (F-R) and Kelen-Tudos (K-T) methods. The reactivity of acrylate was found to be more than that of methacrylate towards acrylonitrile. The reactivity ratio values suggest 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 structural units were evaluated. The molecular weights of the polymers were determined by gel permeation chromatography. The molecular weights of the copolymers increase with the increase of the acrylonitrile content. The solubility parameters were determined with viscometric method. The solubility parameter values of acrylate copolymer are more than the corresponding methacrylate copolymer. 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 T_g values of acrylate copolymers are less than the corresponding methacrylate copolymers. Thermal stability of IBM copolymers is found to be more than that of IBA copolymers. The dielectric properties of the copolymers were also studied. The dielectric loss of the copolymers is found to be shifting to a higher temperature from acrylate to methacrylate copolymers.

Key Words: Acrylonitrile, Isobornyl acrylate, Isobornyl methacrylate, Copolymerization, Reactivity ratios.

INTRODUCTION

The copolymers of isobornylacrylate and methacrylate seem to show high tensile strength, elongation at break and upper service temperature[1]. Introduction of isobornylacrylate and methacrylate into various copolymers seems to modify and improve the properties of a copolymer[2–5]. In our earlier communication[6], the copolymers of isobornyl acrylate and methacrylate with N,N-dimethyl acrylamide have been discussed.

This work describes the synthesis, characterization, reactivity ratios, solution properties, thermal and dielectric properties of the copolymers of isobornyl acrylate and methacrylate with acrylonitrile.

EXPERIMENTAL

Monomer: Acrylonitrile (AN) was recrystallized 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.

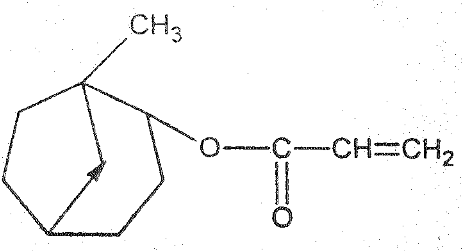
Solvent: The solvent used in copolymerization was DMF which is a reagent grade chemical. This is dried and purified by distillation before use.

Synthesis of copolymers: Polymerization was carried out in N,N-dimethyl formamide (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 copolymer, 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.

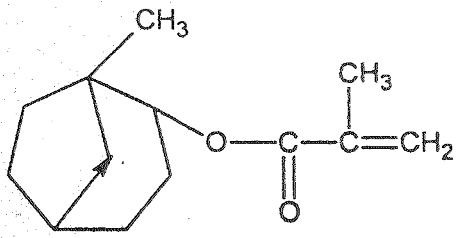
The monomer unit structures are represented as follows:

$H_2C{=}CH{-}CN$

Acrylonitrile



Isobornyl acrylate (IBA)



Isobornyl methacrylate (IBM)

RESULTS AND DISCUSSION

IR spectrum of copolymer of acrylonitrile and isobornyl acrylate (AN—CO—IBA) shows the characteristic bands of both the monomer units. Appearance of strong absorption bands at 2960, 1718, 2244, 1385 cm^{-1} corresponds to methylene (—CH) stretching, >C═O stretching in ester and cyano (—CN) and (—CH_3) methyl stretching vibration, respectively. The appearance of absorption bands corresponding to >C═O and —CN groups and the disappearance of absorption bands corresponding to olefinic bond is the evidence for the formation of ANIBA copolymer.

TABLE-1

LOW CONVERSION COPOLYMERIZATION DATA OF AN WITH IBA AND IBM

Copolymer system	Mole fraction in the feed		Intensity of vinyl proton (3H) (M_1)	Intensity of isobornyl methyl proton (9H) (M_2)	Copolymer composition	
	AN (M_1)	IBA/IBM (M_2)			AN (m_1)	IBA/IBM (m_2)
AN-IBA$_1$	0.867	0.133	8.69	72.06	0.8925	0.1075
AN-IBA$_2$	0.800	0.200	11.809	75.67	0.865	0.135
AN-IBA$_3$	0.734	0.266	18.94	85.32	0.818	0.182
AN-IBA$_4$	0.666	0.333	28.17	94.23	0.770	0.230
AN-IBA$_5$	0.600	0.400	39.71	105.23	0.726	0.274
AN-IBM$_1$	0.867	0.133	10.714	50.83	0.7892	0.210
AN-IBM$_2$	0.800	0.200	9.053	35.67	0.7462	0.2538
AN-IBM$_3$	0.734	0.266	25.24	79.62	0.6829	0.3171
AN-IBM$_4$	0.666	0.333	31.77	89.25	0.644	0.358
AN-IBM$_5$	0.600	0.400	47.74	98.24	0.514	0.485

IR spectra of copolymer of AN and isobornyl methacrylate (AN—CO—IBM) show the characteristic abosorption bands at 2950, 1716, 2241 and 1380 cm^{-1} correspond to methylene (—CH) stretching, >C=O stretching in ester, cyano (—CN) stretching vibrations and —CH_3 stretching vibration. The appearance of absorption bands corresponding to —CN and >C=O and the disappearance of absorption bands corresponding to olefinic bond is the evidence for the formation of ANIBM copolymer.

Determination of copolymer composition

The copolymer compositions were determined by ^{1}H NMR spectra. The distinct peaks due to methyl groups (*ca.* 0.9 to 1.0 ppm, 9H) of IBA and IBM units and CH_2 protons of IBA and IBM units appearing as a doublet at 1.6–1.9 ppm and methylene protons appearing as a triplet at 2.5–3 ppm of the acrylonitrile 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[7] by % IBA or IBM.

$$\text{in AN} = \frac{{}^{1}\text{H-methyl}/9}{{}^{1}\text{H-methyl}/9 + {}^{1}\text{H-methylene}/3}$$

This equation is based on the fact that the methyl group of isobornyl unit corresponds to nine protons and methylene group of AN unit to three protons.

Reactivity ratios

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

TABLE-2

REACTIVITY RATIOS OF AN 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
AN	IBM	0.688	0.16	0.622	0.18
AN	IBM	0.641	0.20	0.631	0.19

In the systems studied the reactivity ratio values of AN are greater than those of IBA and IBM (acrylate and methacrylate) indicating that the copolymer formed will be richer in AN. The product of r_1r_2 values (Table-2), which are less, suggests 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[8, 9] where the alkyl acrylonitriles are straight chain compounds whereas here the acrylate and methacrylate contain fused rings.

The rate of polymerization 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 AN radical. The higher the value of $1/r_1$, the greater the change that the acrylate and methacrylate will add to AN radical. The value of $1/r_1$ for AN-IBA copolymer is 1.5847 and that of AN-IBM copolymer is 1.4105, which clearly shows that acrylate is more reactive than methacrylate towards AN. 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 ploys of m_1 *vs.* M_1 were drawn, in which m_1 is the mole fraction of AN in AN-IBA and An-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. The azeotropic compositions for the two systems are also determined by the following equation[10]:

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

These values of AN-IBA and AN-IBM are 0.708 and 0.687, respectively. For the system AN-IBA, the value indicates that the copolymer is richer in AN below this point and richer in IBA above this point. Similarly, for the system AN-IBM value is 0.687 below which the copolymer is richer in AN and above which it is richer in IBM. This behaviour also suggests the random distribution of monomers in the copolymer.

Sequence length distribution

The mean sequence lengths $\overline{n_1}$ and $\overline{n_2}$ for AN-IBA and AN-IBM copolymer systems have been calculated. Table-3 shows the mean sequence lengths $\overline{n_1}$ and $\overline{n_2}$ for M_1 and M_2 units calculated using equations suggested by Expenyong[11]. For example, at 86.7% AN (13.3% IBA) in the monomer mixture each copolymer segment with M_1 units was approximately five times longer than its adjoining segment with M_2 units. The sequence may be expressed as . . . 2111112 . . . .

This difference between n_1 and n_2 values is increased from 33.3–40.0% to 86.7% of AN. Thus, we can say that AN has a tendency to form more segments than IBA. Hence IBA acts as a retarder in the copolymerization.

TABLE-3

MEAN SEQUENCE LENGTH DISTRIBUTION OF AN-IBA AND AN-IBM COPOLYMERIZATION

Copolymer	$[M_1]$ mol %	$\bar{n}_1$	$\bar{n}_2$	$\bar{n}_1/\bar{n}_2$	$n_1 : n_2$	Distribution
AN-IBA	40.00	1.946	1.1200	1.7375	2 : 1	2112
	33.30	2.262	1.0950	2.0750	2 : 1	2112
	26.60	2.741	1.0680	2.5660	3 : 1	21112
	20.00	3.524	1.0475	3.3600	3 : 1	21112
	13.30	5.110	1.0291	4.9650	5 : 1	2111112
AN-IBM	40.01	1.993	1.1200	1.7790	2 : 1	2112
	33.30	2.324	1.0900	2.1321	2 : 1	2112
	26.60	2.826	1.0650	2.6536	3 : 1	21112
	20.00	3.648	1.0450	3.4900	4 : 1	211112
	13.30	5.8154	1.0270	5.8100	6 : 1	21111112

In case of AN-IBM at 86.7% AN (13.3% IBM) in the monomer mixture each copolymer segment with M_1 units was approximately six times longer than its adjoining segment with M_2 units. The increase in number of AN units in the copolymer with increase in AN in the feed is relatively more than that of AN-IBA system. Thus, the retarding effect of methacrylate is more than that of acrylate.

The number of AN units in copolymer increases with increase in [AN] in the feed, but this is not so for IBA and IBM. Thus IBA and IBM act as retarders in the copolymerization. The ratios of the mean sequence lengths distribution $\bar{n}_1/\bar{n}_2$, which theoretically correspond to the ratio m_1/m_2, where m_1, m_2 are the corresponding compositions of M_1 and m_2 in the copolymer for each monomer mixture, for AN-IBA (or) AN-IBM copolymerization are given in Table-3.

The microstructure of a copolymer is defined by the distribution of the various lengths of the M_1 and M_2 sequences, that is, the sequence-length distributions. The probabilities or mole fractions $(N_1)_X$ and $(N_2)_X$ of forming M_1 and M_2 sequence of length X are given by

$$(N_1)_X = P_{11}^{X-1}, P_{12} \qquad (1)$$

$$(N_2)_X = P_{22}^{X-1}, P_{21} \qquad (2)$$

where the terms P_{11}, P_{12}, P_{22}, P_{21} have the usual significance[12]. Eqns. (1) and (2) allow one to calculate the mole fractions of different lengths of M_1 and M_2 sequences. Figs. 1 and 2 show the sequence-length distributions for AN-IBA and AN-IBM copolymerization respectively of 0.6/0.4 and 0.734/0.266 feed compositions.

From Fig. 1 the most plentiful sequence is M_1 at 51.38% with 24.95, 12.12, 5.89, 2.82, 1.39%, respectively for diad, triad, tetrad, pentad, hexad, M_1 sequences. There are smaller amounts of longer M_1 sequences present in the polymer chain. The distribution for M_2 sequences is much narrower for the less reactive M_2 monomer. Single M_2 units are by far the most plentiful sequence in M_1 at 88.8% with 9.97 and 1.113% respectively of diad and triad sequences for AN-IBA system from feed composition. Similarly, for AN-IBM system from Fig. 2 the most plentiful sequence is M_1 at 35.38% with 22.85, 14.76, 9.53, 6.1 and 3.98% respectively for diad, trad, tetrad, pentad, hexad, heptad, octad, nonad and smaller amounts of longer M_1 sequences. Single M_2 units are by far the most plentiful: 93.88% with 5.74% of diad and 0.33% of triads present in the polymer chain.

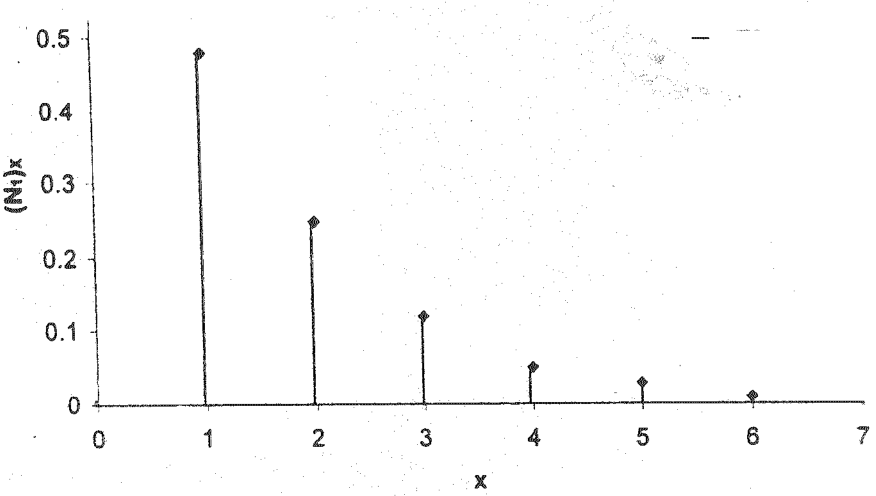


Fig. 1. Sequence-length distribution of AN-IBA copolymer; feed composition 0.60/0.40

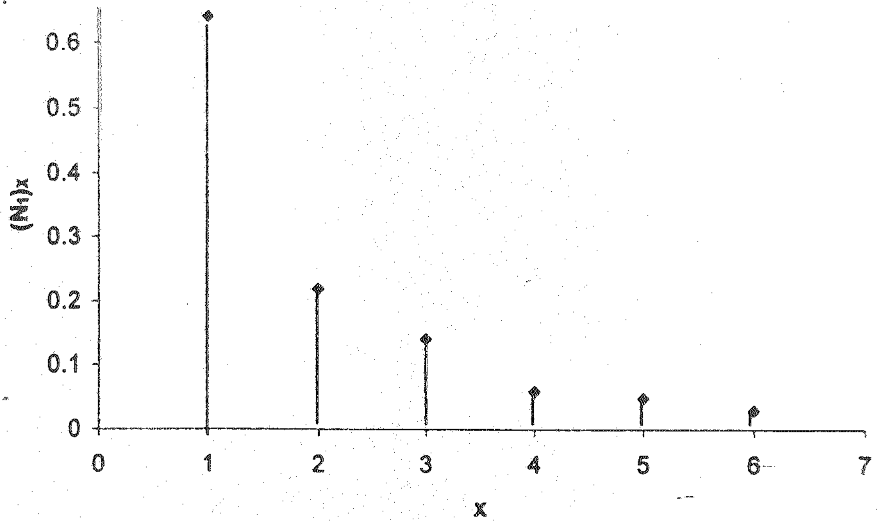


Fig. 2. Sequence-Length Distribution of AN-IBM copolymer; Feed Composition 0.734/0.266

Table-4 summarizes the M_w and M_n values of the copolymers. These values increase with the increase in the AN 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 monodispersed in nature.

TABLE-4
INTRINSIC VISCOSITIES AND MOLECULAR WEIGHTS OF AN-IBA AND AN-IBM COPOLYMERS

Copolymer	[n] d/g	$\overline{M}_w \times 10^{-5}$	$\overline{M}_n \times 10^{-5}$	$\overline{M}_w/\overline{M}_n$
AN-IBA$_1$	0.92	4.3319	2.5961	1.6600
AN-IBA$_2$	0.89	4.2261	2.2261	2.5458
AN-IBA$_3$	0.69	4.0156	2.1996	1.8250
AN-IBA$_4$	0.62	3.9562	2.1978	1.8400
AN-IBA$_5$	0.61	3.7965	2.0511	1.8500
AN-IBM$_1$	0.85	6.9831	4.6633	1.4900
AN-IBM$_2$	0.73	6.1341	4.0894	1.5000
AN-IBM$_3$	0.64	5.5602	3.7068	1.5000
AN-IBM$_4$	0.61	5.0664	3.3552	1.5100
AN-IBM$_5$	0.56	4.1231	2.7143	1.5100

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 the 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 AN content (Table-4). This may be attributed to the greater reactivity of nitrile radical, which facilitates propagation in preference to termination. Thus it can be inferred that with increase in the content of AN the molecular weight of the copolymer is increasing.

Intrinsic viscosities of the copolymers in different solvents have been determined by using extrapolation method. Solubility parameter values are determined from the plot of intrinsic viscosity against solubility parameter of solvents. Solubility parameter values of AN-IBA and AN-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 AN-IBA and AN-IBM are 11.0 and 1.06 $(\text{cal/c})^{0.5}$ respectively (Figs. 3 and 5). From these values it is evident that the solubility parameter value of the acrylate copolymer is more than that of the corresponding methacrylate copolymer.

The glass transition temperatures of the copolymers are summarized in Table-5. These values show that the acrylate copolymers possess lower 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 summarized in Table-5. T_g of the copolymer is increasing with increase in the AN content. Inter- and intra-molecular interactions influence T_g. When nitrile content increases, intra- and inter-molecular interaction increase and the polymer segments become less mobile and T_g occurs at higher temperature[13]; chain rigidity is increasing with increase in the nitrile content of the copolymer and thus T_g is increasing.

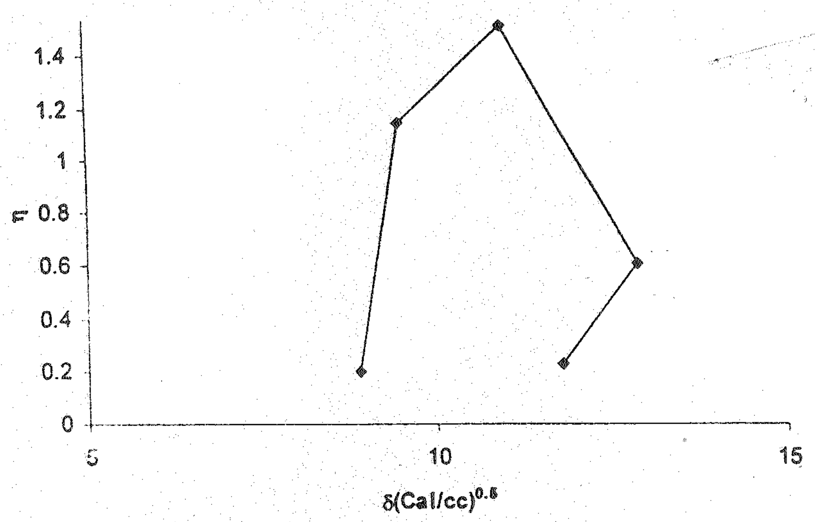


Fig. 3. Plot of intrinsic viscosity of AN-IBA copolymer 0.60/0.40

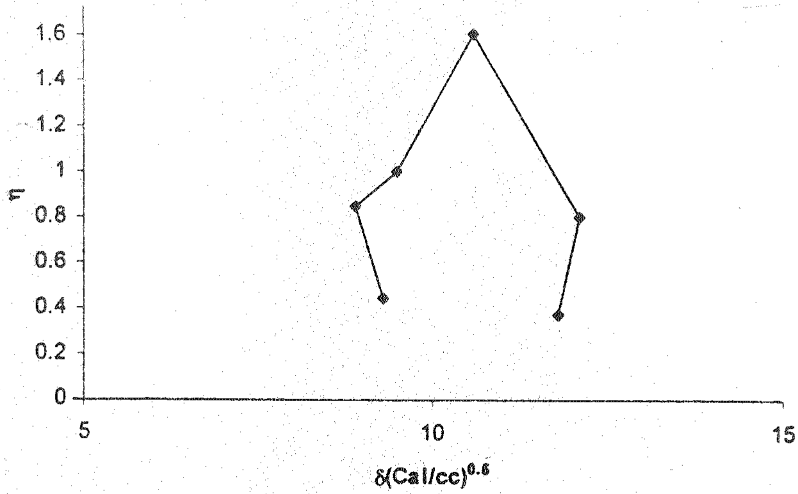


Fig. 4. Plot of intrinsic viscosity of AN-IBM copolymer 0.734/0.266

TABLE-5

VARIATION OF T_g WITH COMPOSITION OF AN-IBA AND AN-IBM COPOLYMERS

Copolymer	T_g(C)	Copolymer	T_g(C)
AN-IBA$_1$	120.69	AN-IBM$_1$	153.51
AN-IBA$_2$	125.69	AN-IBM$_2$	167.44
AN-IBA$_3$	129.05	AN-IBM$_3$	168.64

Thermal stability of the copolymers AN-IBA and AN-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 strucutre (b) nature of the acrylate and methacrylate, and (c) nitrile 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 summarized in Table-6.

TABLE-6
THERMAL BEHAVIOUR OF AN-IBA AND AN-IBM COPOLYMERS

Copolymer	IDT (°C)	IPDT (°C)	Temperature (°C) at 50% wt. loss
AN-IBA$_1$	202.00	366.56	432.34
AN-IBA$_2$	175.37	312.13	405.62
AN-IBA$_3$	169.58	219.80	350.89
AN-IBM$_1$	234.56	344.21	532.55
AN-IBM$_2$	215.24	325.47	413.14
AN-IBM$_3$	190.62	313.99	367.40

The thermal stabilities of AN-IBM copolymers are found to be more than those of AN-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 plots of ε and tan δ against temperature for AN-IBA$_2$ (Fig. 5) show that ε and tan δ are unaffected by temperatures up to 120°C. Beyond that region, both ε and tan δ are increased. A peak due to relaxation is observed in tan δ, known as α-relaxation, at about 135°C, in the rubbery state of the polymer[14, 15]. 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[16]. As the temperature is raised, more

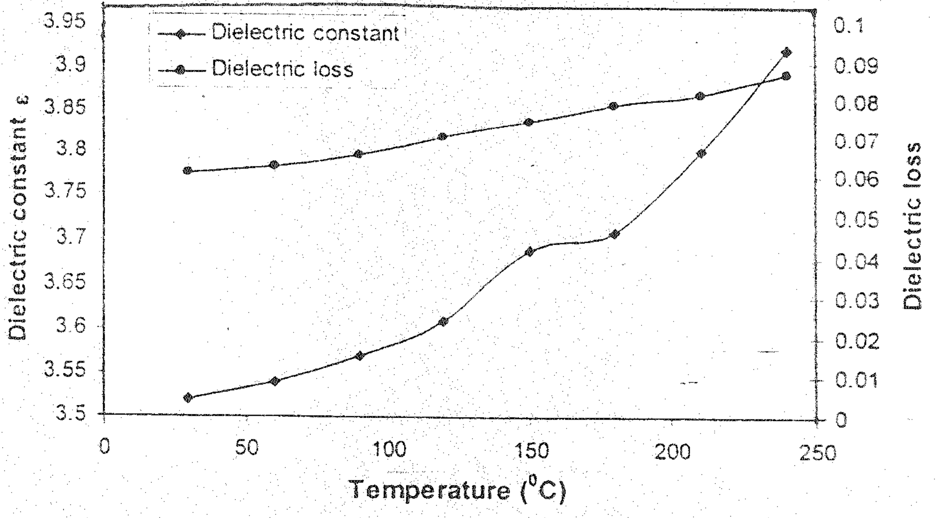


Fig. 5. Typical plot of ε and tan δ against temperature for AN-IBA

and more dipole groups are released and the mobility of polymer segments increases. A similar plot for AN-IBM$_2$ (Fig. 6) shows a similar behaviour but the α-relaxation is at about 145°C. This might be due to the presence of relatively bulkier group present in the IBM unit than in IBA unit.

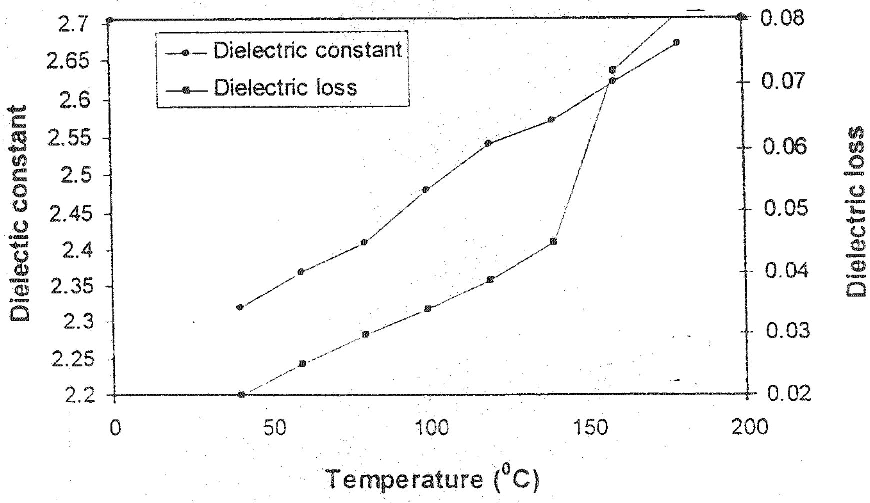


Fig. 6. Typical plot of ε and tan δ against temperature for An-IBM copolymers

ACKNOWLEDGEMENTS

One of the authors (Sridevi) thanks the Principal, Aurora Degree College for encouragement and Head, Department of Chemistry, for providing facilities.

REFERENCES

1. J.M. Yu, Ph. Dubois and R. Jerome, *Macromolecules*, **30**, 6536 (1997).
2. S.C. Fu and K.H. Hsien, *J. Polym. Sci., Part A: Polym. Chem.*, **38**, 954 (2000).
3. P. J. Miller, Matyjaszewshi, Krozysztof, P. Jeffrey, K. Guido and D. Steve, *Polym. Prepr.* (Am. Chem. Soc. Div. Polym. Chem.), **40**, 424 (1999).
4. Kim, Jin-Back, Choi, Jae-Hak, Kim, Hyunwoo, Kwon, Young-Gil, Polymer Journal Society of Polymer Science, Japan (Tokyo), 31, 695.
5. Matyjaszewshi, Krozysztof, Miller and J. Peter, *Macromolecules*, **32**, 6526 (1999).
6. T. Sreelatha and P. Raghunatha Rao, *Proc. Natl. Acad. Sci., Sec. A* (in press).
7. E. Raji Reddy and P. Raghunath Rao, *J. Polym. Mater.*, **11**, 279 (1994).
8. B. Srinivasulu, P. Raghunath Rao and E.V. Sundaram, *J. Polym. Mater.*, **8**, 175 (1991).
9. B. Srinivasulu and P. Raghunath Rao, *Die Angewandte Makromole Kulare Chemie*, **51**, 192 (1991).
10. V.R. Gowrikar, N.V. Viswanathan and J. Sreedhar, Poly. Sci. New Age International Limited, New Delhi, 206 (1996).
11. K.I. Ekpenyong, *J. Polym. Sci., Polym. Chem. Ed.*, **23**, 125 (1985).
12. M. Veda, T. Suzuki, M. Takabashi, Zao Baugli and K. Koyama, *Macromolecules*, **19**, 558 (1986).
13. A. Tager, *Physical Chemistry of Polymers*, **11**, 319 (1978).
14. A. Adam, *Kolloid Zeitschrift Zeitshrift Polym.*, **180**, 11 (1962).
15. A. Tanaka and Y. Ishida, *J. Phys. Soc. (Japan)*, **15** (1960).
16. A.K. Gupta, R.P. Singhal and A.K. Agarwal, *Polymer*, **22**, 285 (1981).

(*Received*: 29 August 2005; *Accepted*: 25 April 2006) AJC-4802