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Radiation-Induced Copolymerization of Acrylonitrile with Methyl Acrylate: Synthesis and Characterization

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RADIATION-INDUCED COPOLYMERIZATION OF ACRYLONITRILE WITH METHYL ACRYLATE: SYNTHESIS AND CHARACTERIZATION

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ABSTRACT

Radiation-induced copolymerization of acrylonitrile with methyl acrylate was carried out in aqueous medium at room temperature. Different compositions of the copolymer were prepared and characterized by IR, $^1\text{H-NMR}$, thermal, and dielectric studies. NMR spectroscopy was used to determine the composition and stereochemistry of the copolymer. Glass transition temperature values (T_g) were determined by DSC. Dielectric studies were carried out to understand the segmental motions and the effect of composition on dielectric loss.

INTRODUCTION

Acrylonitrile-based copolymers have a variety of applications in the textile industry, housewares, and custom molding products [1, 2]. Acry-

lonitrile homopolymer, because of its combination of high melting point, high melt viscosity, and poor thermal stability, has few applications. By copolymerizing acrylonitrile with other monomers like acrylates, the deficiencies of acrylonitrile homopolymer have been tempered and desirable properties have been achieved [3]. In the present investigation, the spectral, thermal, and electrical properties of acrylonitrile-methyl acrylate (AM) copolymer systems are studied.

EXPERIMENTAL

Acrylonitrile (A) (BDH) and methyl acrylate (M) (BDH) were purified by washing three times with 5% NaOH and then several times with distilled water. The monomers were distilled and stored at low temperatures. All radiation-induced copolymerization reactions were carried out under nitrogen. Cobalt-60, gamma chamber, supplied by the Bhabha Atomic Research Centre, Trombay, with a dose rate of 0.16 ± 0.02 Mrd/h was used for this purpose. All reactions were carried out at room temperature. The monomers were mixed in their reactivity ratio proportions in the presence of water and exposed to radiation. The copolymer sample obtained was purified by dissolving it in dimethylformamide (DMF) and precipitating it with methanol. The purified polymers were dried at 50°C under vacuum to constant weight. Different copolymers were prepared by changing the composition of the initial monomer feed. The acrylonitrile-methyl acrylate copolymers prepared were AM_1 (50:50), AM_2 (60:40), AM_3 (70:30), and AM_4 (80:20).

The copolymers formed were characterized by IR and $^1\text{H-NMR}$ analysis. $\text{DMSO-}d_6$ was used as the solvent in NMR analysis.

The glass transition temperatures, T_g , of the copolymers were determined with a differential scanning calorimeter (DSC) at a heating rate of $10^\circ\text{C}/\text{min}$. Thermogravimetric (TG) analysis was carried out for the AM_1 composition copolymer in a nitrogen atmosphere at a heating rate of $10^\circ\text{C}/\text{min}$. The activation energy for this process was calculated.

A systematic study of dielectric constant (ϵ) and dielectric loss ($\tan \delta$) over a wide range of frequency and temperature was made. Dielectric measurements were made with a GR 1620 A capacitance bridge in the 10^2 – 10^5 Hz frequency range and the 30 – 150°C temperature range. An external oscillator (Agronic) was used at higher frequencies. Polymer samples were taken in the form of pellets pressed at constant pressure. Aluminum foils were used on both sides of the samples to ensure good contact and to remove any air gaps between the sample and the elec-

trodes. The samples were dried before making measurements. The temperature was measured by using a copper-constantan thermocouple and a digital panelmeter.

RESULTS AND DISCUSSION

The IR spectrum of the copolymer sample was recorded between 400–4000 cm^{-1} (Fig. 1). Strong absorption bands at 2950, 2240, 1730, and 1450 cm^{-1} correspond to $>\text{CH}_2$ stretching, $-\text{C}\equiv\text{N}$ stretching, $>\text{C}=\text{O}$ stretching, and $>\text{CH}$ deformation vibrations. The characteristic absorption band of the hydroxyl group shows the formation of OH radicals in the radiolysis of water. This has also been demonstrated by Dainton [4].

The main chain of the AM copolymer contains the following structural units:

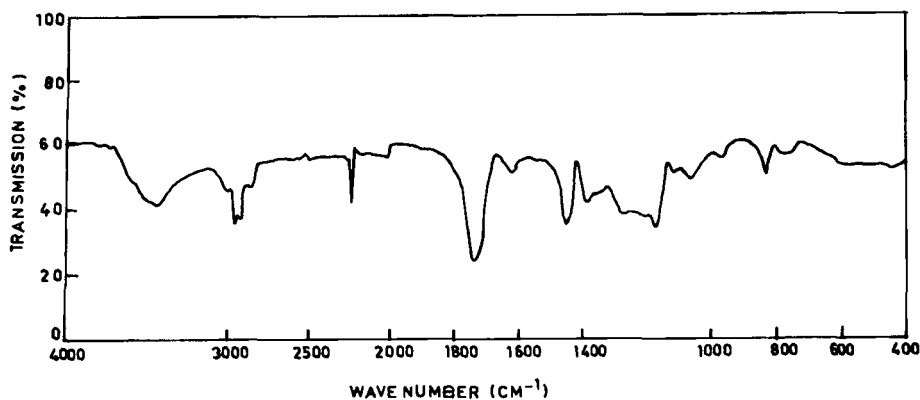
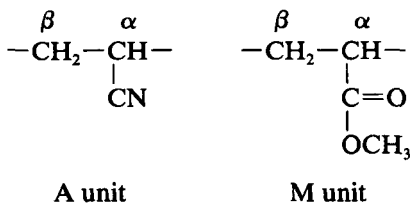


FIG. 1. Typical IR spectrum of AM_1 copolymer.

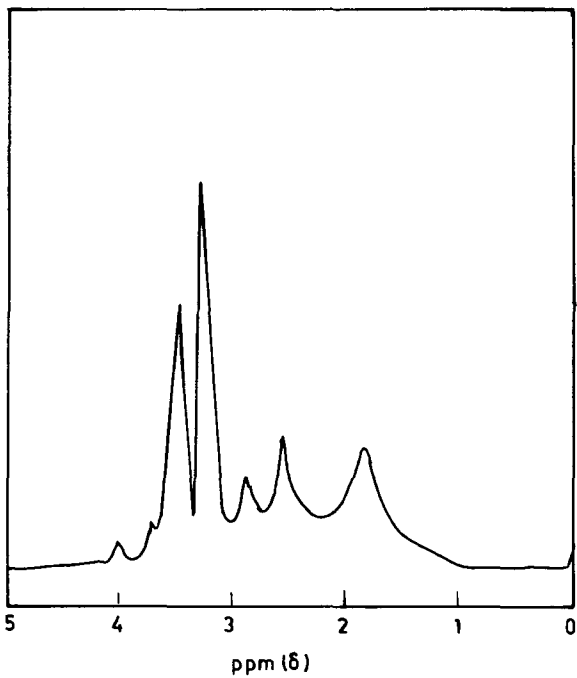


FIG. 2a. $^1\text{H-NMR}$ spectrum of AM copolymer (30:70).

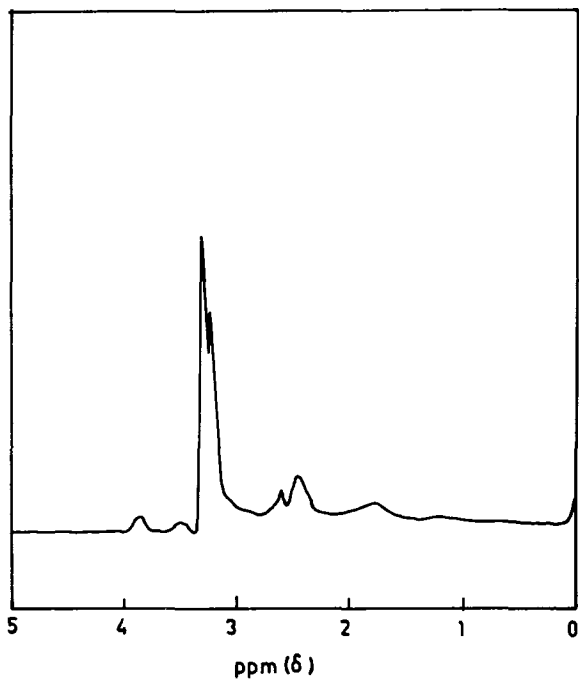


FIG. 2c. $^1\text{H-NMR}$ spectrum of AM_2 copolymer.

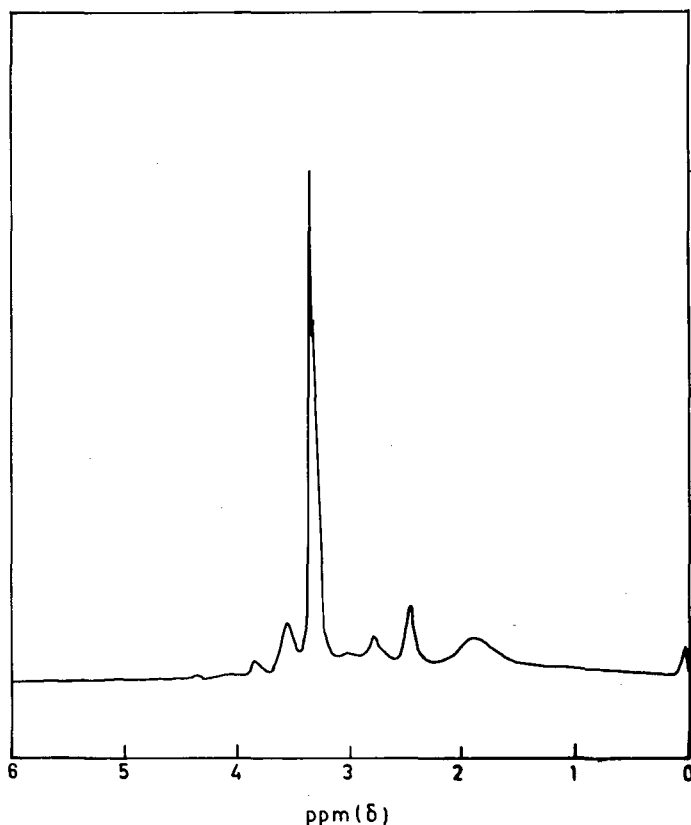


FIG. 2b. ¹H-NMR spectrum of AM₁ copolymer.

The distribution of protons in the two units is an important means of distinguishing the monomers in the copolymer chain. In the above units the chemical environment of the α, β -protons is almost identical. Hence, in the ¹H-NMR spectra of AM copolymers with different compositions, the methylene protons of acrylonitrile merge with the methylene proton signals of methyl acrylate. The situation is similar with methyne protons. Methoxy protons of M appear downfield whereas methylene and methyne protons of A and M appear upfield.

In the ¹H-NMR (Fig. 2b) spectrum of AM₁, the methoxy protons of methyl acrylate appear at 2.6–3.6 δ and the methylene and methyne pro-

tons appear in the 1.7–2.6 δ region. The appearance of methoxy protons as multiple peaks indicates that a copolymer is formed [5, 6]. In the case of the homopolymer of methyl acrylate, methoxy protons appear as a single peak. Compositional analysis of the copolymer has been made using the methoxy proton signal of methyl acrylate in relation to the rest of the main-chain protons from the $^1\text{H-NMR}$ spectra (Figs. 2a and 2c). Triad distribution in the copolymers of acrylonitrile (A) and methyl acrylate (M) has been studied by using the three methoxy signals centered at 3.5 δ , 3.2 δ , and 2.8 δ , which are assigned to MMM, MMA, and MAM types of triads, respectively [7].

From the $^1\text{H-NMR}$ spectra it is observed that the integration magnitude of peaks at 3.5 δ and 2.8 δ decreases while that at 3.2 δ increases with a decrease in the methyl acrylate content in the feed. This type of dependence of intensities with composition was observed by Ito et al. [6]. The location of the MMM peak corresponds to the methoxy peak in poly(methyl acrylate).

Theoretically, there are four kinds of triads along a copolymer chain, i.e., MMM, MMA, AMM, and AMA. Each triad may be written as consisting of four kinds of configurations by employing the representation of Nishioka et al. [5, 8] (see Fig. 3). The appearance of methoxy protons as three peaks suggests that it is possible to distinguish three main kinds of methyl acrylate units spectroscopically as suggested by Bovey [9].

Structures (1), (2), (3), (4), (6), (7), and (10) constitute the peak at 3.5 δ . In Structures (6), (7), and (10), A units are opposite those of the central M units of interest, so diamagnetic shielding by such A units may be small. Structures (11) and (12) are responsible for 3.2 δ , and Structures (5), (8), and (9) are responsible for the peak at 2.8 δ [10].

The glass transition temperatures of the copolymers increase with increasing acrylonitrile content (Table 1). Thermogravimetric analysis of the copolymers showed a single-stage weight loss. The rate of weight loss (dw/dt) was calculated from the thermogram, and when it was plotted against the temperature (Fig. 4), the activation energy for decomposition was found to be 158.4 kJ/mol by using the method of Kharkhanawala et al. [11].

The dielectric constant values measured at room temperature were found to be independent of frequency; the values are given in Table 1. Typical plots of ϵ and $\tan \delta$ against temperature for AM₄ composition (Fig. 5) show that initially ϵ and $\tan \delta$ are unaffected by temperatures up to 100°C. Beyond that, both ϵ and $\tan \delta$ increase. A peak due to relaxation, known as α -relaxation, is observed in $\tan \delta$ at 140°C in the rubbery

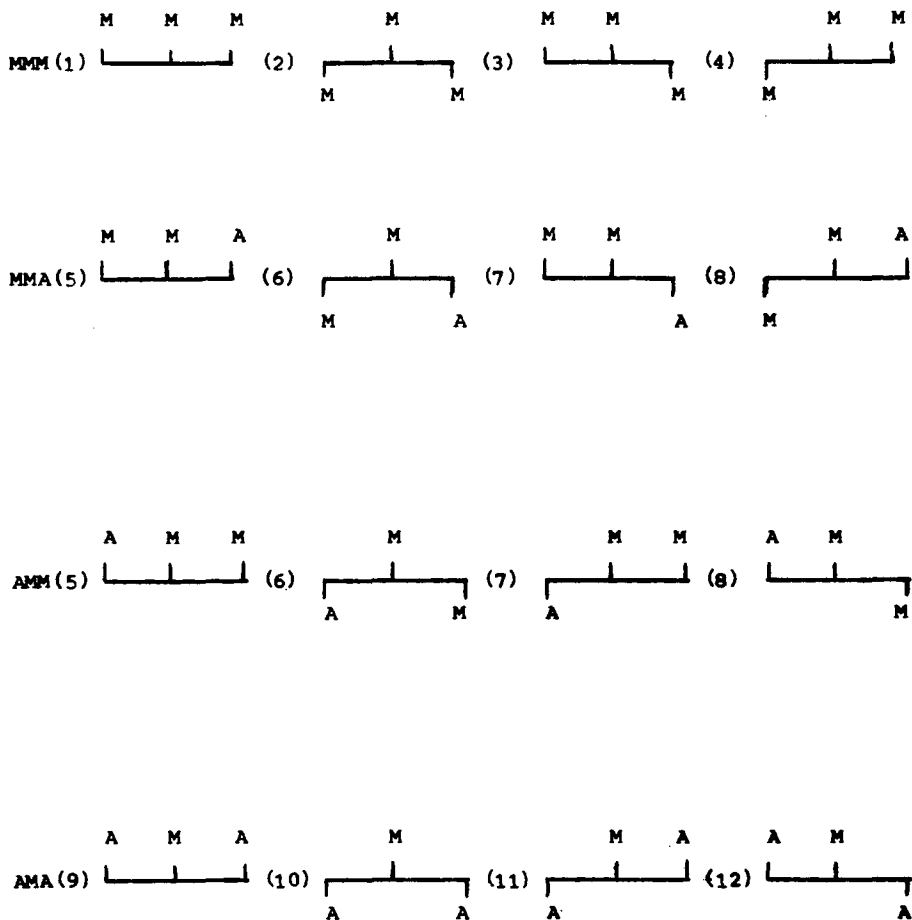
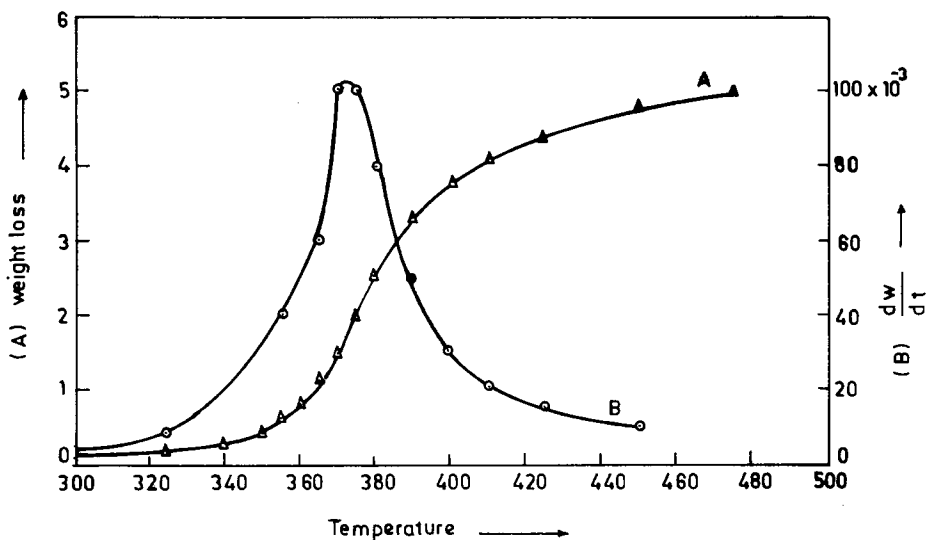


FIG. 3. Four kinds of configurations.

polymer state [12, 13]. This temperature is higher than the glass transition temperature of the polymer obtained by any static method. At lower temperatures the molecular chains are not only immobile but are also tightly bound at some points due to dipole-dipole interactions [14]. As the temperature increases, more and more dipole groups are released and the mobility of polymer segments increases. For AM_4 , $\tan \delta_{\max}$ occurs at 140°C at a constant frequency of 50 kHz.

TABLE 1

Copolymer	Mole fraction of A in feed	Mole fraction of A in AM	Conversion, %	T_g	ϵ
AM ₁	0.50	0.36	8.3	70.43	2.45
AM ₂	0.60	0.46	9.0	72.96	2.57
AM ₃	0.70	0.62	8.7	81.20	2.53
AM ₄	0.80	0.70	9.3	—	2.45

FIG. 4. Plot of (dw/dt) against temperature for AM₁ copolymer.

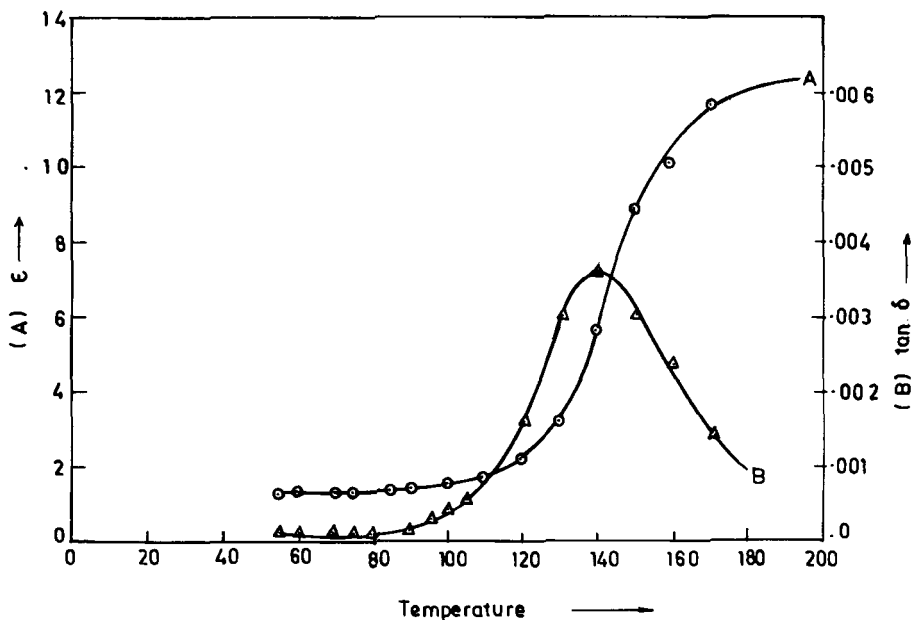


FIG. 5. Typical plot of ϵ and $\tan \delta$ against temperature for AM_4 copolymer.

Variation of $\tan \delta$ with temperature for AM_1 was studied at 1, 5, 10 and 50 kHz (Fig. 6). $\tan \delta_{\max}$ was found to shift toward higher temperatures with an increase in frequency. Absorption maxima were observed at 95, 100, 107, and 116°C for frequencies of 1, 5, 10, and 50 kHz, respectively. A similar trend was observed for other compositions.

The variations of $\tan \delta$ with temperature for AM_1 , AM_2 , AM_3 , and AM_4 at a constant frequency of 50 kHz was studied (Fig. 7). The $\tan \delta_{\max}$ value shifts toward higher temperatures with an increase in acrylonitrile content. Maximum values are observed at 116, 123, 128, and 140°C for AM_1 , AM_2 , AM_3 , and AM_4 , respectively. Dipole-segmental loss depends on the chemical constitution of polymers, and this 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. The exchange of nonpolar or less polar substituents for polar substituents increases intra- and intermolecular interactions [15]. Thus, inclusion of a larger number of acrylonitrile

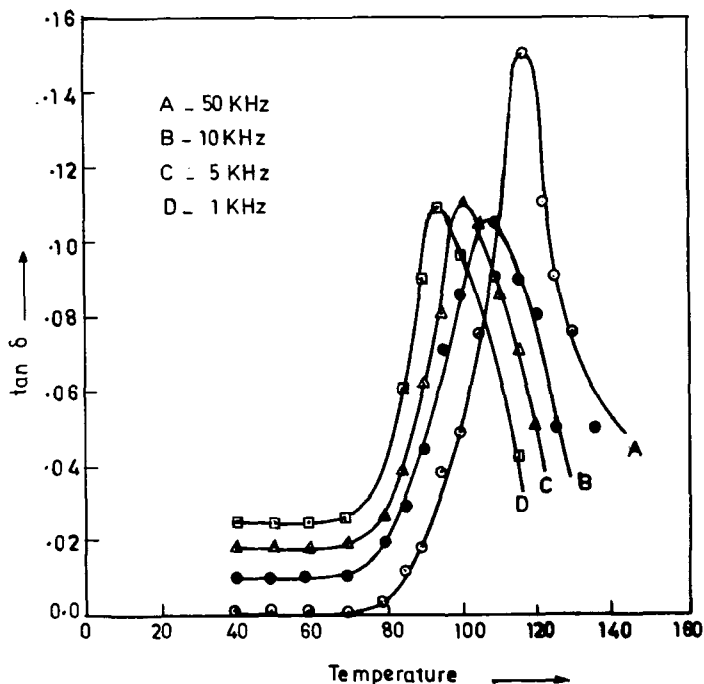


FIG. 6. Plot of $\tan \delta$ against temperature at different frequencies for AM₁ copolymer.

units into a copolymer leads to a shift in $\tan \delta_{\max}$ toward higher temperatures. The rigidity of the polymer chain increases as the number of $-\text{CN}$ substituents in the copolymer grows [16]. Thus, the kinetic rigidity of a polymer chain results in a shift of the $\tan \delta_{\max}$ temperature.

CONCLUSIONS

The methoxy peak of methyl acrylate in $^1\text{H-NMR}$ is shown to be useful in composition and microstructure analyses of acrylonitrile copolymers. Evidence for copolymer formation is provided by the appearance of methoxy protons as a triplet. T_g values increase with an increase in the acrylonitrile content of the copolymer. The dielectric constant and loss

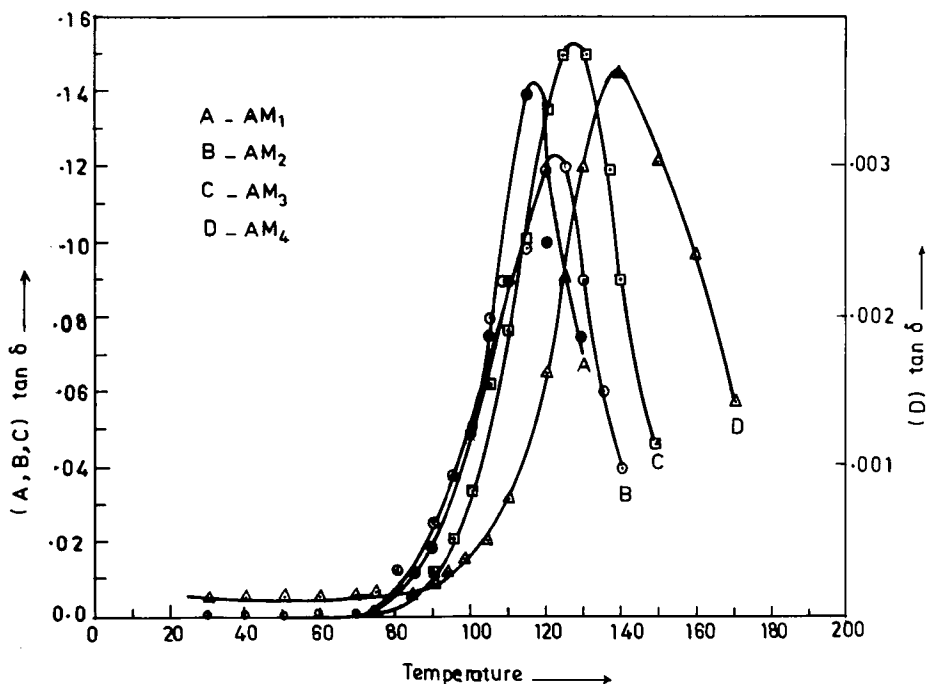


FIG. 7. Plot of $\tan \delta$ against temperature for different compositions of AM copolymer.

factor were found to be temperature dependent. The $\tan \delta_{\max}$ values of these copolymers were found to shift toward higher temperatures with an increase in the frequency of the electric field and the acrylonitrile content of the copolymers. The variation in T_g with copolymer composition was in consonance with $\tan \delta_{\max}$ variation.

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