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Novel Copolymers of N-(4-Bromophenyl)-2-Methacrylamide with 2-Acrylamido-2-Methyl-1-Propanesulfonic Acid

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The new acrylamide monomer, N-(4-Bromophenyl)-2-methacrylamide (BrPMAAm) has been synthesized by reacting 4-Bromoaniline with methacryloyl chloride in the presence of triethylamine(NR_3) at 0–5°C. The radical-initiated copolymerization of (BrPMAAm), with 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) has been carried out in dimethylformamide (DMF) solution at 70 ± 1°C using 2,2′-azobisisobutyronitrile (AIBN) as an initiator with different monomer-to-monomer ratios in the feed. The copolymers were characterized by FTIR, ^{1}H- and ^{13}C-NMR spectroscopy. The copolymer composition was evaluated by nitrogen content (N for AMPS-units) in polymers led to the determination of reactivity ratios. The monomer reactivity ratios for BrPMAAm (M_1)-AMPS (M_2) pair were computed using the Fineman-Ross (F-R), Kelen-Tüdös (KT) and Extended Kelen-Tüdös (EKT) methods. These parameters were also estimated using a non-linear computational fitting procedure, known as reactivity ratios error in variable model (RREVM). The mean sequence lengths determination indicated that the copolymer was statistically in nature. By TGA and DSC analyses, the thermal properties of the polymers have been studied. The antimicrobial effects of polymers were also tested on various bacteria, and yeast.

Keywords: N-(4-bromophenyl)-2-methacrylamide; thermogravimetric analysis; monomer reactivity ratios; antimicrobial effects

1 Introduction

Several studies have been done in our laboratories on the synthesis of N-monosubstituted (meth)acrylamides (1–3) and their radical copolymerization with commercial monomers. These studies clearly show that the nature, as well as position of the substituent, had a large effect on monomer reactivity ratios, glass transition temperatures and antimicrobial properties. Copolymers with reactive or functional monomers are gaining importance steadily. The potentially wide range of applications for functionalized polymeric materials has made these materials important. In recent years, some comprehensive work has been published on functional monomers and their polymers (4–7). 2-Acrylamido-2-methyl-1-propanesulphonic acid (AMPS) is a relatively strong acid (8) that has had a wide variety of applications (as the acid or its salts or as a comonomer) including packaging films (9), foam stabilizers (10), photographic materials (11), and water absorbents (12, 13). Copolymers with 2-acrylamido-2-methyl-1-propane sulfonic acid (AMPS) was found to be highly useful. Copolymers of AMPS with ethylene dimethacrylate have been used to make contact lenses (14), and poly(AMPS-graft-styrene) gives self-reinforced hydrogels (15). The understanding of copolymerization kinetics has gained great importance in recent decades. Because of this fact, the prediction of monomer reactivity ratios becomes a valuable quantitative aspect. Moreover, copolymerization is an important and useful way to develop new materials. Copolymerization modulates both the intramolecular and intermolecular forces exercised between like and unlike polymer segments. Therefore, properties such as the glass transition temperature, melt point, solubility, crystallinity, permeability, adhesion, elasticity, and chemical reactivity may be varied within wide limits (16). Most existing procedures for calculating reactivity ratios can be classified as linear least-squares (LLS), and non-linear least-squares (NLLS) methods. It is accepted that LLS methods such as those proposed by Finemann and Ross (17), and by Kelen and Tüdös (18), can only be applied to experimental data at sufficiently low conversion, because the calculation is based on the differential copolymerization equation (19, 20). The only LLS method, as an exception, is an extended Kelen-Tüdös method (21), which involves a rather more complex calculation.

The copolymerizability of vinyl monomers with a bulky substituent that also carries a highly electronegative atom

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like nitrogen and, electronegative halogen like bromo is not yet discussed. The possible effect of such a pendant group as the backbone with respect to reactivity is significant. Most of the polymers are produced by free radical polymerization. This technology has advantages such as versatility, simplicity, compatibility with many functional groups, tolerance to impurities as well as polar and non-polar polymerization media. As a disadvantage, the copolymers obtained are, in general, heterogeneous with very limited control over the molar mass, constitution, and chain architecture. The growing market of well-defined materials has become the driving force for the renaissance to study free radical polymerizations in terms of both synthetic possibilities and mechanistic understanding (22, 23).

We report here the synthesis and characterization of BrPMAAm monomer, as well as homopolymer and copolymers of BrPMAAm with AMPS using different feed ratios. The copolymer composition was determined by elemental analysis. The effect of BrPMAAm content on the thermal properties of resulting copolymers was investigated. Homopolymer and copolymers were also tested for their antimicrobial properties against microorganisms such as *Staphylococcus aureus COWAN I*, *Bacillus subtilis ATCC 6633*, *Escherichia coli ATTC 25922*, *Klebsiella pneumonia FMCS*, *Pseudomonas aeruginosa DSM 50071*, and yeast, *Candida tropcalis ATCC 13803*, *Candida globrata ATCC 66032*, and *Candida albicans CCM 314*.

2 Experimental

2.1 Materials

4-Bromoaniline (Merck), methacryloyl chloride (Alfa Aesar), 2-acrylamido-2-methyl-1-propanesulfonic acid (Merck, 99%) was used without further purification.

2,2′-Azobisisobutyronitrile (AIBN) was recrystallized from chloroform-methanol.

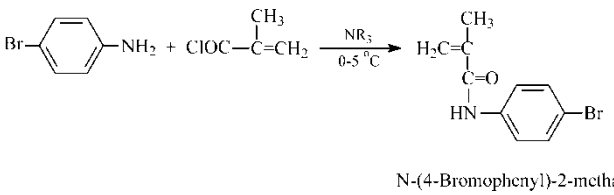
N,N-dimethylformamide, diethylether, and benzene (Merck), were analytical grade commercial products and used as received, unless otherwise noted.

2.2 Synthesis of N-(4-Bromophenyl)methacrylamide (BrPMAAm) Monomer

To a well-stirred solution of 0.1 mole 4-bromoaniline and 0.3 mole of triethylamine in 200 ml N,N-dimethylamine, 0.1 mole of methacryloylchloride was added dropwise under cooling in ice bath (0–5°C), (Scheme 1). After the complete addition of methacryloylchloride, the reaction mixture was stirred for 12 h at room temperature, then filtered and evaporated with a rotavapour. A yellow product was obtained and recrystallized from ethanol as a yellow powder (yield 76%).

2.3 Copolymerization

Homo- and copolymerization were carried out in dimethyl formamide (DMF) using 2,2′-azobisisobutyronitrile (AIBN) as an initiator. Predetermined quantities of N-(4-Bromophenyl)-2-methacrylamide, 2-acrylamido-2-methyl-1-propanesulphonic acid, DMF, and AIBN were mixed in a round-bottomed flask equipped with mechanical stirrer and reflux condenser. The solution was purged with nitrogen for about 10 min, and the reaction mixtures were purged again for several minutes prior to heating. The reaction mixture was heated at 70°C with constant stirring. The mixtures were then cooled to room temperature and slowly poured, with constant stirring, into a large excess of diethylether that was used as a nonsolvent. Solid polymers were purified by repeated precipitation with the diethylether from solution in DMF and finally dried under vacuum.



Sch. 1. Synthesis of N-(4-Bromophenyl)-2-metacrylamide (BrPMAAm).

2.4 Characterization Techniques

Infra-red spectra were measured on a Jasco 460 Plus FT-IR spectrometer. ^{1}H- and ^{13}C-NMR spectra of the polymers were recorded in DMSO-d_6 with tetramethylsilane as the internal standard using a Gemini Varian 200 MHz NMR spectrometer. Thermal data were obtained by using a Setaram Labsys TG-DSC/DTA thermobalance in N_2 atmosphere. Elemental analyses were carried out by a LECO CHNSO-932 auto microanalyzer.

3 Results and Discussion

N-(4-Bromophenyl)-2-metacrylamide (BrPMAAm) was prepared according to Scheme 1.

The structure of N-(4-Bromophenyl)-2-metacrylamide was confirmed by FTIR and ^{1}H- and ^{13}C-NMR spectra. The ^{1}H-NMR and ^{13}C-NMR spectrum of BrPMAAm are shown in Figure 1.

FTIR (cm^{-1}, KBr): 3420 (NH); 3110 and 3046 (=C-H); 2985, 2920 (C-H); 1690 (C=O amide); 1633 (C=C olifinic); 1598, 1500 and 1408 (C=C aromatic); $1380_{(s)}$ and $1445_{(as)}$ (CH_3 bending); 806, 735 and 700 (C-H out of plane bending); 496 (C=C out of plane bending).

^{1}H-NMR (ppm, TMS in $CDCl_3$): 9.6 (NH, 1H); 7.3 (aromatic, 2H); 7.8 (aromatic, 2H); 5.3 (CH_2=, 1H); 5.8 (CH_2=, 1H); 2.0 (CH_3, 3H).

^{13}C-NMR (ppm, TMS in $CDCl_3$): 168.2 (C=O of amide); 135.0 (=C); 126.0 (=C H_2), 118.2138.1, 142.4 (aromatic carbons); 78.0 ($CDCl_3$); 18.12 (α-methyl C).

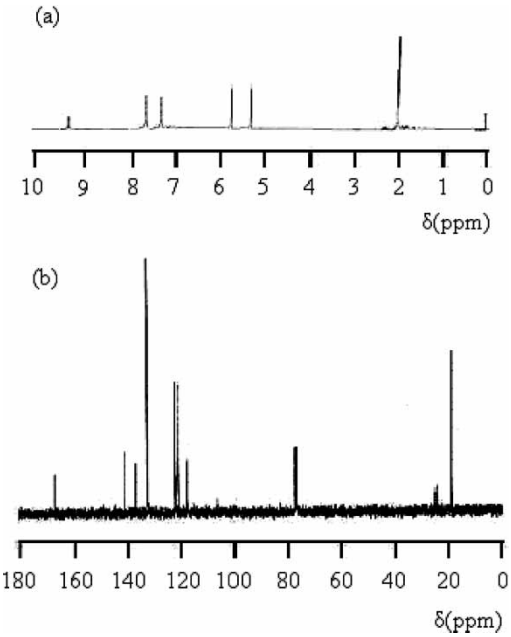


Fig. 1. (a) ^{1}H-NMR and (b) ^{13}C-NMR spectrum of BrPMAAm.

3.1 Copolymer Characterization

The copolymeric units of BrPMAAm with AMPS can be represented according to Scheme 2.

The structures of the copolymers were investigated by infra red spectroscopy. The FTIR spectrum of poly(BrPMAAm-co-AMPS) as an example shows a strong band at 3430 cm^{-1} which is attributed to υ_{NH}, a strong band at 1680 cm^{-1} characteristic for the carbonyl amide and finally a strong band at 1100 cm^{-1} which is attributed to υ_{SO}. The ^{1}H-NMR and ^{13}C-NMR spectrum of poly(BrPMAAm-co-AMPS) [0.47:0.53] and its attributions are shown in Figure 2.

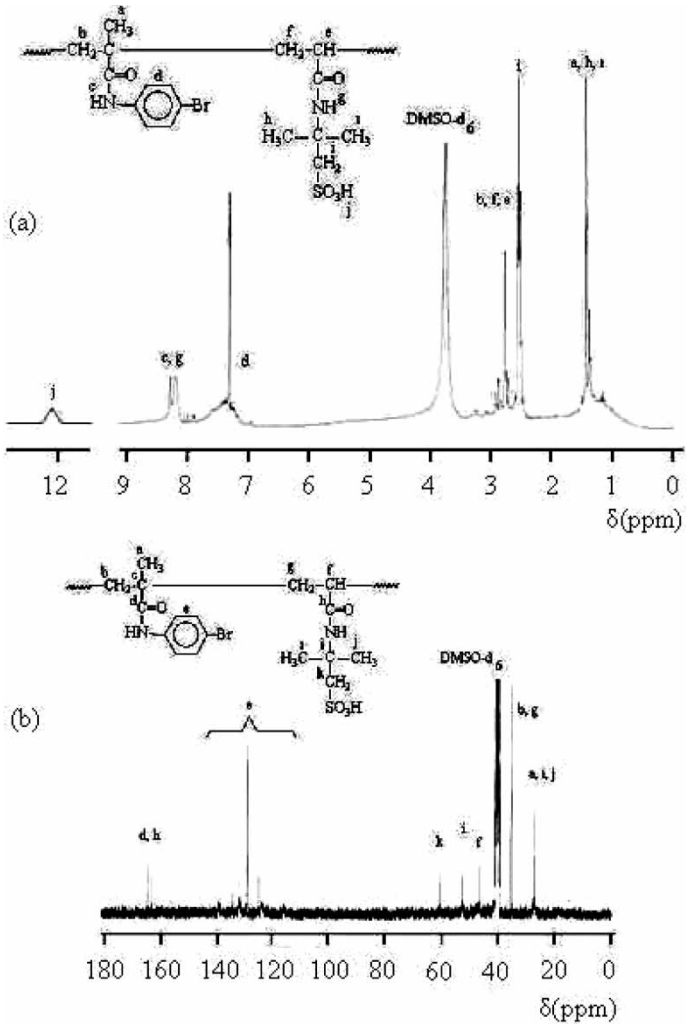
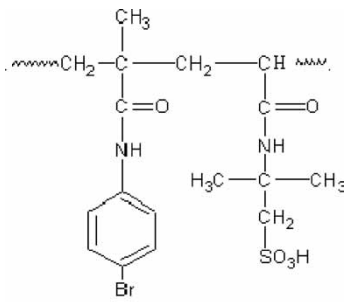


Fig. 2. (a) ^{1}H-NMR spectra and (b) ^{13}C-NMR spectra of copoly(BrPMAAm-co-AMPS); m_1:m_2: [0.47:0.53].

3.2 Copolymer Composition and Monomer Reactivity Ratios

The copolymer compositions of poly(BrPMAAm-co-AMPS) system studied were calculated from sulphur content. The analytical data for copolymerization of BrPMAAm with AMPS as an example are illustrated in Table 1.



poly(BrPMAAm-co-AMPS)

Sch. 2. The structure monomeric units of the copolymer.

The monomer reactivity ratios (r_1 and r_2) were deduced by using Fineman-Ross (17), Kelen-Tüdös (18) and extended Kelen-Tüdös (21) methods. The copolymerization diagram for copolymerization system presented in Figure 3 indicates that the copolymerization proceeds statistically with azeotropic points at molar ratio of 0.4. To determine more reliable values of monomer reactivity ratios, a non-linear error-in-variables model (EVM) method is used utilizing the computer program, RREVM (24). Various statistical treatments of the feed and copolymer compositions can be used to determine monomer reactivity ratios. The nonlinear methodology used selected values of r_1 and r_2, where the sum of the squares of the differences between the observed and the computed polymer compositions was minimized. With this criterion for the nonlinear least-squares method of analysis, the values for the monomer reactivity ratios were unique for a given set of data. The program produces monomer

Table 1. Summary of composition, solubility parameters and DSC parameters of the Poly(BrPMAAm-co-AMPS) System[a]

Sample	M_{BrPMA}[b]	m_{BrPMA}[c]	Conv. (%)	δ (cal/cm^3)$^{1/2}$	T_g (°C)[d]	ΔH_o^d (J/g)[d]	ΔCp (J/g · K)[d]
Copoly-1	0.10	0.25	10.4	12.64	128	1.8088 (Endo)	−0.3032
Copoly-2	0.20	0.32	12.4	12.69	134	3.7185 (Endo)	−0.1628
Copoly-3	0.25	0.36	9.6	12.68	140	2.5250 (Endo)	−0.2124
Copoly-4	0.30	0.38	8.3	12.72	146	3.0138 (Endo)	−0.1880
Copoly-5	0.40	0.40	11.2	12.61	151	2.2320 (Endo)	−0.2520
Copoly-6	0.50	0.47	10.8	12.60	156	1.7475 (Endo)	−0.2843
Copoly-7	0.60	0.53	8.9	12.65	163	2.0211 (Endo)	−0.2622
Copoly-8	0.70	0.59	9.8	12.58	170	2.8822 (Endo)	−0.1882
Copoly-9	0.75	0.62	10.7	12.59	177	3.4454 (Endo)	−0.1443
Copoly-10	0.80	0.71	11.4	12.71	180	3.2020 (Endo)	−0.2060
Copoly-11	0.90	0.78	8.6	13.37	181	4.1220 (Endo)	−0.2441
BrPMA	1.0	1.0	88.4	12.58	185	5.4642 (Endo)	−0.0742
AMPS	1.0	1.0	85.5	12.70	123	2.5212 (Endo)	−0.3545

[a]Polymerization conditions: tetrahydrofurane solution; temperature: 70 ± 1°C; initiator:AIBN (0.1%, based on total molar of monomers).
[b]The molar fraction of BrPMAAm at feed.
[c]The molar fraction of BrPMAAm in copolymer, obtained from elementel analysis.
[d]Obtained from DSC.

reactivity ratios for the monomers in the system with a 95% joint confidence limit determination. The joint confidence limit is a quantitative estimation of the validity of the results of the experiments and the calculations performed. This method of data analysis consists of obtaining initial estimates of the monomer reactivity ratios for the system and experimental data of comonomer charge amounts and comonomer amounts that have been incorporated into the copolymer, both in molar fractions. Tidwell and Mortimer (25) produced a nonlinear least-squares method that allowed rigorous applications of statistical analysis for reactivity ratios r_1 and r_2. This method is a modification or extension of the curve-fitting model and allows the calculations to be quantitatively analyzed. Extensive calculations are needed, but a computer program by A.Penlidis (24) permits rapid data analysis of the nonlinear calculations. The 95% joint confidence region for the determined r_1 and r_2 values using RREVM are shown in Figure 4. The r_1 and r_2 values from methods such as F-R, K-T, EKT and RREVM are presented in Table 2.

The value of r_1 and r_2 is less than one, which indicates that the system copolymerizes statistically.

The microstructure of a polymeric material plays an important role in the behavior of the material toward a variety of biological systems and could be especially important in copolymerizations with monomers of different

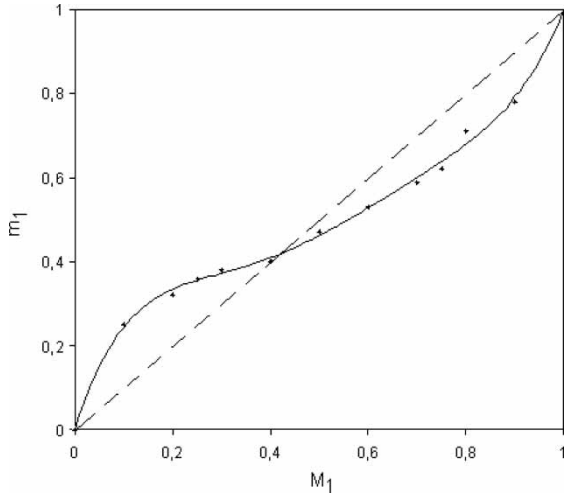


Fig. 3. Copolymer composition diagram for poly(BrPMAAm-co-AMPS) system. (M_1: Feed composition in mole fraction for BrPMAAm; m_1: Copolymer composition in mole fraction for BrPMAAm).

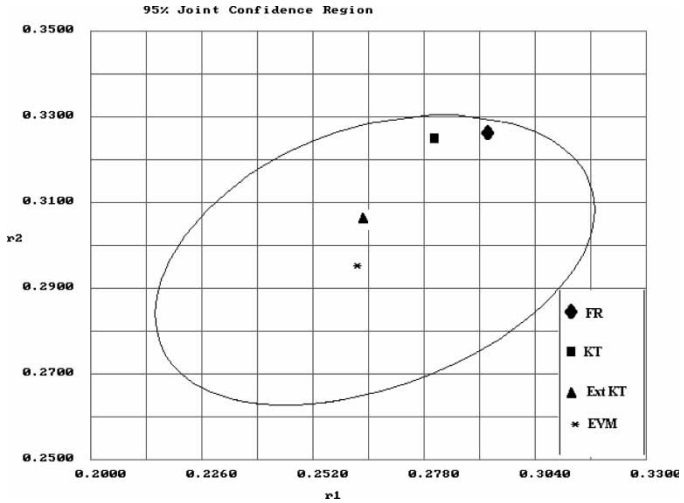


Fig. 4. 95% joint confidence region of r_1 and r_2 values by RREVM for BrPMAAm-AMPS copolymer system.

Table 2. Comparison of the monomer reactivity ratios of BrPMAAm with AMPS by various methods

System	Methods	r_1[a]	r_2[a]	r_1r_2	$1/r_1$	$1/r_2$
Copoly(BrPMA-AMPS)	F-R	0.3001	0.3257	0.0977	3.3322	3.0703
	K-T	0.2786	0.3260	0.0908	3.0675	3.0675
	Ext.K-T	0.2598	0.3086	0.0802	3.8491	3.2404
	RREVM	0.2626	0.2952	0.0775	3.8080	3.3875

[a] r_1 and r_2 are the monomer reactivity ratios of BrPMAAm and AMPS, respectively.

reactivities (26). This implies that the type of copolymer prepared (i.e., random, alternating, or block) may affect the response elicited by the material in a biological environment. Monomer reactivity ratios provide a tool for estimating the average compositions of copolymers and the relative placement of reactive or functional monomers along the polymer chain (26). The reactivity ratio values are also valuable because the final composition of a copolymer is not simply dependent on the amounts of the two monomers present; this is especially true for monomers displaying substantial differences in the copolymerization rates. The final composition of a copolymer also depends on the method of monomer introduction, that is, whether the monomers are added all at once or incrementally over the course of the copolymerization. Both the composition and placement of monomers are dependent on the relative reactivity of each monomer in the system toward the growing polymer radicals, and vice versa.

3.3 Determination of the Solubility Parameters

The solubility parameters of the polymers were determined by using a titration method (27) at 25°C from a solubility test using DMSO as solvent and diethylether as non-solvent. The solubility parameters (δ) values are presented in Table 2.

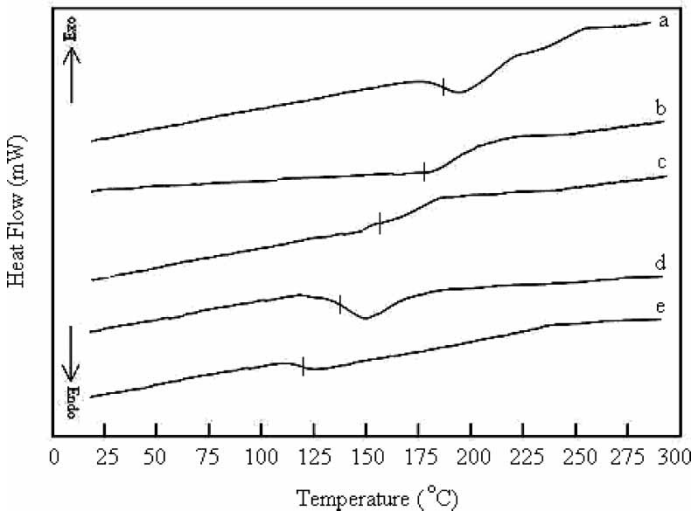


Fig. 5. DSC thermograms of investigated copolymers; (a) poly(BrPMAAm), (b–d) poly(BrPMAAm-co-AMPS): [0.62:0.38], [0.47:0.53],[0.36:0.64], (e) poly(AMPS).

3.4 Thermal Properties

The glass transition (T_g) temperatures were determined by a Setaram 131 DSC. Samples of about 5–8 mg held in sealed aluminum crucibles and the heating rate of 20°C/min under a dynamic nitrogen flow ($5\,l \cdot h^{-1}$) were used for the measurements. From DSC measurements T_g was taken as the midpoint of the transition region. For comparison, homopolymers of BrPMAAm and AMPS were also synthesized under the same conditions. Polymer glass transition temperature, which represents the molecular mobility of polymer chains, is an important phenomenon that influences the material properties and potential applications of a given polymer (28). The characteristics of the homopolymers are presented in Table 1. The gradual increase in the T_g of the copolymer was observed with an increase in the mol percent of BrPMAAm in the copolymer (Table 1) indicating that the presence of sterically bulky bromophenyl group in the copolymer increases the T_g of the copolymer. High T_g of the copolymers (Table 1) in comparison with that of polystyrene ($T_g = 95$°C) indicates substantial decrease of chain mobility of the copolymer due to high dipolar character of the structural unit.

The DSC thermograms of polymers indicated endothermic degradation. Representative DSC thermograms of polymers

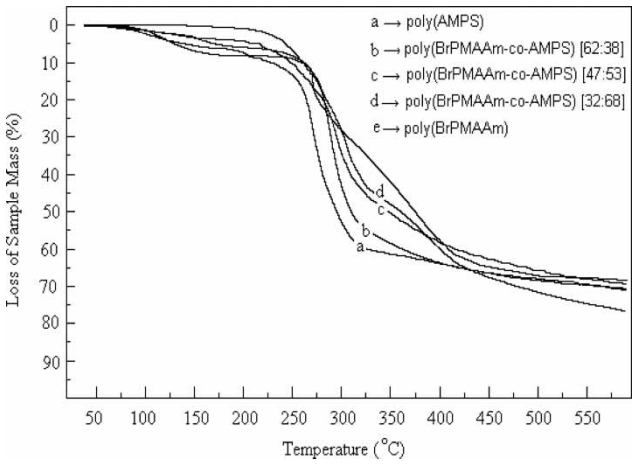


Fig. 6. TGA curves of investigated polymers.

Table 3. Antimicrobial activity of compounds

	E. coli	*Kleb.*	*Pseudo*	*Staph*	*Bacill*	*C. glo*	*C. tro*	*C. albi*
Copoly-1	—	—	—	8	—	—	12	—
Copoly-2	—	—	—	8	—	—	10	—
Copoly-3	—	—	—	—	—	—	8	—
Copoly-4	—	—	—	—	—	—	8	—
Copoly-5	—	—	—	—	—	—	8	—
Copoly-6	—	—	—	—	—	—	8	—
Copoly-7	—	—	—	—	—	—	—	—
Copoly-8	—	—	—	—	—	—	—	—
Copoly-9	—	—	—	—	—	—	—	—
Copoly-10	—	—	—	—	—	—	—	—
Copoly-11	—	—	—	—	—	—	—	—
KAN	19	19	20	21	22	22	22	22
AMP	20	21	20	22	23	22	23	21

Compound concentration: 100 μ/disk.

are given in Figure 5. Data analysis was carried out with the Setaram software package. The enthalpy changes (ΔH_o^d) and heat capacity (ΔCp) during thermal degradation obtained from the DSC thermograms of polymers are given in Table 2.

As evidenced from Figure 6, TGA curves have characteristic three-step decomposition regions. The first weight loss region appears around 70–150°C associated with dehydration of partially degradated of amide groups; secondary weight loss occurring around 150–300°C can be related to possible decarboxylation and/or other reactions of side-chain units and degradation of sulfonic groups; at last weight loss around 315–450°C indicate the main-chain degradation reactions and breakdown of the polymer backbone (17). The increasing thermal stability at higher temperatures may probably be because of the presence of bromophenyl group and -SO_3H and -COOH groups in the side chain, which form crosslinks.

3.5 Antimicrobial Screening

The biological activities of polymers were tested against different microorganisms using DMSO as the solvent. The sample concentrations was 100 μg. The antibiotic sensitivity of the polymers were tested by using the antibiotic disk assay as described (29). Muller-Hinton Agar 1.0% (w/v) beef extract, 2.0% (w/v) bactopeptone, 1.0% (w/v) glucose, 2.0% (w/v) agar was purchased from Difco. 1.5 ml of each prepared different cell culture was transferred into 20 ml of Muller-Hinton Agar (MHA) and mixed gently. The mixture was inoculated into the plate. The plates were rotated firmly and allowed to dry at room temperature for 10 min. Prepared antibiotic disks (100 μg) were placed on the surface of the agar medium (29). The plates were kept at 5°C for 30 min then incubated at 35°C for 2 days. If a toxic compound leached out from the disc the microbial growth was inhibited around the sample. The width of this area expressed the antibacterial or antifungal activities by diffusion. The zones of inhibition of the microorganisms growth of the standard samples, investigated polymers were measured with a millimeter ruler at the end of incubation period. The data reported in Table 3 are the average data of three experiments. The results were standardised against Kanamycin and Amphicillin under the same conditions. The first six copolymers showed selective antimicrobial activities. The results show that the all the copolymers did not inhibit the growth of the test microorganisms [except *Staphylococcus aureus COWAN I (bacteria) and*, Candida tropcalis ATCC 13803 (yeast)].

4 Conclusions

The antimicrobial activity on the homo- and copolymers of BrPMAAm with AMPS was obtained. As the percentage of AMPS in the copolymers increases, the effectiveness of the copolymers to inhibit the growth of the microorganisms increases. Although the sulfur and nitrogen content of the polymers appears to be the most important component to impart antimicrobial properties, it is to be remembered that the conformation the polymers acquired under experimental conditions is a factor for their antigrowth activity.

5 Acknowledgements

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