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SHORT COMMUNICATION

Reactivity ratio of novel acrylic copolymer by NMR spectroscopy

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Abstract The monomer 4-methylcoumarylacrylate (4-MCA) was synthesized from 7-hydroxy-4-methylcoumarin and characterized by conventional methods. Homo and copolymers of 4-methylcoumarylacrylate and styrene were synthesized with different feed ratios using *N*,*N*-dimethylformamide (DMF) as a solvent and 2,2′-azobisisobutyronitrile as an initiator at 70°C.The resulting polymers were characterized by infrared spectroscopy. Copolymer compositions were determined by nuclear magnetic resonance spectroscopy. The monomer reactivity ratios were determined by applying the conventional linearization method of Fineman–Ross and Kelen–Tudos. The reactivity ratios values of 4-methylcoumarylacrylate and styrene obtained from F–R plot are 1.36 and 0.62, respectively, and from K–T plot 1.24 and 0.58, respectively.

Keywords Copolymer Composition · Reactivity ratio

Introduction

Acrylic and methacrylic esters are readily copolymerized with a wide variety of monomers. The copolymers of acrylic or methacrylic esters have been used for variety of applications [1–3]. Acryalte homopolymers along with their copolymers are used in various fields such as films, fibers, filaments, coating, lithography, lacquers, adhesives, printing inks, and binders [4–6]. Copolymerization is one of the important techniques in affecting desired changes in the properties of the polymers synthesized. YH Mi [7] has synthesized a new type foil or paper-laminating adhesive from VAc and Acrylic acid. Widmaier and coworkers [8] prepared adhesives having good adhesion to paper from copolymers of N-vinyl pyrrolidone and acrylate esters. Many copolymers of acrylic and methacrylic esters have been synthesized and characterized, and their biocidal properties have been investigated by Patel et al. [9].

Coumarin and its derivatives have attracted considerable attention because of their various physiological and biochemical properties. Coumarin itself inhibits the germination and subsequent root growth of plants. Coumarins have interesting cytogenetic properties [10]. God [11] synthesized homo and copolymer of 3-acrylamino benzyl coumarin with methyl methacrylate by free radical solution polymerization in dimethyl formamide solution in which coumarin contains vinyl polymers as a side chain. Lee and coworkers [12] prepared coumaryl acrylate by reacting 7-hydroxy coumarin with acryloyl chloride and from this they synthesized poly (cinnam-4-yl methyl methacrylate). The thermal stability of these polymer films as photo alignment layer was also checked.

Since coumarin has antimicrobial activity, it was thought appropriate to incorporate this moiety in copolymer frame. The synthesis and characterization of 4-methylcoumaryl acrylate (MCA), the homopolymer of MCA, and the copolymers of MCA with styrene (Sty) are communicated here. The copolymer composition was obtained from ^{1}H-NMR spectroscopy. The ^{1}H-

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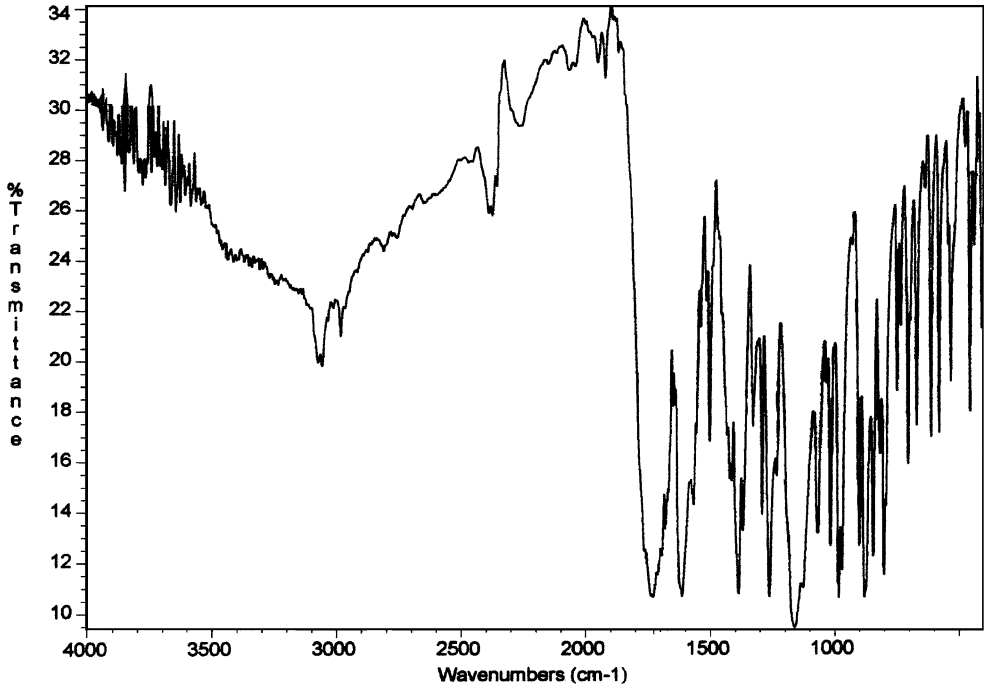


Fig. 1 FT-IR spectrum of monomer 4-MCA

NMR technique is very versatile for determination of composition of monomers and reactivity ratios of monomers. Reactivity ratios were calculated by applying conventional linearization methods of Fineman–Ross and Kelen–Tudos. The biocidal properties of these polymers have also been investigated and will be communicated shortly.

Experimental

Materials

Analytical grade reagent acrylic acid, benzoyl chloride (chiti chem.), 2,2′-azobisisobutyronitrile(AIBN, Aldrich), styrene, and hydroquinone (S.D. Fine Chemicals) were used.

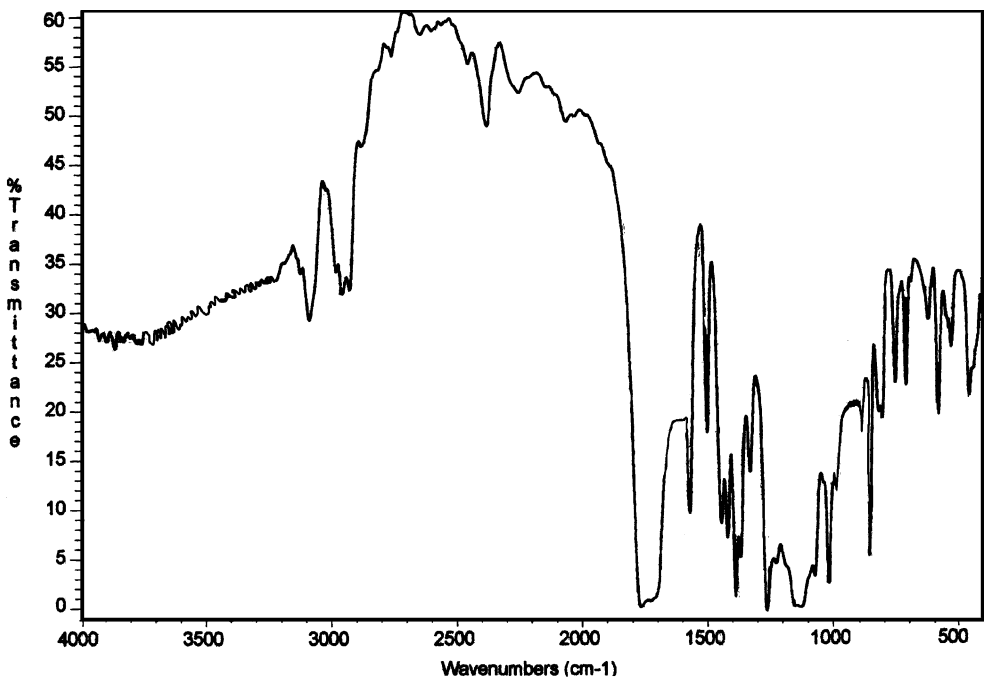


Fig. 2 FT-IR spectrum of homopolymer 4-MCA

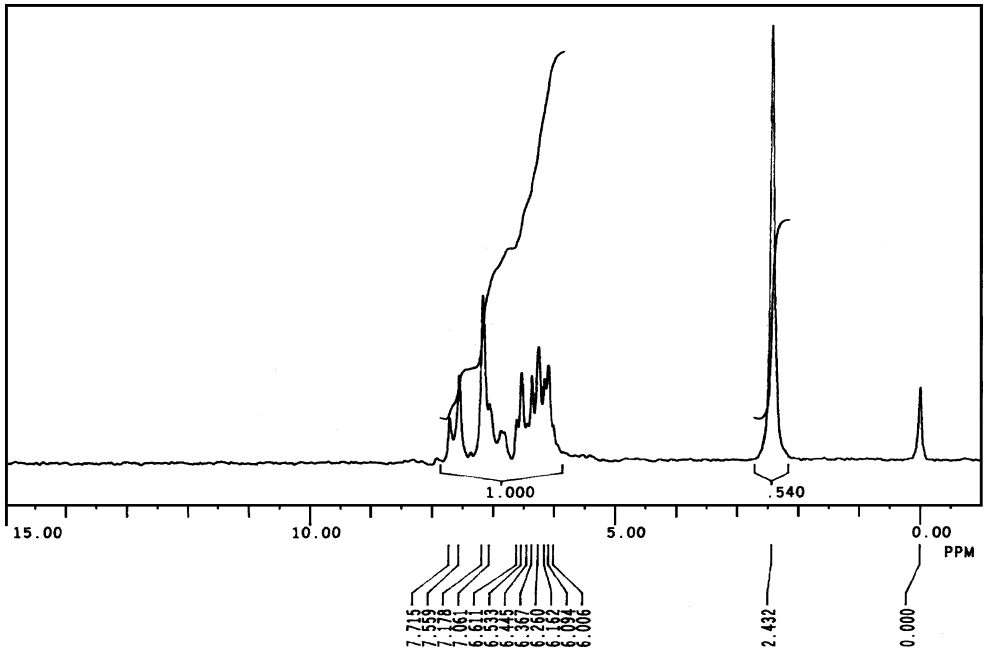


Fig. 3 ^{1}H-NMR spectrum of monomer 4-MCA

Characterization

Perkin Elmer (Spectrum GX, USA) Fourier transform infrared (FT-IR) spectrophotometer was used to record the infrared spectrum of homo and copolymers on solid KBr pellets. Copolymer composition and reactivity ratios were determined using ^{1}H-NMR (60 MHz) spectrophotometer. The ^{1}H-NMR spectra of monomer and polymers are also obtained. HPLC (Perkin Elmer, Series200 USA) was used to determine chromatographic purity of the monomer 4-MCA.

Synthesis of 7-hydroxy-4-methylcoumarin

7-Hydroxy-4-mehtylcoumarin was prepared according to the process reported in the literature [13]. Two hundred fifty microliters of concentrated sulfuric acid (H_2SO_4) was added to a 1-l three-necked flask fitted with a thermometer, a mechanical stirrer, and a dropping funnel. The flask was immersed in an ice bath. Solution containing (0.23 mol) of resorcinol and (0.26 mol) of ethyl acetoacetate was added dropwise to the flask maintained at temperature less than 10°C with constant stirring. The reaction mixture was kept

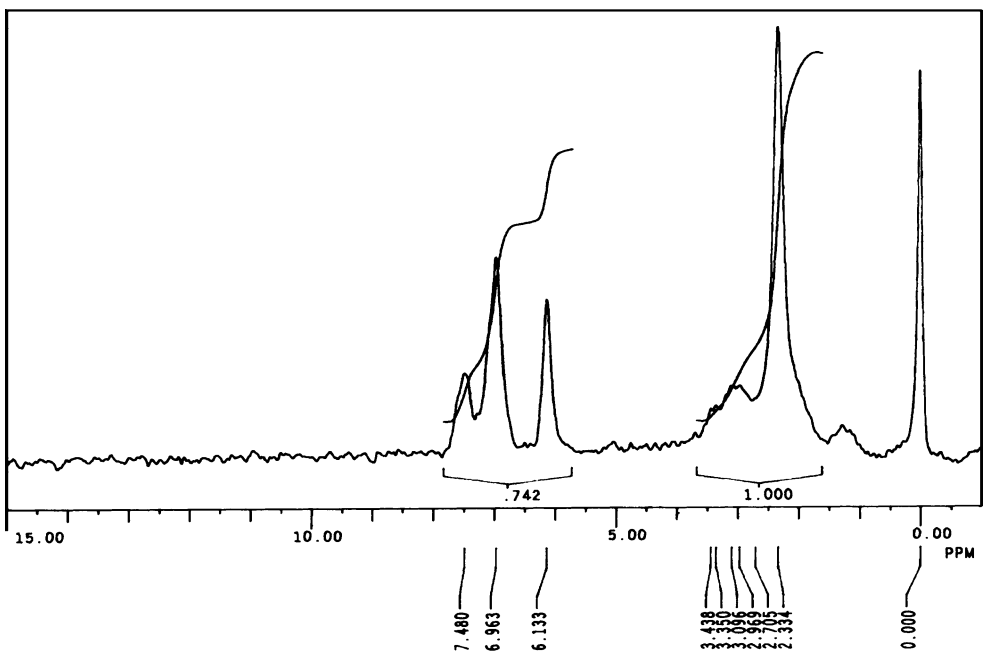
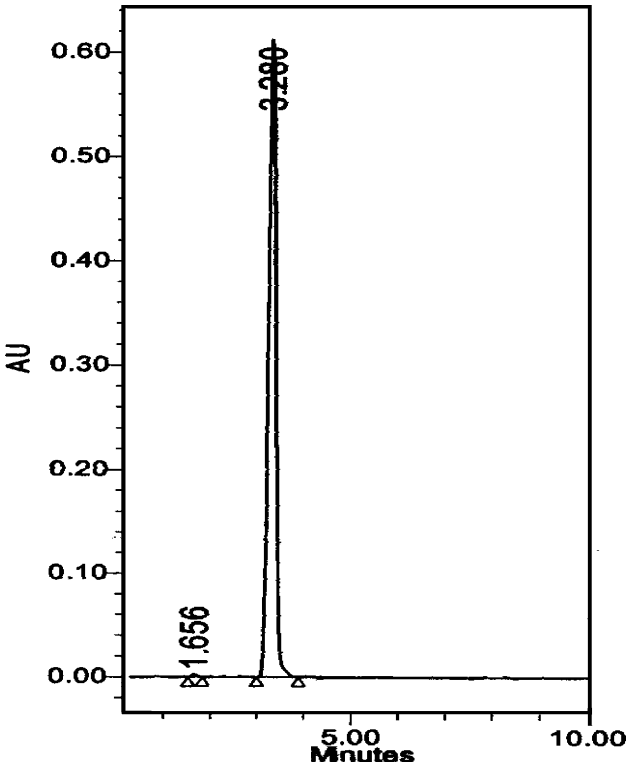


Fig. 4 ^{1}H-NMR spectrum of homopolymer 4-MCA



Peak No	RT min:sec	Height	Area	Amount % Area
1	1:656	2484	19644	0.113
2	3:280	612869	17364427	99.887

Fig. 5 HPLC chromatogram of monomer 4-MCA

for about 18 h at room temperature after completion of addition of the reagents. The contents of the flask were poured in crushed ice water mixture when the product separated out. The crude product was dissolved in 5% aqueous sodium hydroxide solution. H_2SO_4 (2M) was added to the solution until acidic. The product obtained was filtered, dried and recrystallized from 95% ethanol (yield: 97%).

IR of 7-hydroxy-4-methylcoumarin (cm^{-1}): 3,190 (ν_{-OH}), 1,683 ($\nu_{C=O}$), 3,067 (–CH stretching vibration of the aromatic ring), CH_3 confirmed by absorption band at 1,375, 1,214 (asymmetric ν_{C-O-C}), 1,134 (symmetric ν_{C-O-C}).

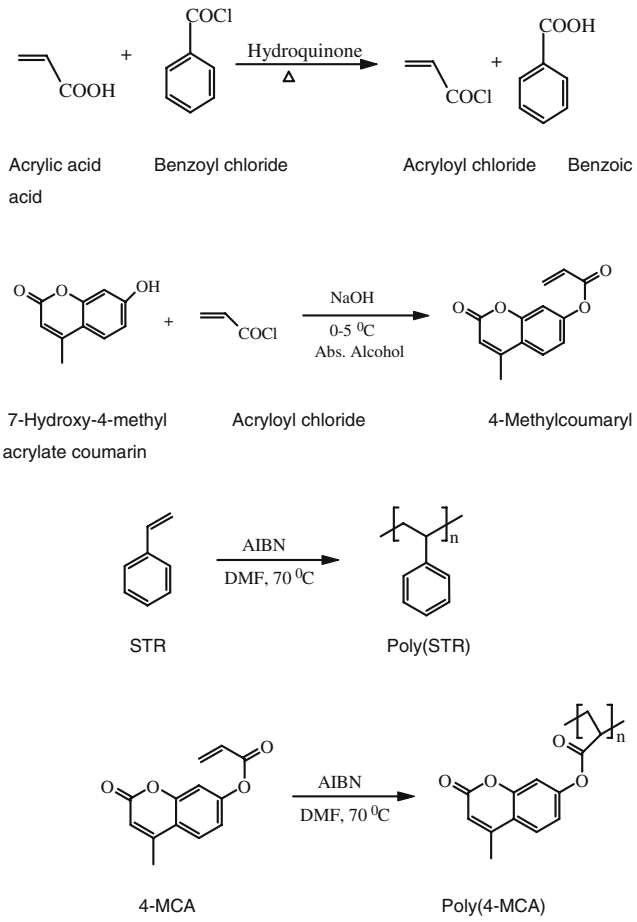
^{1}H-NMR of 7-hydroxy-4-methylcoumarin (δ) (60 MHz): 6.074 (1H, CH=), 7.529 (1H, Ar–H), 6.904 (1H, Ar–H), 6.758 (1H, Ar–H), 3.223 (1H,–OH), 2.402 (3H, CH_3).

Synthesis of acryloyl chloride

Acryloyl chloride was prepared according to the process reported in the literature [14]. A mixture of acrylic acid (1 mol), benzoyl chloride (2 mol), and hydroquinone (0.0025 mol) was distilled at a fairly high rate through an effective column. The distillate was collected in the temperature range between 70°C and 80°C. The crude product was redistilled through the same column. The pure acryloyl chloride was distilled out at 72–76°C. The product yield was 85%.

Synthesis of 4-methylcoumarylacrylate (4-MCA)

Absolute alcohol (550 ml) and NaOH (0.1 mol) were added to a 1-l three-necked flask equipped with stirrer, thermometer, and guard tube, and the contents were stirred until all the NaOH dissolved. 7-Hydroxy-4-methylcoumarin (0.1 mol) was added to this. The reaction mixture was heated to 60°C for 30 min with stirring, cooled to room temperature and then to 0–5°C. Freshly prepared acryloyl chloride (0.11 mol) was added drop wise over a period of 60 min to the cooled reaction mixture. The temperature was maintained around 0–5°C during the addition. After completion of addition, reaction mixture was stirred for 90 min and was poured into crushed ice water mixture where a white-colored product separated out. It was filtered through buckner funnel, the product was washed thoroughly with cold water. It was dried at 40°C in vacuum and recrystallized from methanol (yield: 89%, HPLC purity: 99.89%)



Scheme 1 Reaction scheme

Table 1 F–R and K–T parameters for copolymers of 4-MCA with STR

Sample code no.	4-MCA M_1 mole	STY M_2 mole	Composition of 4-MCA in copolymer m_1	X	Y	F	G	ξ	η
2	0.5	0.5	0.512	1.00	1.049	0.953	0.047	0.760	0.037
3	0.4	0.6	0.426	0.67	0.742	0.599	−0.232	0.666	−0.257
4	0.3	0.7	0.330	0.43	0.493	0.372	−0.441	0.553	−0.656
5	0.2	0.8	0.221	0.25	0.284	0.220	−0.631	0.423	−1.212
6	0.1	0.9	0.115	0.11	0.130	0.095	−0.743	0.240	−1.879

Where $m_2=1-m_1$; $X=M_1/M_2$; $Y=m_1/m_2$; $F=X^2/Y$; $G=X(Y-1/Y)$; $\xi=F/\alpha+F$; $\eta=G/\alpha+F$ and $\alpha=[F_M \bullet F_m]^{1/2}$
M_1 Mole fraction of 4-MCA in feed, M_2 Mole fraction of STY in feed, m_1 Mole fraction of 4-MCA in copolymer

The formation of 4-MCA was confirmed by IR and ^{1}H-NMR spectra.

IR of 4-MCA (cm^{-1}): 3,073(–CH stretching vibration of the aromatic ring), 2,986(ν_{-C-H}), 1,737 ($\nu_{C=O}$; broad), 1,630 ($\nu_{C=C}$), 1,240 (asymmetric ν_{C-O-C}), 1,142 (symmetric ν_{C-O-C}), 890 (–CH bending mode of vinyl group), 730 (C–H rocking mode of vinyl group). The absorption bands at ~1,375 confirmed the CH_3 group. The absorption at 1,585 and 1,502 cm^{-1} are aromatic breathing frequencies. Figures 1 and 2 show the IR spectrum of Homo and monomer 4-MCA.

^{1}H-NMR of 4-MCA (δ) (60 MHz): 6.094 (1H, –CH=), 2.432 (3H, CH3), 6.260 (1H), and 6.533 (1H; nonequivalent methylene protons), 7.061–7.715 (3H, aromatic protons). Figures 3 and 4 show ^{1}H-NMR spectrum of monomer and homopolymer of 4-MCA.

Homo and copolymerization

Homo and copolymerization were carried out in solution using free radical polymerization technique. HPLC chromatogram of monomer 4-MCA which show in Fig. 5. Appropriate quantity of 4-MCA, Sty, *N,N*-dimethylformamide (DMF), and AIBN were mixed in round bottom flask equipped with stirrer and reflux condenser. The reaction mixture was heated at 70°C for 5 to 6 h under stirring. It was then poured in a large volume of methanol with stirring when the polymer precipitated out. It was filtered and washed with methanol. Solid polymer is purified by repeated precipitation by methanol from solution in DMF and finally dried under vacuum. The synthesis of homo and copolymer is represented in Scheme 1.

Copolymer composition and reactivity ratios

The ^{1}H-NMR spectroscopy is well established as a convenient method for determining the compositions of constituent monomer units in a copolymer [15]. The use of ^{1}H-NMR spectroscopy for determination of copolymer composition in acrylate or methacrylate systems has been documented [16, 17]. The chemical composition of the copolymers depends on the degree of incorporation of the comonomers and also on the relative reactivity between them. The F-R and K-T parameters for copolymers of 4-MCA with STR show in Table 1 and reactivity ratio values for poly(4-MCA-co-STR) show in Table 2.

The distribution of protons in the two units is distinguishing monomers in the copolymerization. The aliphatic protons of both the monomers are almost indistinguishable. Grassie et al. [18] calculated the molar ratio of methyl methacrylate and methacrylic acid by the use of total proton differences. Narsimhaswamy and coworkers [19] developed a method for the determination of copolymer composition in the copolymer of phenyl methacrylate and glycidyl methacrylate.

The average composition of monomer units in the copolymer chain was determined from the corresponding ^{1}H-NMR spectra. The assignment of the resonance peaks in the ^{1}H-NMR spectrum leads to accurate evaluation of each monomeric content incorporated into the copolymer chains. Thus, the mole fraction of 4-MCA in the copolymer was calculated by measuring the integral peak height of total aromatic protons to total aliphatic protons of the copolymer chain using following equation.

$$C = \frac{\text{Intensity of aromatic protons } (I_{AROMATIC})}{\text{Intensity of aliphatic protons } (I_{ALIPHATIC})} \quad (1)$$

Now let m_1 be the mole fraction of 4-MCA and then $1 - m_1$ will be that of Sty. There are three and five aromatic protons in 4-MCA and Sty, respectively. 4-MCA has seven aliphatic protons while Sty has three of the same. The composition data of 4-MCA show in Table 3.

$$C = \frac{3m_1 + 5(1 - m_1)}{7m_1 + 3(1 - m_1)} \quad (2)$$

Table 2 Reactivity ratio values for poly(4-MCA-*co*-STR)

Method	Reactivity ratio	
	r_1 r_2	r_2
F–R	1.36	0.62
K–T	1.24	0.58

Table 3 Composition data for free radical copolymerization of 4-MCA with STY in DMF at 70±1 °C

Polymer code	M_1	M_2	Conversion (%)	Intensities of protons		C	m_1
				I_{Ar}	I_{Al}		
1	1.0	–	–	–	–	–	–
2	0.5	0.5	8.88	3.00	6.1031	0.5816	0.512
3	0.4	0.6	9.01	3.00	6.138	0.5740	0.426
4	0.3	0.7	8.25	3.00	5.7492	0.5148	0.330
5	0.2	0.8	9.12	3.00	5.5621	0.5188	0.221
6	0.1	0.9	8.37	3.00	5.356	0.5392	0.115
7	–	1.0	–	–	–	–	–

M_1 Mole fraction of 4-MCA in feed, M_2 Mole fraction of STY in feed, m_1 Mole fraction of 4-MCA in copolymer

$$m_1 = \frac{5 - 3C}{4C + 2} \tag{3}$$

The composition of 4-MCA in copolymer were obtained with the help of the above equation (Eq. 3) and converted into the appropriate units. The overlay spectrum for composition (2, 3, 4, 5, 6, 7) of 4-MCA show in Fig. 6.

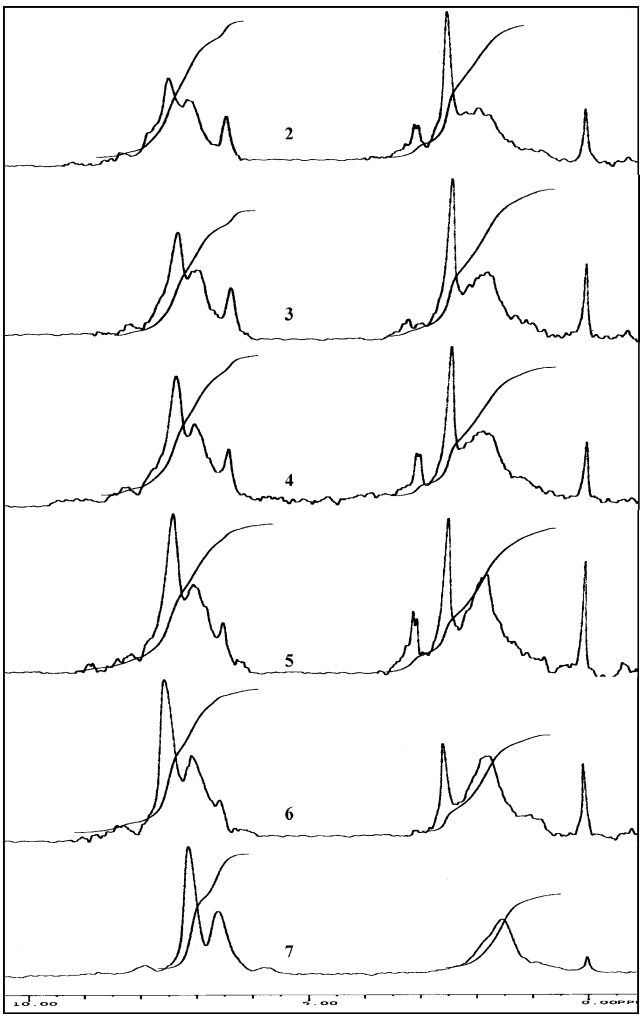


Fig. 6 ^{1}H-NMR spectrum of poly(STR) and poly(4-MCA-*co*-STR)

Results and discussion

The main evidence of the polymer formation is certainly the disappearance of some characteristic signals of the double bond in the IR spectrum and this fact was effectively observed in the present investigation. Thus, the absorption bands at 890 and 730 cm^{-1} assigned respectively to the C–H bending and C–H rocking mode of vinyl group and the stretching vibration of C=C at 1,630 cm^{-1} disappeared in the IR spectrum of poly(4-MCA). The formation of polymer, i.e., poly(4-MCA) is evident from the disappearance of signals at 6.260 (1H), 6.367, and 6.533 (δ) (2H) due to vinyl protons in ^{1}H-NMR and the appearance of broad signals at 3.350 (δ) (1H, –CH) and 2.969–3.096 (δ) (2H, –CH_2). In poly(4-MCA) the aromatic protons are assigned around 6.963–7.480 (δ).

The reactivity ratio of 4-MCA and Styrene were determined by the application of conventional linearization methods such as Fineman–Ross (F–R) [20] and Kelen–Tudos (K–T) [21]. The reactivity of the monomers 4-MCA and Sty were found to be 1.36 and 0.62, respectively. From the reactivity ratio value, r_1 is greater than r_2. Thus, Sty is found to be slightly less reactive than 4-MCA. Since, the values of r_1 and r_2 are less than 1; the system gives rise to

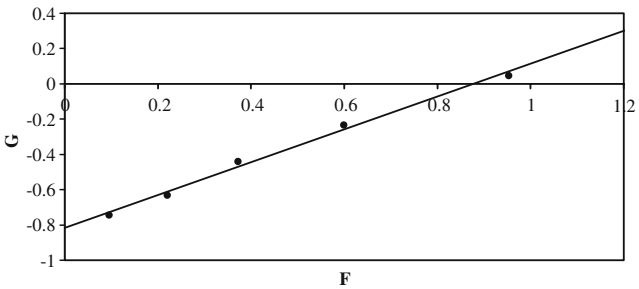


Fig. 7 F–R plot for poly(4-MCA-*co*-STR)

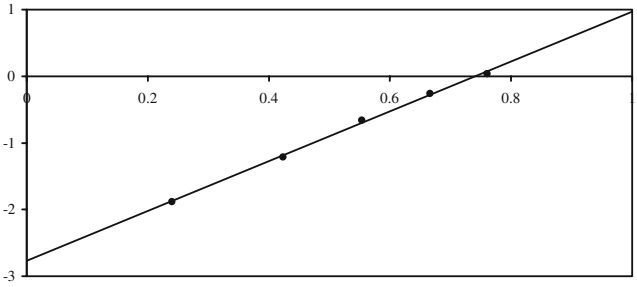


Fig. 8 K–T plot for poly(4-MCA-*co*-STR)

azeotropic polymerization at particular composition of monomer. F-R plot for poly(4-MCA-co-STR) and K-T plot for poly(4-MCA-co-STR) show in Figs. 7 and 8.

$$N_1 = \frac{1 - r_2}{2 - r_1 - r_2} \tag{4}$$

Where, N_1=mole fraction of monomer 4-MCA in feed.

From Eq. 4, the value of N_1 is 0.720. When the mole fraction of monomer 4-MCA in the feed is 0.720, the copolymer formed will have the same composition of the feed. When the mole fraction is less than 0.720, the copolymer will be richer in 4-MCA monomeric unit where as the copolymer is richer in Sty monomeric unit if the molefraction is greater than 0.720. Since the product r_1r_2 is less than 1, the system follows a random distribution.

Conclusion

The monomer 4-MCA was synthesized, characterized, and copolymerized with styrene using different feed ratio by free radical solution polymerization. Conventional methods were employed to characterize the polymers. The reactivity ratio styrene is slightly less reactive then 4-MCA. The system gives rise to azeotropic polymerization at particular composition of monomer. The product r_1r_2 is less than 1, which indicates that the system follows a random distribution.

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References

1. Kine BB, Nivak RW (1986) Encyclopedia of polymer engineering, 2nd edn. Wiley, New York, p 234
2. Shantha KL, Harding DRK (2003) Euro Poly J 39:63
3. Pan HZ, Yu SY, Li WJ, Li FM (2002) Polymer preprints 43 (2):260
4. Thamazharsi S, Rami Reddy AV (1992) Euro Poly J 28:119
5. Omidin H, Hashemi SA, Sammes PG, Meldrum I (1999) Polymer 40:1753
6. Lengu A, Neckers DC (1995) J Coat Technol 67:29
7. Jiaonianji Z, Mi-Ya-Ha (2002) Chem Abstr 137(10):141370e
8. Widmaier R, Schneider T, Mathauer K, Burghardt A (2004) PCT int. Appl. 140(23):37–940
9. Patel SA, Shah BS, Patel PM, Patel RM (2004) Iran Polym J 13 (6):445–453
10. Sharma AK, Bal AK (1953) Stain Tech 8:255
11. God S (1993) Khim Flak 85:77–83
12. Lee J, Kim H (2001) Bull Korean Chem Soc 22(2):179–181
13. Furniss BS, Hannaford AJ, Smith PWG, Tatchell AR (1989) AR Vogel's Text book of Practical Organic Chemistry, 5th edn. Pearson, Singapore
14. Stempel GH, Cross RP Mareioll RP (1950) J Ame Chem Soc 72:2299
15. Ivin KJ, Pitchumani S, Reddy RC, Rajadurai S (1981) Eur Poly J 17:341
16. Tocx JCJF, Velden VGPM, German AL (1988) Polymer 29:1675
17. Rudin A, Driscoll KFO, Rumack (1981) MS Polymer 22:740
18. Grassie N, Torrance BJD, Fortune JD, Gemmell JD (1965) Polymer 6:633
19. Narsimhaswamy T, Sumathi SC, Reddy BSR (1991) Polymer 32 (18):3426
20. Kelen T, Tudos F (1975) J Macro Sci Chem A 9:1
21. Broido A (1969) J Polym Sci A 2(7):176