

4-Chloro-3-methylphenyl Methacrylate Copolymers with 2,4-Dichlorophenyl Methacrylate: Synthesis, Characterization, and Antimicrobial Activity

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ABSTRACT: 4-Chloro-3-methylphenyl methacrylate (CMPM) and 2,4-dichlorophenyl methacrylate (2,4-DMA) were synthesized by reacting methacryloyl chloride with 4-chloro-3-methylphenol (CMP) and 2,4-dichlorophenol (2,4-DP), respectively. Homo and copolymers of CMPM and 2,4-DMA were obtained from different monomer feed ratios, using 2,2'-azobisisobutyronitrile as initiator in toluene at 70°C. IR-spectroscopy was employed to characterize the resulting homo and copolymers. Copolymer compositions were determined by ultraviolet (UV) spectroscopy. Fineman–Ross method was used to calculate the reactivity ratios of the

monomers. Average molecular weight and polydispersity index were obtained by gel permeation chromatography (GPC). Thermogravimetric analyses (TGA) and differential thermal analysis (DTA) of copolymers were carried out under a nitrogen atmosphere. Antimicrobial effects of the homo and copolymers were also investigated for various microorganisms such as bacteria, fungi, and yeast. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 439–448, 2006

Key words: copolymerization; thermal properties; gel permeation chromatography (GPC)

INTRODUCTION

Copolymerization is one of the most successful and powerful methods for effecting systematic changes in polymer properties.¹ Acrylic and methacrylic esters are readily polymerized or copolymerized with a wide range of other monomers. The copolymers of acrylic and methacrylic esters have found use in various applications.^{2,3} Because of their excellent biocompatibility and long term stability, the polymeric systems based on acrylic derivatives are increasingly being used as biomaterials for clinical application.⁴ Phenyl acrylate copolymers crosslinked with divinylbenzene are used as polymer supports for pharmacological drugs.⁵

Chlorine containing phenyl methacrylate and its polymers has received considerable attention in recent years due to their varied applications.^{6,7} These chemicals find application as biocides. Many chlorine containing polymers possessing antimicrobial property have been reported.^{8,9} Pleurdean et al.¹⁰ report the synthesis of acrylic esters, useful as biocides, by reacting pentachloro phenol, *p*-chloro-*m*-cresol and *o*-phenyl phenol with acryloyl chloride. Strum¹¹ reported about 38 esters useful as commercial bactericides and fungicide. These esters were prepared by halogenation

or nitration of 5-acetyl-8-hydroxy quinoline followed by esterification with acryloyl chloride or acetyl chloride.

Acrylate and methacrylate vinyl esters are readily polymerized by free radical polymerization to form linear, branched, or network polymers.¹² Reddy¹³ and coworkers have prepared new chlorine containing polymers. These authors examined the biological activity of these polymers, and they showed good biological activity. Ibrahim and coworkers^{14,15} prepared new methacrylate monomers, their derivatives, and polymers. These authors have determined reactivity ratio of monomers and studied the biological activity of polymers. These polymers showed good biological activity.

We report here the synthesis and characterization of monomers 4-Chloro-3-methylphenyl methacrylate (CMPM) and 2,4-dichlorophenyl methacrylate (2,4-DMA), their homo polymers, and copolymers, using different feed ratio. The copolymer composition was obtained by UV-spectroscopy and molecular weight was determined by gel permeation chromatography (GPC). The results of thermal analysis on polymers are also included in this article. Homo and copolymers were also tested for their antimicrobial properties against microorganisms such as bacteria (*Bacillus subtilis*, *Escherichia coli*, and *Staphylococcus citreus*), fungi (*Aspergillus niger*, *Sporotrichum pulverulentum*, and *Trichoderma lignorum*), and yeast (*Candida utilis*, *Saccharomyces cerevisiae*, and *Pichia stipitis*).

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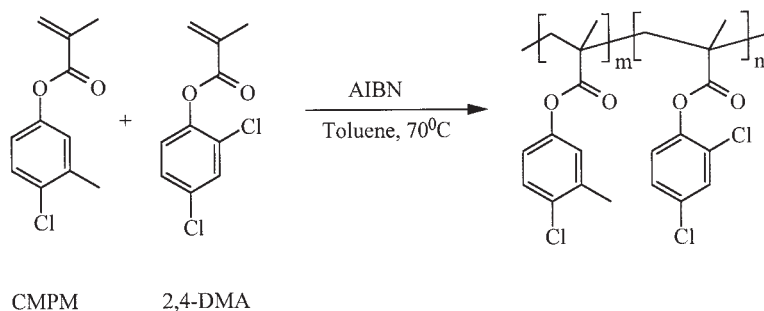


Figure 1 Scheme of Poly (CMPM-co-2,4-DMA) synthesis.

EXPERIMENTAL

Materials

4-Chloro-3-methylphenol (CMP) and 2,4-dichlorophenol (S.D. fine chemicals), 2,2'-azobisisobutyronitrile (AIBN, Aldrich), methacrylic acid, and benzoyl chloride (chiti chem.) have been used without any further purification. Solvents were purified by fractional distillation.

Synthesis of methacryloyl chloride

Methacryloyl chloride was prepared by adopting the standard procedure given by Stempel et al.¹⁶

Synthesis of CMPM

The esterification was performed with methacryloyl chloride and CMP. Absolute alcohol (400 mL) and NaOH (0.2 mol, 8.0 g) were added to a three-necked flask, equipped with stirrer, condenser, and thermometer. The flask was placed in a waterbath. The contents of the flask were stirred until all the NaOH dissolved. To this, CMP (0.2 mol, 42.1 g) was added. The reaction mixture was heated to 60°C for 30 min with stirring, cooled to room temperature, and then to 0–5°C by ice. Freshly prepared methacryloyl chloride (0.21 mol, 20.5 mL) was added drop wise within 60 min to the cooled reaction mixture. The reaction temperature was maintained through out the addition. Reaction mixture was then stirred for 90 min and it was poured into crushed ice-water mixture, when a light yellow color liquid product settled down. It was extracted with ether. The lower aqueous layer is separated. The remaining solution is transferred to a Petri dish to allow evaporation of ether at room temperature and then dried over anhydrous calcium chloride in vacuum desiccator. The boiling point of this monomer was found to be 230°C; yield 75%.

Synthesis of 2,4-DMA

Same experimental procedure as described for monomer CMPM was followed to synthesize 2,4-DMA. The

monomeric ester 2,4-DMA was prepared by drop wise addition of equimolar quantity of methacryloyl chloride to the sodium salt of 2,4-dichlorophenol (2,4-DP) in absolute alcohol at 0–5°C with constant stirring. It was then poured into crushed ice-water mixture, when a cream colored product separated out. It was filtered out, washed thoroughly with cold water, dried at 35°C in vacuum, and recrystallized from petroleum ether. The melting point was 53.5°C; yield 86%.

Characterization of monomers CMPM and 2,4-DMA

The monomers were characterized by FTIR and ¹H-NMR spectroscopy. IR spectra of monomers were recorded using NICOLET 400D FTIR spectrophotometer. ¹H-NMR spectra of monomers were recorded on HITACHI-R-1500 FT-NMR spectrometer (60 MHz) using CDCl₃ as solvent and tetramethylsilane as an internal standard.

Characterization of monomer CMPM

The IR spectrum of monomer CMPM is shown in Figure 2(a). The important absorptions are:

FTIR (cm⁻¹): 2925 (ν_{CH_3}), 1743 ($\nu_{\text{C=O}}$), 1642 ($\nu_{\text{C=C}}$), 1232 (asymmetric $\nu_{\text{C-O-C}}$) and 1160 (symetric $\nu_{\text{C-O-C}}$), 980 (—CH bending mode of vinyl group), 720 (rocking mode of vinyl group), 670 ($\nu_{\text{C-Cl}}$), 1590 and 1488 (bands due to phenyl ring).

The NMR spectrum of CMPM is shown in Figure 2(b). The resonances are:

¹H-NMR (δ ppm) (60MHz): 2.275 (6H) (methyl protons), 6.949 (1H) and 6.533 (1H) (nonequivalent methylene protons), 6.670–7.217 (3H) (aromatic protons).

Characterization of monomer 2,4-DMA

The IR spectrum of monomer 2,4-DMA is shown in Figure 3(a). The important absorptions are:

FTIR (cm⁻¹): 2925 (ν_{CH_3}), 1743 ($\nu_{\text{C=O}}$), 1642 ($\nu_{\text{C=C}}$), 1333 (asymmetric $\nu_{\text{C-O-C}}$) and 1232 (symetric $\nu_{\text{C-O-C}}$), 890 (—CH bending mode of vinyl group), 720 (rocking mode of vinyl group), 670 ($\nu_{\text{C-Cl}}$), 1590 and 1488

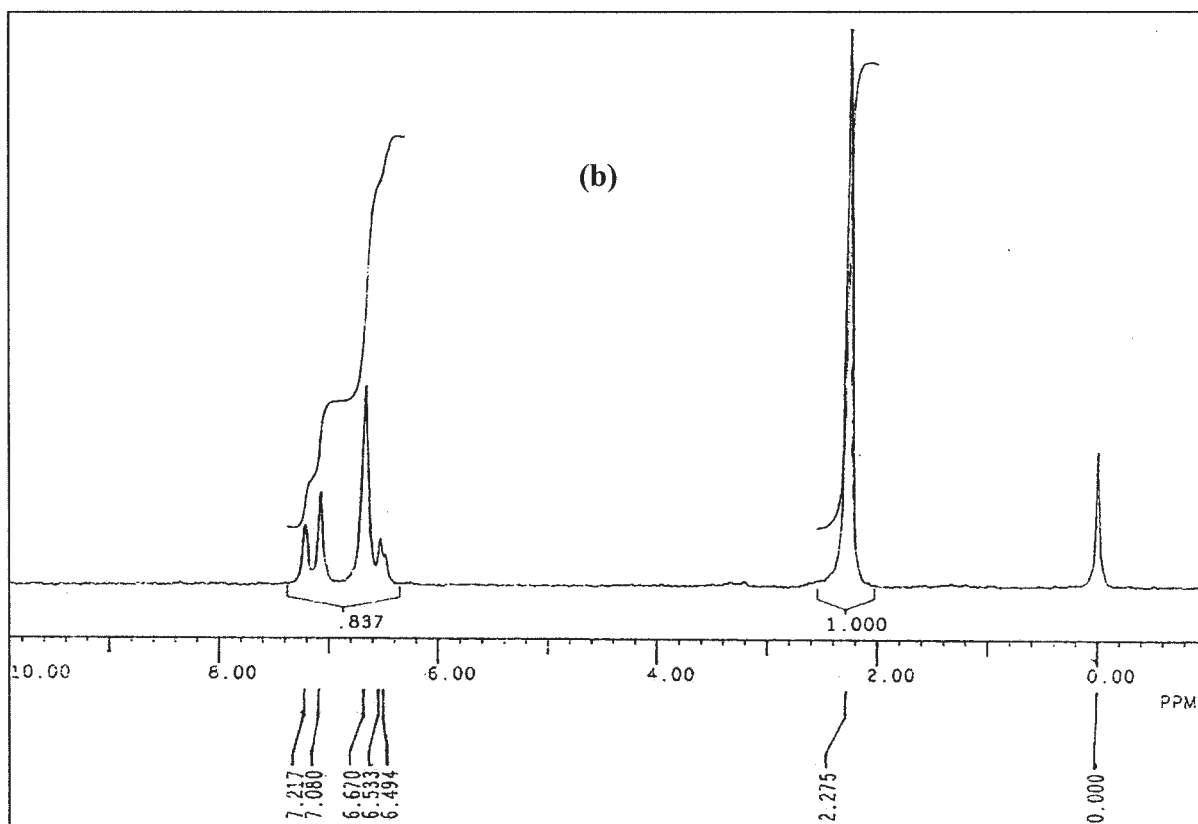
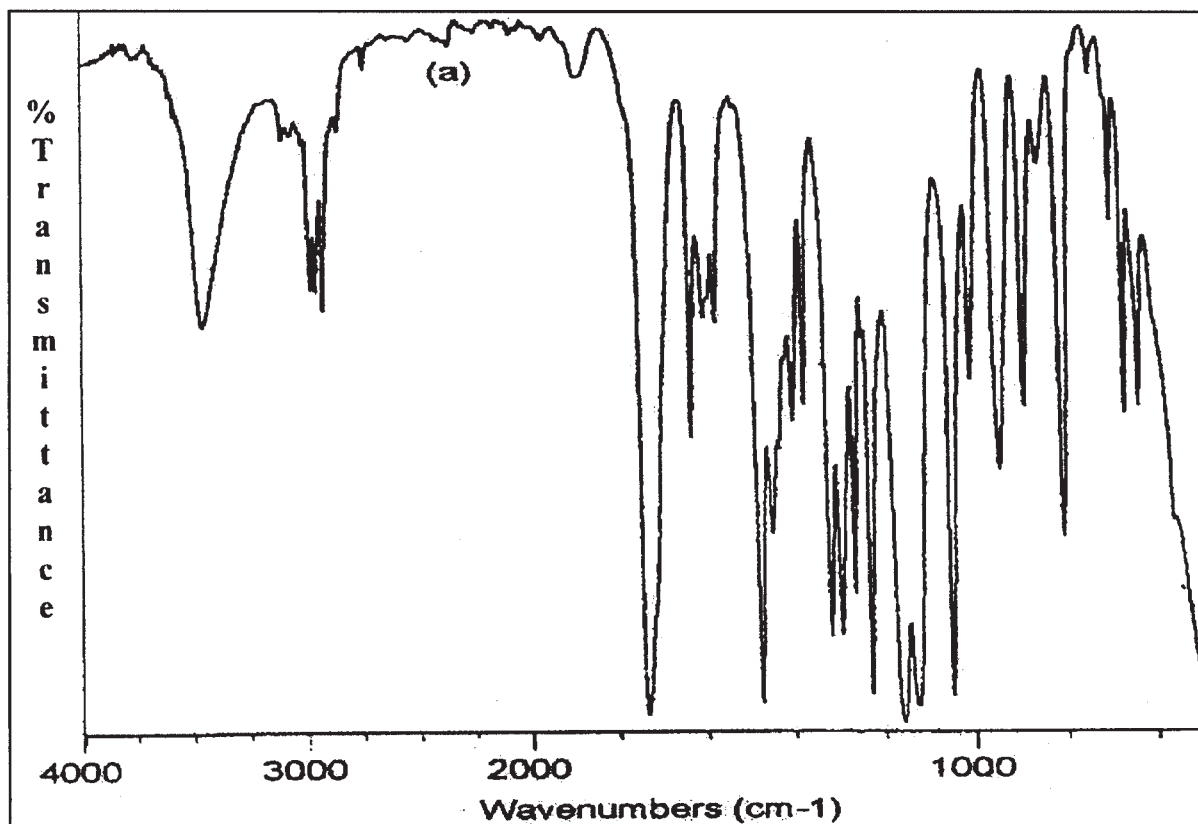


Figure 2 (a) IR spectrum of monomer CMPM (b) $^1\text{H-NMR}$ spectrum of monomer CMPM.

TABLE I
Copolymer Composition and Reactivity Ratios of Copolymers of CMPM and 2,4-DMA

| Sample code no. | Monomer feed composition | | Conversion (%) | Composition of CMPM in the copolymer $[m_1]$ | $m_2 = 1 - m_1$ | $F = M_1/M_2$ | $f = m_1/m_2$ | $H = F^2/f$ | $G = F(f-1)/f$ | $\eta = G/\alpha + H$ | $\xi = H/\alpha + H$ | Reactivity ratio | | | | | |
|-----------------|--------------------------|------------------------|----------------|--|-----------------|---------------|---------------|-------------|----------------|-----------------------|----------------------|------------------|-------|-------|-------|-------|-------|
| | CMPM $[M_1]$ (mole) | 2,4-DMA $[M_2]$ (mole) | | | | | | | | | | F-R | K-T | r_1 | r_2 | r_1 | r_2 |
| M-1 | 1.0 | — | — | — | — | — | — | — | — | — | — | — | — | — | — | — | — |
| M-2 | 0.2 | 0.8 | 9.25 | 0.246 | 0.754 | 0.25 | 0.326 | 0.192 | -0.517 | -0.462 | 0.172 | 0.793 | 0.707 | 0.760 | 0.688 | — | — |
| M-3 | 0.4 | 0.6 | 7.86 | 0.423 | 0.577 | 0.67 | 0.733 | 0.612 | -0.244 | -0.159 | 0.398 | — | — | — | — | — | — |
| M-4 | 0.5 | 0.5 | 8.38 | 0.510 | 0.490 | 1.0 | 1.041 | 0.961 | 0.039 | 0.021 | 0.509 | — | — | — | — | — | — |
| M-5 | 0.6 | 0.4 | 8.20 | 0.583 | 0.417 | 1.5 | 1.398 | 1.609 | 0.427 | 0.168 | 0.635 | — | — | — | — | — | — |
| M-6 | 0.8 | 0.2 | 9.43 | 0.782 | 0.218 | 4.0 | 3.587 | 4.461 | 2.885 | 0.536 | 0.828 | — | — | — | — | — | — |
| M-7 | — | 1.0 | — | — | — | — | — | — | — | — | — | — | — | — | — | — | — |

(bands due to phenyl ring). The band 1160 cm^{-1} also might have some contribution for symmetric $\nu_{\text{C-O-C}}$.

The NMR spectrum of 2,4-DMA is shown in Figure 3(b). The resonances are:

$^1\text{H-NMR}$ (δ ppm) (60 MHz): 2.080 (3H) (methyl proton), 6.416 (1H) and 5.811 (1H) (nonequivalent methylene protons), 7.383–7.471 (1H) (aromatic proton), 7.031–7.236 (2H) (aromatic proton).

Copolymerization

Copolymers of CMPM with 2,4-DMA having different feed composition were synthesized by free radical polymerization in toluene, using AIBN as free radical initiator. The feed composition of both the monomer and comonomer is given in Table I. Appropriate quantities of monomer, comonomer, toluene (10 mL), and AIBN (0.5% of total monomers) were mixed in round bottom flask equipped with mechanical stirrer and reflux condenser. The reaction mixture was heated to 70°C for 5 h with stirring. It was then cooled to room temperature and the resulting polymer solution was slowly poured in a large volume of methanol with stirring, when the polymer precipitated out. It was filtered and washed with methanol. Solid polymers were purified by repeated precipitation by methanol from solution in DMF and finally dried. Reaction scheme (Fig. 1) shows the reaction leading to the formation of copolymers of CMPM with 2,4-DMA. The yield of copolymers varies from 78 to 85%.

Characterization

Infrared spectra of solid samples in KBr pellets were recorded with a NICOLET-400D FTIR spectrophotometer. Shimadzu-160-A recording UV-visible spectrophotometer was used to determine copolymer composition and reactivity ratios. Molecular weights of the polymers were determined by GPC (Waters 600 E) equipped with a 410-RI detectors calibrated with polystyrene standard. Thermogravimetric analysis was performed with Du Pont-951 thermal analyzer at a heating rate of $10^\circ\text{C}/\text{min}$ in static air atmosphere. Differential thermal analysis (DTA) traces were obtained with Du Pont-9900 differential thermal analyzer at a heating rate of $10^\circ\text{C}/\text{min}$ in nitrogen atmosphere. A heating rate of $10^\circ\text{C}/\text{min}$ and a sample size of 10 ± 1 mg were used in each experiment. Intrinsic viscosity (η) of the copolymers was measured in toluene solvent at $(25 \pm 0.1)^\circ\text{C}$ using an Ubbelohde suspension level viscometer.

Antimicrobial activity

The homo and copolymers prepared were tested for their antimicrobial activity against bacterial strain (*B. subtilis*, *E. coli*, and *S. citreus*), fungal strain (*A. niger*, *S.*

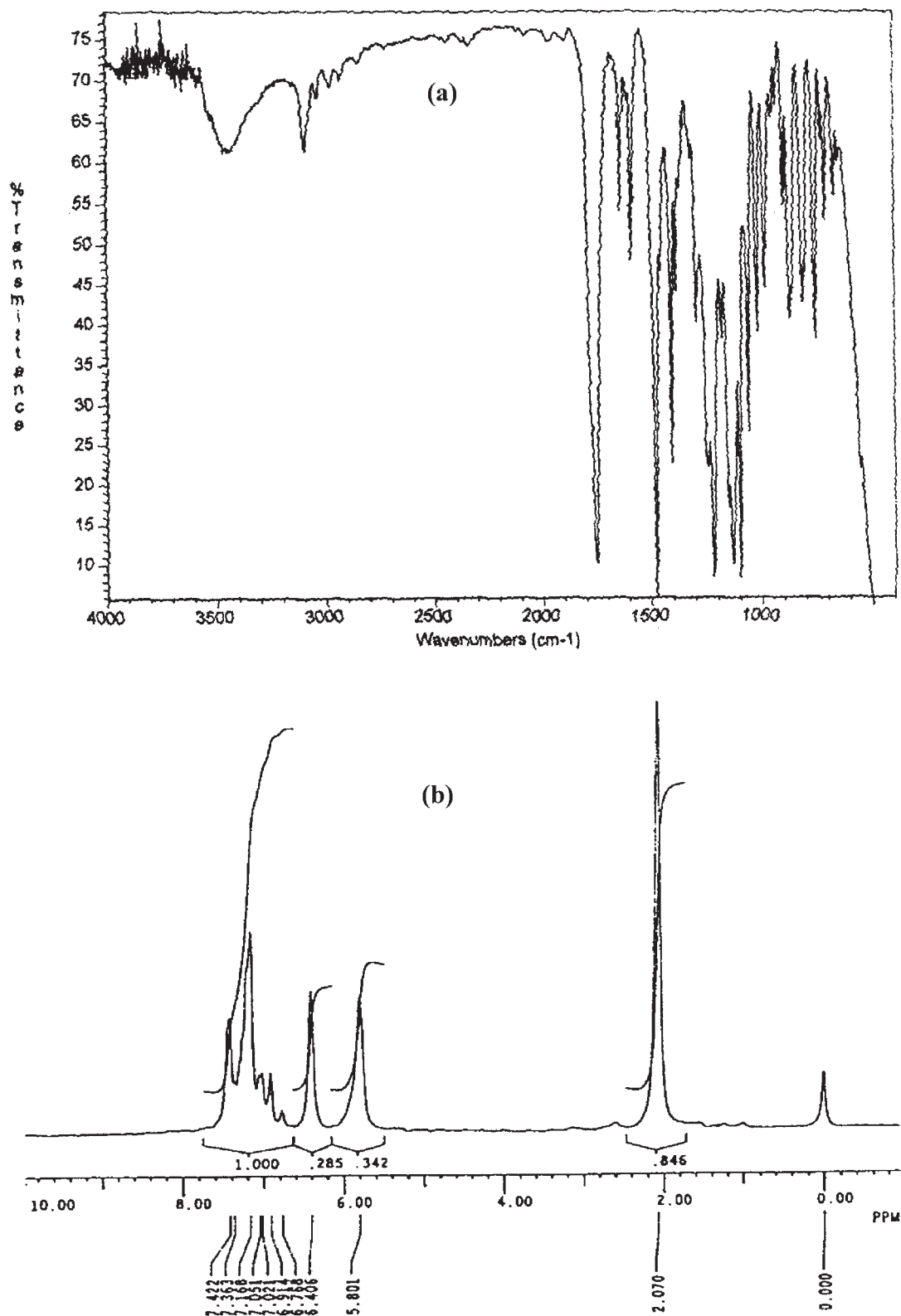


Figure 3 (a) IR spectrum of monomer 2,4-DMA (b) $^1\text{H-NMR}$ spectrum of monomer 2,4-DMA.

pulverulentum, and *T. lignorum*) and yeast strain (*C. utilis*, *S. cerevisiae*, and *Pichia stipitis*). These microorganisms were grown in Nutrient broth (N-broth), Sub-

ourand's dextrose broth, and yeast extract peptone dextrose (YEPD) media with or without indicated polymer. The content of the flasks were incubated in a

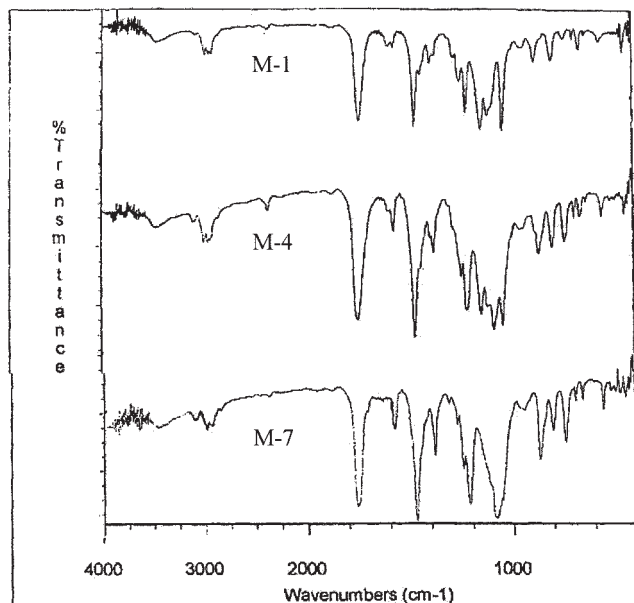


Figure 4 IR spectra of homo and copolymers of CMPM with 2,4-DMA.

shaker at room temperature. At specific time intervals (20–48 h), the optical density was measured at 660 nm for bacteria and yeast cultures. The fungal cultures were harvested after 48 h and the dry cell mass was determined gravimetrically. The details of experimental procedure have been reported elsewhere.^{17,18}

RESULTS AND DISCUSSION

The copolymers of CMPM with 2,4-DMA were synthesized by taking different mole fraction of the monomers in the feed ranging from 0.2 to 0.8 (Table I). To satisfy the differential copolymerization equation, the reaction time was so selected as to have less than 10% wt conversion. The copolymers and homopolymers are characterized by IR technique and a brief discussion of the important absorptions is given here.

The IR spectra of copolymers are shown in Figure 4. The IR spectrum of poly(CMPM) is almost similar to that of poly(2,4-DMA) and shows all the characteristic absorption (Fig. 4). All the resins show the C—H stretching frequency of the aromatic moiety at ~ 3000 cm^{-1} . The C—H stretching vibrations of the aliphatic group appear in the range of 3000 – 2900 cm^{-1} . Bands at 1380 and 1467 cm^{-1} could be assigned as the C—H bending vibration of methyl and methylene group.¹⁹ The strong absorption at 1770 cm^{-1} is mainly due to the C=O stretching of the ester moiety. In the copolymers and homo polymers as well, the C=O stretching frequency shows blue shifts (30 – 40 cm^{-1}) compared with the same in the monomers. The monomers are α,β -unsaturated ketones, and on polymerization, this α,β -unsaturation is lost, thereby leading to increase in C=O stretching. The aromatic ring vibrations in these polymers are assigned at approximately 1600 and 1500 cm^{-1} . The C—O—C stretching vibrations are attributed to the strong absorption in the region 1300 – 1150 cm^{-1} , where as the sharp band at 680 cm^{-1} was due to C—Cl.²⁰ The absence of band at 1642 cm^{-1} in the polymers indicated that the vinyl group took part in polymerization.

Copolymer composition and reactivity ratios

The average composition of each copolymer sample was determined from the corresponding UV-spectrum. The assignment of the absorption in the UV-spectrum allows accurate determination of the content of each kind of monomeric unit incorporated into the copolymer chains. The λ_{max} for poly(CMPM) was found at 267 nm, while that of poly(2,4-DMA) was observed at 275 nm. The UV-spectra of different composition of copolymers are shown in Figure 5. The agreement between the two concentrations was good. The composition of the copolymers of CMPM and 2,4-DMA were obtained from the UV-spectral data. From monomer feed ratio and copolymer composi-

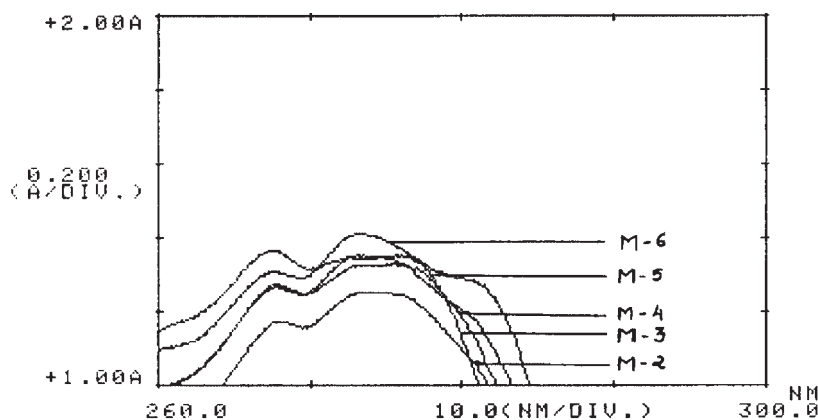


Figure 5 UV spectra for copolymers of CMPM with 2,4-DMA.

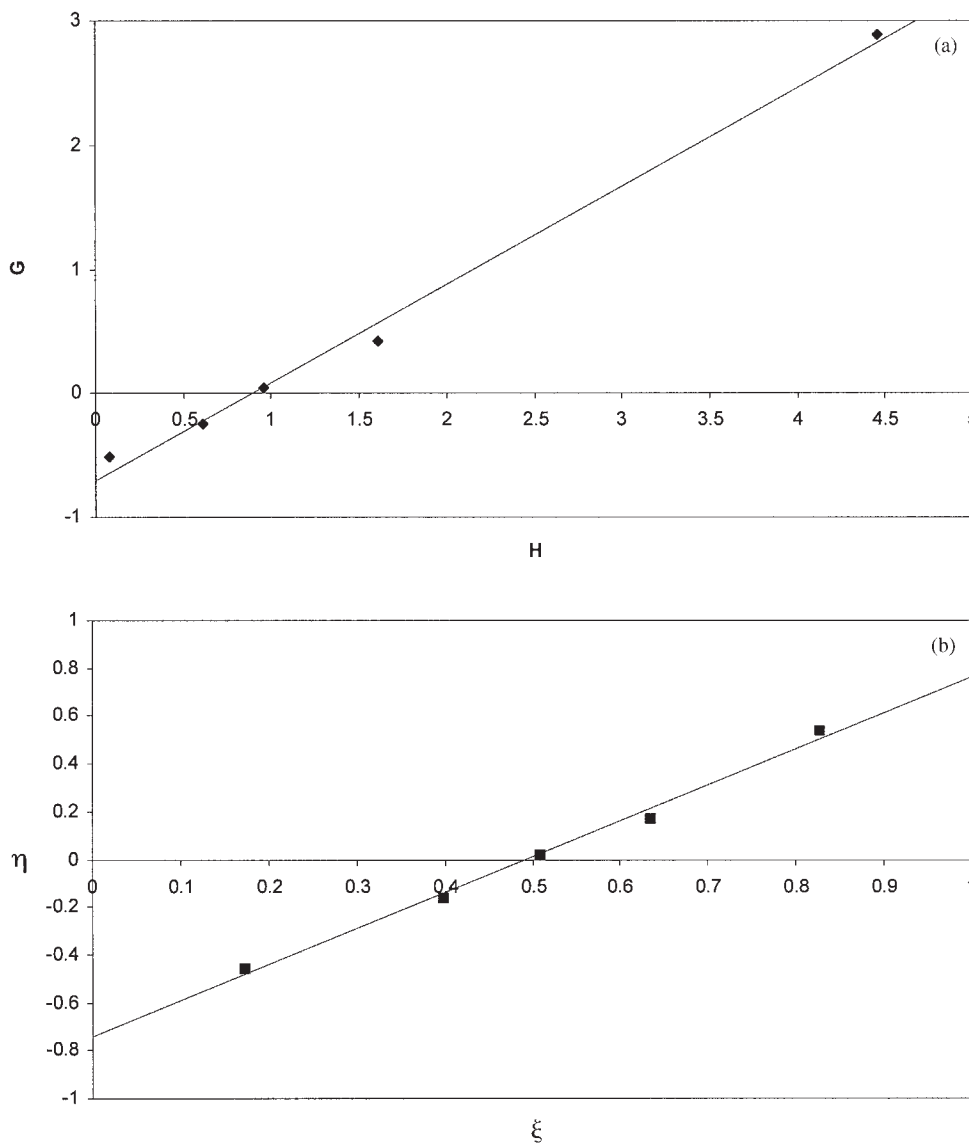


Figure 6 (a) F-R plot for poly(CMPM-co-2,4-DMA) (b) K-T plot for poly(CMPM-co-2,4-DMA).

tion, the reactivity ratios of CMPM and 2,4-DMA were determined by Fineman–Ross method²¹ and are shown in Table I. The reactivity ratios were also obtained by Kelen–Tudos²² method. The values are shown in Table I. The reactivity ratios obtained by these two methods agree well. The reaction time was selected in such a way that conversion was less than 10% in weight. This was done to satisfy the differential copolymerization equation for calculation of reactivity ratio.²¹ A plot of G versus H in F–R method was a straight line shown in Figure 6(a). The intercept at y -axis gives the value of $-r_2$ and the slope gives the value of r_1 . Similarly in K–T method, by plotting η against ξ , a straight line is obtained as shown in Figure 6(b), which when extrapolated to $\xi = 0$ and $\xi = 1$ gives $-r_2/\alpha$ and r_1 , respectively. When r_1 and r_2 are less than 1, the system gives rise

to azeotropic polymerization at a particular composition of the monomer, which is calculated using the equation²³

$$N_1 = \frac{(1 - r_2)}{(2 - r_1 - r_2)} = 0.586$$

where N_1 is the mole fraction of CMPM in the feed.

When the mole fraction of the monomer CMPM in the feed is 0.586, the copolymer formed will have the same composition as that in the feed. When the mole fraction of CMPM in the feed is less than 0.586, the copolymer is relatively richer in this monomeric unit than the feed. When the mole fraction of the monomeric CMPM in the feed is above 0.586, the copolymer is relatively richer in 2,4-DMA monomeric units.

TABLE II
Average Molecular Weights by GPC Data for the Copolymers of CMPM with 2,4-DMA

| Sample code no. | M_n | M_w | Polydispersity (M_w/M_n) | Intrinsic viscosity [η] dL g ⁻¹ |
|-----------------|--------|--------|------------------------------|---|
| M-1 | 44,011 | 45,811 | 1.041 | 0.210 |
| M-2 | 33,001 | 36,429 | 1.104 | 0.170 |
| M-3 | 34,506 | 37,869 | 1.097 | 0.178 |
| M-4 | 36,609 | 38,788 | 1.059 | 0.186 |
| M-5 | 36,902 | 39,191 | 1.062 | 0.189 |
| M-6 | 37,400 | 39,801 | 1.061 | 0.192 |
| M-7 | 45,609 | 46,710 | 1.024 | 0.230 |

Molecular weight and viscosity measurement

The number- and weight-average molecular weight of poly(CMPM), poly(2,4-DMA), and five samples of copolymers were obtained from GPC. The polydispersity index of homo and copolymers varied in the range of 1.024–1.104. The intrinsic viscosities (η) were obtained by extrapolating $\eta_{sp} C^{-1}$ to zero concentration. The molecular weights and viscosities are presented in Table II.

Thermal analysis

Thermogravimetric analysis

The results of thermogravimetric analysis (TGA) of poly(CMPM), poly(CMPM-co-2,4-DMA) (20 : 80, 50 : 50, 80 : 20 monomer feed ratio), and poly(2,4-DMA) are presented in Table III. The data clearly indicate that all polymers undergo single-step decomposition in the temperature range of 207–472°C. The activation energy (E_A) was calculated by Broido's method,²⁴ which lies in the range 102–117 kJ mol⁻¹. The integral procedural decomposition temperature (IPDT) was calculated by Doyle's method.²⁵ IPDT express the overall thermal stability of the polymer and it varies between 297 and 394°C for these polymers.

TABLE III
TGA Data for Poly(CMPM), Poly(2,4-DMA), and Their Copolymers

| Sample code no. | % Weight loss at various temperature (°C) | | | | Decomposition temperature range (°C) | T_{Max}^a (°C) | T_{50}^b (°C) | IPDT ^c (°C) | Activation energy ^d (E_A) (kJ mol ⁻¹) |
|-----------------|---|-------|-------|-------|--------------------------------------|------------------|-----------------|------------------------|--|
| | 250 | 350 | 450 | 550 | | | | | |
| M-1 | 0.98 | 7.27 | 87.20 | 89.41 | 320–472 | 399 | 396 | 394 | 102 |
| M-2 | 14.25 | 29.45 | 96.14 | 98.05 | 207–414 | 382 | 370 | 297 | 103 |
| M-4 | 8.10 | 60.38 | 98.16 | 99.69 | 250–428 | 360 | 338 | 335 | 117 |
| M-6 | 16.11 | 59.11 | 97.20 | 99.81 | 217–424 | 355 | 330 | 332 | 111 |
| M-7 | 2.60 | 20.11 | 98.03 | 98.79 | 240–429 | 395 | 387 | 384 | 104 |

^a Temperature for maximum rate of decomposition.

^b Temperature for 50% weight loss.

^c Integral procedural decomposition temperature.

^d By Broido's method.

TABLE IV
DTA Data for Poly(CMPM), Poly(2,4-DMA) and Their Copolymers

| Sample code no. | T_1^a (°C) | T_2^b (°C) | T_p^c (°C) | Activation Energy ^d (E_A) (kJ mol ⁻¹) | Reaction order |
|-----------------|--------------|--------------|--------------|--|----------------|
| M-1 | 400 | 540 | 445 | 103 | 1 |
| M-2 | 385 | 455 | 426 | 104 | 1 |
| M-4 | 376 | 492 | 422 | 115 | 1 |
| M-6 | 372 | 442 | 418 | 110 | 1 |
| M-7 | 388 | 515 | 440 | 106 | 1 |

^a Starting Temperature of DTA.

^b Ending Temperature of DTA trace.

^c Peak maxima Temperature of DTA trace.

^d Activation Energy by Reich's method.

Differential thermal analysis

DTA data of poly(CMPM), poly(CMPM-co-2,4-DMA) (20 : 80, 50 : 50, 80 : 20 monomer feed ratio) and poly(2,4-DMA) are presented in Table IV. The activation energy for thermal degradation and reaction order were obtained by Reich's method.²⁶ The activation energy for thermal degradation of polymers ranged from 103 to 115 kJ mol⁻¹.

Antimicrobial activity

The antimicrobial activity of homo and copolymers of CMPM and 2,4-DMA was investigated. The results obtained are presented in Figures 7, 8, and 9. It has been suggested that presence of chlorine in a compound is of prime importance for its antimicrobial activity.^{27,28} All the copolymers systems showed almost similar antimicrobial properties against bacteria, fungi, and yeast. Poly(CMPM) allowed about 18–23% growth of bacteria, 20–24% growth of fungi, and 21–24% growth of yeast, while 11–16% growth of bacteria, 15–19% growth of fungi, and 13–16% growth of yeast, respectively, was pos-

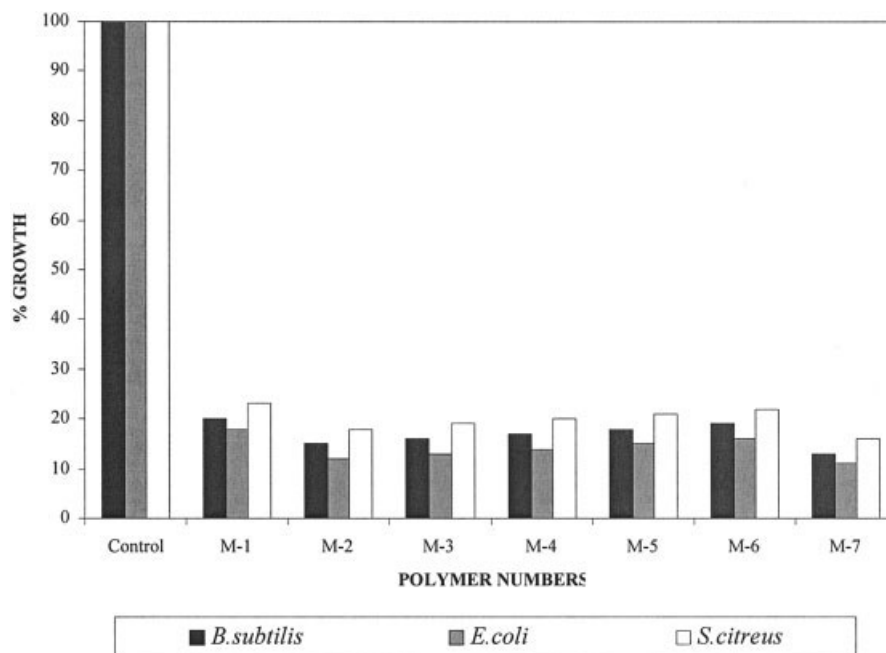


Figure 7 Effect of homo and copolymers on percentage growth of bacteria.

sible in poly(2,4-DMA). The poly(2,4-DMA) is found to be more effective in inhibiting the growth of microorganisms than that of poly(CMPM), this may be traced to the high chlorine content of poly(2,4-DMA). As the percentage of CMPM in the copolymers increases, the effectiveness of the copolymers to inhibit the growth of microorganisms decreases

as expected. The inhibition property of the polymers is as follows:

$$M-7 > M-2 > M-3 > M-4 > M-5 > M-6 > M-1$$

This clearly demonstrates that as the chlorine content in the polymer decreases, the inhibiting property also decreases.

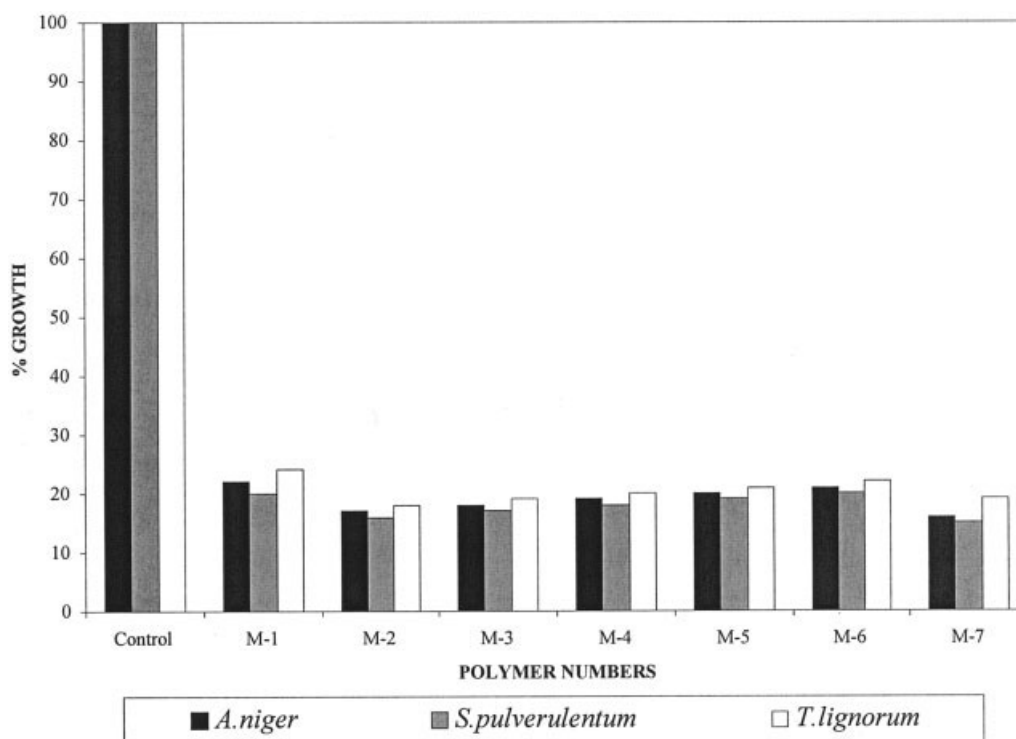


Figure 8 Effect of homo and copolymers on percentage growth of fungi.

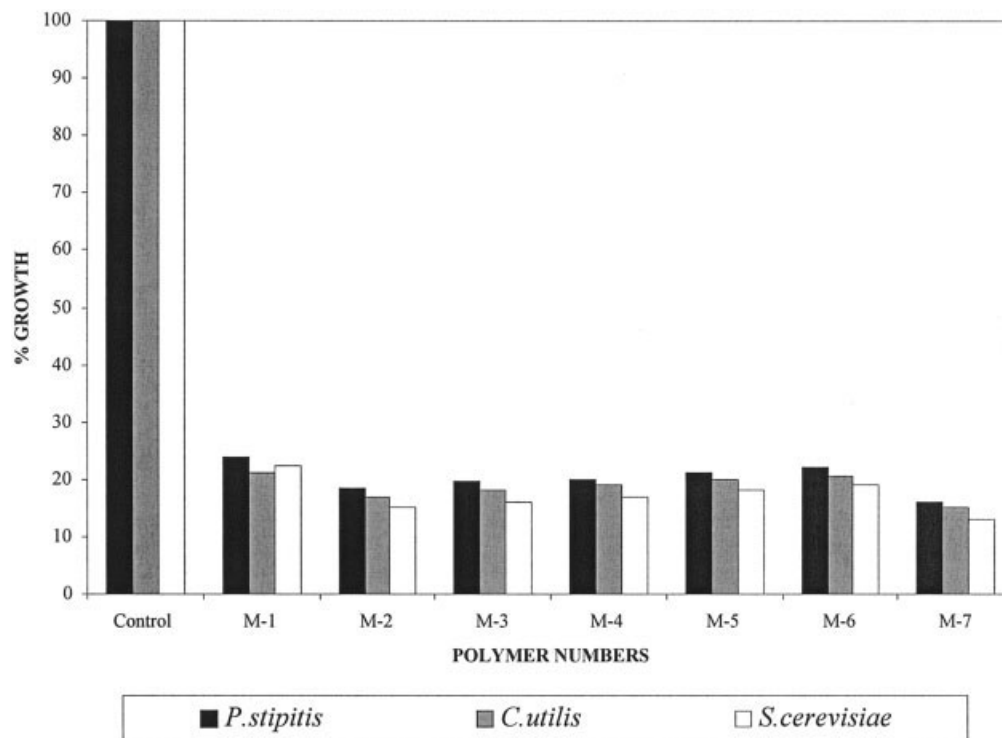


Figure 9 Effect of homo and copolymers on percentage growth of yeast.

CONCLUSIONS

The new acrylate based homo and copolymer was synthesized by free radical solution polymerization technique. The monomers and copolymers were characterized by spectroscopic methods. The reactivity ratio of CMPM (r_1) is greater than that of 2,4-DMA (r_2) and the product of reactivity ratio was less than 1. This shows that the monomers were distributed in the copolymer chain in a random fashion. The number-average molecular weight (M_n) and weight average molecular weight (M_w) were in the range of 33,001–45,609 and 36,429–46,710, respectively. Thermal analyses showed that all the polymers undergo single-step degradation. The chlorine content of the polymers appears to be the most important component to impart the antimicrobial activity. It is hoped that such chlorine containing copolymers will find use as antimicrobial agents.

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