

# Reactivity Ratios and Thermal and Dielectric Studies of *n*-Butyl Methacrylate and Methacrylamide Copolymers

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## SYNOPSIS

Free-radical copolymerization of *n*-butyl methacrylate (B) and methacrylamide (M) was carried out in the presence of 2,2'-azobisisobutyronitrile (AIBN) in dimethyl formamide (DMF) at 60°C. The percentage composition of the copolymers was established by elemental analysis. The reactivity ratios as determined by the Finemann-Ross (F-R) and the Kelen-Tüdös (K-T) methods are  $r_1$  (B) =  $2.75 \pm 0.01$ ,  $r_2$  (M) =  $0.2 \pm 0.01$  and  $r_1 = 2.70 \pm 0.05$ ,  $r_2 = 0.19 \pm 0.02$ , respectively. The copolymers were characterized by IR, <sup>1</sup>H-NMR, thermal, and dielectric studies. Glass transition temperature ( $T_g$ ) values were determined by DSC. Dielectric studies were carried out to understand the segmental motions and the effect of composition on dielectric loss. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

Acrylic copolymers have acquired prime importance in various avenues of industrial applications.<sup>1-3</sup> They serve as basic materials for the preparation of formulations that are used as base and top coats in the leather industry. Saini et al.<sup>4</sup> studied the free-radical copolymerization of methacrylamide and methyl methacrylate. Copolymerization of methacrylamide with methyl methacrylate,<sup>5</sup> sodium methacrylate,<sup>6</sup> methacrylic acid,<sup>7</sup> and methyl vinyl ketone<sup>8</sup> were also studied. Copolymerization of methacrylamide with acrylamide, methyl acrylate, and methacrylic acid were also studied by various workers.<sup>9</sup> In our earlier work, we reported the copolymerizations of methacrylamide with ethyl methacrylate<sup>10</sup> and acrylamide with *n*-butyl methacrylate.<sup>11</sup> In the present investigation, reactivity ratios were determined to discover the type of copolymers formed and thermal properties were studied to assess the thermal stability of the copolymer as a function of composition. In addition, dielectric studies were carried out to investigate segmental motions and

the effect of frequency and composition on dielectric loss.

The degradation of *n*-butyl methacrylate (B)-methacrylamide (M) copolymers in which the reaction between neighboring units in the polymer chain plays a significant part in the degradation process was undertaken. Previously reported examples have included the homopolymers polyacrylamide,<sup>12</sup> polymethacrylamide,<sup>13</sup> and the copolymer systems methacrylic acid-methacrylonitrile,<sup>14</sup> vinyl chloride-methyl methacrylate,<sup>15,16</sup> methyl methacrylate-methacrylic acid,<sup>17</sup> and methacrylamide with methyl methacrylate.<sup>18</sup>

## EXPERIMENTAL

*n*-Butyl methacrylate (B) (Aldrich) was freed from the inhibitor by 5% sodium hydroxide and water and dried over calcium chloride and distilled twice under reduced pressure. Methacrylamide (M) (Merck) was crystallized from chloroform before polymerization. 2,2'-azobisisobutyronitrile (AIBN) (Fluka) was crystallized by methanol. DMF was reagent grade and was purified by distillation before use.<sup>19</sup>

All the experiments were performed in glass tubes that were filled with dry monomers, solvent, and

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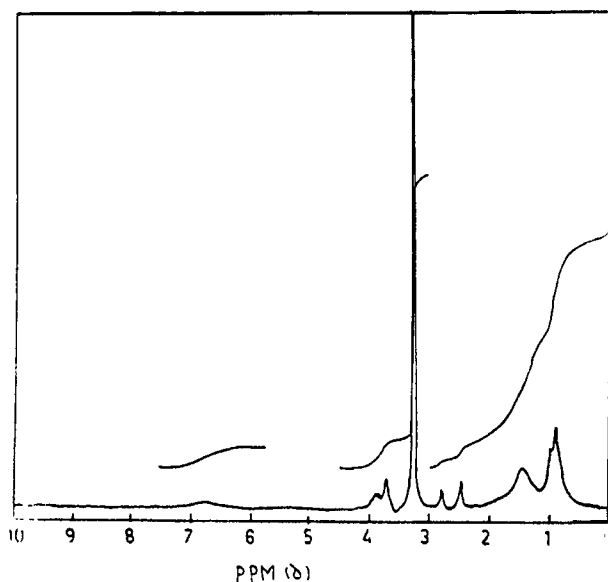


Figure 1  $^1\text{H-NMR}$  of BM copolymer.

initiator. The total monomer concentration was maintained at 1.25  $M$ , while the ratio  $[\text{B}]/[\text{M}]$  was varied. The initiator was used at 0.6 g/L of solvent. The tubes were then sealed in a nitrogen atmosphere and immediately introduced into the thermostat at 60°C temperature. The reaction was to proceed to less than 10% conversion, and the copolymers were precipitated using the excess volume of water as nonsolvent. The residue was filtered, washed, and dried. Reprecipitation was done from DMF solution.

The copolymers were characterized by IR and  $^1\text{H-NMR}$  spectroscopy. The IR absorptions were obtained in a KBr disc using a Perkin-Elmer Model 283 spectrophotometer.  $^1\text{H-NMR}$  spectra were recorded from  $\text{DMSO-}d_6$  solution using an 80 MHz Varian spectrometer.

The nitrogen content of the copolymer samples was determined by a Carlo-Erba Model 1106 ele-

mental analyzer to obtain data on the copolymer compositions. The  $r$ -values for the B-M system in DMF were obtained by Fineman-Ross<sup>20</sup> (F-R) and Kelen-Tüdös<sup>21</sup> (K-T) methods.

The glass transition temperatures,  $T_g$ , of the copolymers were determined by differential scanning calorimeter (DSC) using V2.2A DuPont 9900. For each DSC experiment, 1–2.5 mg samples were used with a heating rate of 8°C/min.

Thermogravimetric analysis (TGA) was done using V2.2A DuPont 9900 in air at a heating rate of 8°C/min. Powdered samples, 13–21 mg, were used. Copolymers with three varying feed ratios were analyzed thermally. Integral procedural decomposition temperature<sup>22</sup> (IPDT) values calculated from the TG curves were used to compare the thermal stabilities of polymers.

A systematic study of dielectric constant ( $\epsilon$ ) and dielectric loss ( $\tan \delta$ ) over a wide range of frequency and temperature was carried out. Dielectric measurements were made with a GR 1620 A capacitance bridge in the frequency range  $10^2$ – $10^5$  Hz and temperature range 30–150°C. Polymer samples were taken in the form of pellets pressed at a constant pressure. Aluminum foils were used on either side of the samples to ensure good contact and to improve the air gaps between the samples and electrodes. The samples were dried before measurements. Temperature was measured using a copper-constantan thermocouple.

## RESULTS AND DISCUSSION

The IR spectra of copolymers show strong absorptions bands at 2960, 1720, 1660, and 1470  $\text{cm}^{-1}$ , corresponding to methylene C—H stretching, carbonyl stretching in ester, carbonyl stretching in amide, and —OCH<sub>2</sub> stretching vibrations, respectively.

Table I Copolymerization of *n*-Butyl Methacrylate–Methacrylamide; Temperature = 60 ± 1°C; AIBN = 0.6 g/L

Copolymer	Feed Composition in Mol Fraction		$N$ (%)	Copolymer Composition in Mol Fraction		$T_g$ (°C)
	$[\text{B}] M_1$	$[\text{M}] M_2$		$[\text{B}] M_1$	$[\text{M}] M_2$	
BM <sub>1</sub>	0.602	0.397	1.90	0.82	0.18	76
BM <sub>2</sub>	0.400	0.599	3.69	0.67	0.33	80
BM <sub>3</sub>	0.302	0.698	4.57	0.61	0.39	83
BM <sub>4</sub>	0.252	0.748	5.35	0.55	0.45	85
BM <sub>5</sub>	0.201	0.798	6.48	0.48	0.52	88

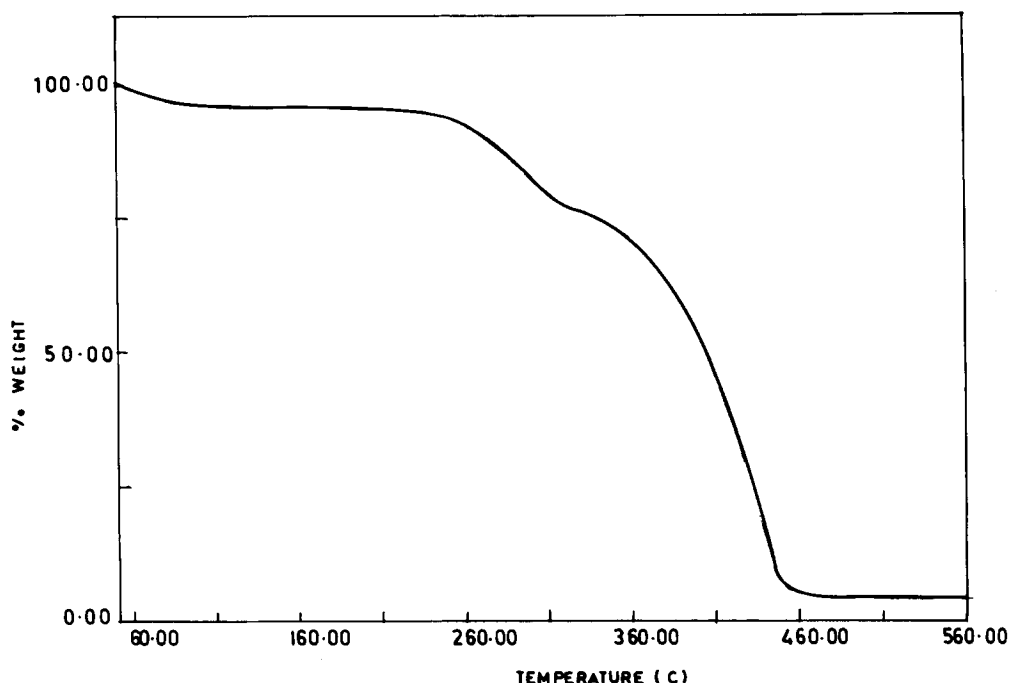


Figure 2 TGA of BM<sub>4</sub> copolymer.

In <sup>1</sup>H-NMR (Fig. 1), —OCH<sub>2</sub> protons of *n*-butyl methacrylate appear at 3.6–4.0 δ.<sup>23,24</sup> β-Methylene protons appear in the region of 1.2–1.9 δ; α-methyl protons and CH<sub>3</sub> protons of the alkyl part of the ester appear at 0.7–1.1 δ. Methylene protons of the alkyl part of the ester appear in the region of 2.4–2.9 δ. Amide protons of methacrylamide appear at 6.2–7.2 δ. The presence of —OCH<sub>2</sub> protons of *n*-butyl methacrylate and amide protons of methacrylamide shows the formation of copolymers.

The composition of the copolymers formed with varying feed composition was determined by nitrogen estimation (Table I). These data were used for the evaluation of reactivity ratios of the B–M system by F–R and K–T methods.

The values of *r*<sub>1</sub> (B) and *r*<sub>2</sub> (M) so obtained were, respectively, 2.75 ± 0.01 and 0.2 ± 0.01 by F–R and 2.70 ± 0.05 and 0.19 ± 0.02 by K–T methods. For this system, the product of *r*<sub>1</sub> and *r*<sub>2</sub> remains less than unity, indicating that the copolymers are weakly ordered with a predominantly random distribution of the monomeric units in the polymer chain. The high value of *r*<sub>1</sub> indicates that the probability of *n*-butyl methacrylate entering into the copolymer chain is higher than that of methacrylamide. The copolymer formed is therefore richer in *n*-butyl methacrylate than in the feed.

The glass transition temperatures (*T*<sub>g</sub>'s) of the copolymers increased with an increase in methac-

rylamide content (Table I). The root cause for such an increase is probably due to the increased intermolecular interactions of amide groups.

The TG curve of the BM<sub>4</sub> copolymer is given in Figure 2. The results of the integral procedural decomposition temperature (IPDT) and the decomposition temperatures for various copolymer compositions are summarized in Table II. It is shown from the table that the first-stage decomposition temperature (IDT<sub>1</sub>) increases with an increase in methacrylamide content in the feed. This may be because higher methacrylamide content in the copolymer facilitates intermolecular hydrogen bonding. The TGA curve shows a two-stage breakdown, in which a significant portion of weight loss is seen at about 260–310°C. At 310°C is a plateau region of stability followed by further degradation to essentially zero weight at 460°C. This is indicative of an

Table II Dielectric Constant (ε) and Thermal Behavior of BM Copolymer

Copolymer	IDT <sub>1</sub> (°C)	IDT <sub>2</sub> (°C)	IDPT (°C)	ε
BM <sub>3</sub>	220.0	335.8	418.04	3.77
BM <sub>4</sub>	230.4	332.7	395.02	3.89
BM <sub>6</sub>	237.1	320.3	364.09	3.54

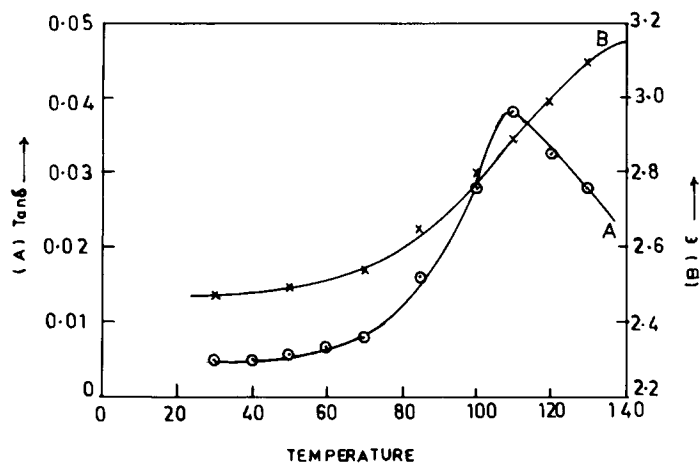


Figure 3 Typical plot of  $\tan \delta$  and  $\epsilon$  vs. temperature for  $BM_3$  copolymer.

imidization process of the methacrylamide with adjacent methacrylamide (to lose  $NH_3$ ) or adjacent *n*-butyl methacrylate (to lose *n*-BuOH) forming the cyclic imide. This process gives an initial weight loss (first step in the TGA curve). The cyclization process (imidization) actually stabilizes the resulting polymer substantially toward further degradation. Further, the TGA weight loss temperatures in air at 1, 10, and 50% from Figure 2 are compared with poly(methyl methacrylate) (PMMA).<sup>18</sup> The initial 1% weight loss temperatures are much lower than that of PMMA because cyclization and devolatilization is the major process. However, the 50% weight loss temperature of the methacrylamide/butyl methacrylate copolymer is significantly higher than that of PMMA due to the stabilization of the partially cyclized polymer by imide groups. Similar observations were made by Jamieson and McNeill<sup>17</sup>

in the two-step TGA decomposition thermogram, which is the result of methyl methacrylate/methacrylic acid copolymers by the anhydridization process. Since the IPDT value is a measure of thermal stability of a polymer, it is evident from the data that the decreasing trend of IPDT values with increasing content of methacrylamide in the copolymers indicates a decrease in thermal stability.

The dielectric constant values measured at room temperature are given in Table II. A plot of  $\epsilon$  and  $\tan \delta$  against temperature for the  $BM_3$  composition (Fig. 3) shows that initially  $\epsilon$  and  $\tan \delta$  are unaffected by temperature up to 70°C. Beyond that region, both  $\epsilon$  and  $\tan \delta$  increase. A peak due to relaxation is observed in  $\tan \delta$ , known as  $\alpha$ -relaxation, at 110°C, in the rubbery state of the polymer.<sup>25,26</sup> This temperature is higher than the glass transition temperature for the polymer obtained by any static method.

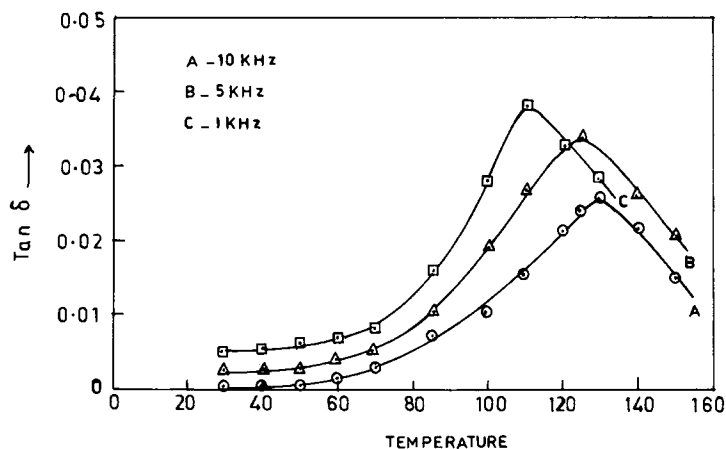


Figure 4 Plot of  $\tan \delta$  vs. temperature at different frequencies for BM copolymer.

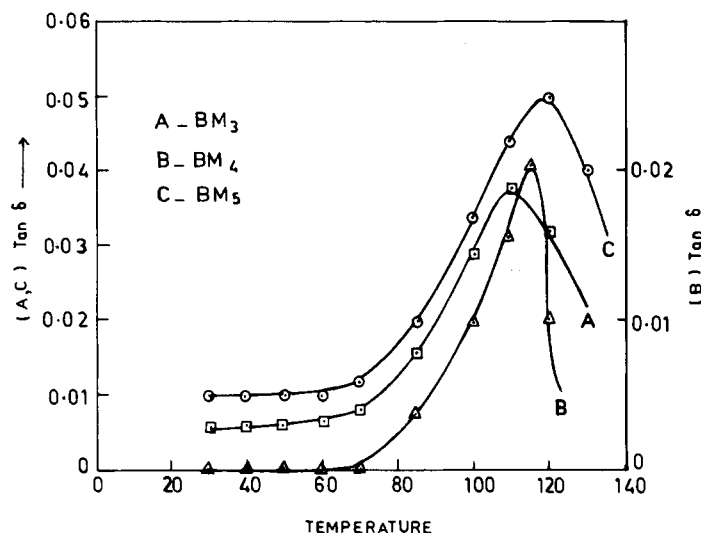


Figure 5 Plot of  $\tan \delta$  vs. temperature for different compositions of BM copolymer.

At lower temperatures, molecular chains are not only immobile but also tightly bound at some points due to dipole-dipole interactions.<sup>27</sup> As the temperature is increased, more and more dipole groups are released and the mobility of polymer segments increases. For BM<sub>3</sub>,  $\tan \delta_{\max}$  is occurring at 110°C at a constant frequency of 1 kHz.

Variation of  $\tan \delta$  with temperature for BM<sub>3</sub> was studied at three different frequencies, namely, 1, 5, and 10 kHz (Fig. 4).  $\tan \delta_{\max}$  is found to shift toward higher temperatures with an increase in the frequency. The absorption maxima are observed at 110, 125, and 130°C for frequencies 1, 5, and 10 kHz, respectively. A similar trend was observed for other compositions.

Variations of  $\tan \delta$  with temperature for different compositions, viz., BM<sub>3</sub>, BM<sub>4</sub>, and BM<sub>5</sub>, at a constant frequency of 1 kHz have been studied (Fig. 5). With an increase in the content of methacrylamide, the  $\tan \delta_{\max}$  values shift toward higher temperatures. The maximum values are observed at 110, 115, and 120°C for BM<sub>3</sub>, BM<sub>4</sub>, and BM<sub>5</sub> compositions, respectively. Dipolesegmental loss depends on the chemical constitution of the polymers, which influences intra- and intermolecular interactions. The greater the intra- and intermolecular interactions, the less mobile are the repeating units and the higher is the temperature at which  $\tan \delta_{\max}$  occurs.<sup>28</sup> Thus, inclusion of a higher number of methacrylamide units into the copolymer leads to a shift in  $\tan \delta_{\max}$  toward higher temperatures.

In conclusion, we can state that  $T_g$  values have been found to increase with an increase in the content of methacrylamide of the copolymer and ther-

mal stability depends on the methacrylamide content of the copolymer. The dielectric constant and loss factor were found to be temperature-dependent.

$\tan \delta_{\max}$  of these copolymers were found to shift toward higher temperatures with increase in the frequency of the electric field and increase in the content of methacrylamide of the copolymer.

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## REFERENCES

1. H. S. Payne, *Organic Coating Technology*, Wiley, New York, 1964, Vol. I, p. 536.
2. C. R. Martens, *Technology of Paints, Varnishes and Lacquers*, Teinhold, New York, 1968, p. III.
3. H. Warson, *The Application of Synthetic Resin Emulsions*, Ernest Bean, London, 1972, p. 215.
4. G. Saini, A. Leoni, and S. Franco, *Makromol. Chem.*, **147**, 213 (1971).
5. E. N. Zilberman, R. A. Novolokina, and N. A. Abramova, *Vysokomol. Swed. Ser. B.*, **25**(4), 279 (1983).
6. A. A. Shubin, V. N. Kisel'nikov, V. V. Vyalkov, and G. N. Shavareva, *Izv. Vyssh. Uchebn. Zaved. Khim. Tekhnol.*, **26**(10), 1249 (1983).
7. S. K. Chatterjee, A. Malhotra, and D. Yadav, *J. Polym. Sci. Polym. Chem. Ed.*, **22**(12), 3697 (1984).
8. N. Yamashita, K. Ikezawa, S. I. Ayukawa, and T. Maeshima, *J. Macromol. Sci. Chem.*, **A21**(5), 621 (1984).
9. J. Brandrup and E. H. Immergut, Eds., *Polymer Handbook*, Wiley-Interscience, New York, 1966.
10. B. Srinivasulu, P. Raghunath Rao, and E. V. Sundaram, *J. Polym. Mater.*, **7**, 77 (1990).

11. B. Srinivasulu, P. Raghunath Rao, and E. V. Sundaram, *Eur. Polym. J.*, **9**, 979 (1991).
12. J. B. Gilbert et al., *Polymer*, **3**, 1 (1962).
13. K. Crauwels and G. Smets, *Bull. Soc. Chim. Belg.*, **59**, 182 (1956).
14. N. Grassie and I. C. McNeill, *J. Polym. Sci.*, **27**, 207 (1958).
15. N. L. Zutty and F. Welch, *J. Polym. Sci. A1*, 2289 (1963).
16. J. Guillot, M. Bert, J. Vialle, and A. Guyot, *Eur. Polym. J.*, **8**, 641 (1972).
17. A. Jamieson and I. C. McNeill, *Eur. Polym. J.*, **10**, 217 (1974).
18. N. Grassie, I. C. McNeill, and J. Samsson, *Eur. Polym. J.*, **14**, 931 (1978).
19. *Vogel's Text Book of Practical Organic Chemistry*, 4th ed., B. S. Furniss and A. J. Hannaford, Eds., ELBS and Longman, London, 1980, p. 277.
20. M. Fineman and S. D. Ross, *J. Polym. Sci.*, **5**, 259 (1950).
21. T. Kelen and F. Tüdös, *J. Macromol. Sci. Chem.*, **A-9**, 1 (1975).
22. C. D. Doyle, *Anal. Chem.*, **33**, 77 (1961).
23. R. M. Silverstein, G. C. Bassler, and T. C. Morrill, *Spectroscopic Identification of Organic Compounds*, 4th ed., Wiley, New York, 1981.
24. S. Pitchumani, C. Rami Reddy, and S. Rajadurai, *J. Polym. Sci. Polym. Chem. Ed.*, **20**, 277 (1982).
25. A. Adam, *Kolloid Z. Z. Polym.*, **180**, 11 (1962).
26. T. Tanaka and Y. Ishida, *J. Phys. Soc., Jpn.*, **15**, 161 (1960).
27. A. K. Gupta, R. P. Singhal, and V. K. Agarwal, *Polymer*, **22**, 285 (1981).
28. A. Tager, *Physical Chemistry of Macromoles*, Mir, 1978, p. 318 Moscow.

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