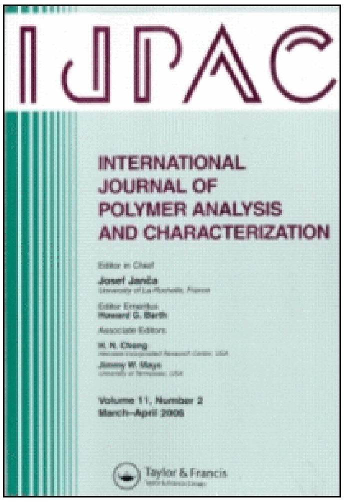

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Crystalline Amphiphilic (Maleanilic acid-*ran*-styrene) Copolymers: Structural and Kinetic Properties

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Abstract: A series of amphiphilic (maleanilic acid-*ran*-styrene) copolymers composed of hydrophobic and hydrophilic moieties were prepared by radical copolymerization using different molar feed ratios of maleanilic acid and styrene. The obtained copolymers were structurally examined by FT-IR, TGA, XRD, and SEM. The weight average molecular weight (M_w) was determined by light scattering method in DMSO and found to lie in the range of 20,000–334,000 g/mol depending upon the molar feed ratio of the maleanilic acid and styrene monomers. The reactivity ratios and *Q*-*e* scheme values for the copolymerization process showed a random arrangement of repeating units. The corresponding activation energies for the degradation process ($E_{a,d}$) for maleanilic acid and styrene fractions in the copolymer were determined from the TGA data and found to be 57.1 and 89.5 kJ/mol, respectively. The SEM and XRD data show that these copolymers exhibit a rigid rock-like texture with different degree of percent crystallinity. The hydrophilic moiety (−COOH) in these copolymers was found to play a crucial role in determining their crystallinity and textural morphology. The implication of the presence of the hydrophobic and hydrophilic groups in close proximity is discussed.

Keywords: Amphiphilic; Maleanilic acid; *Q*-*e* scheme values

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INTRODUCTION

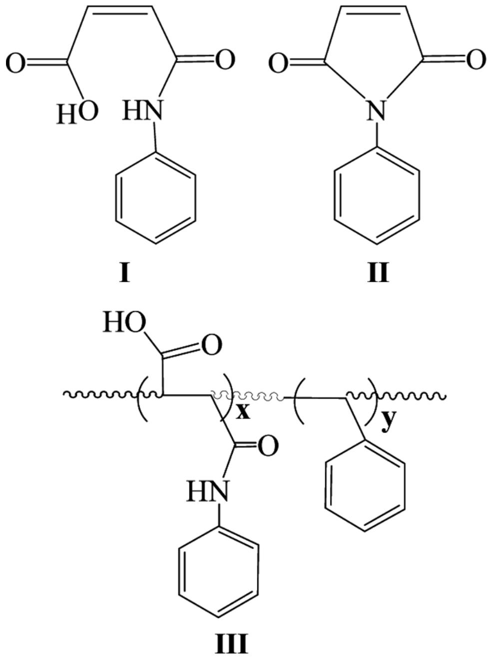
Monomers with two or more different reactive functionalities that can be further modified via grafting, curing, and attaching/anchoring organic and inorganic additives have attracted increasing interest in recent years.[1–6] In particular, amphiphilic monomers that simultaneously have both hydrophobic and hydrophilic moieties are of special interest in cosmetic preparations, nanoparticle coating technology, enzyme immobilization, phase-transfer agents, and other applications.[4–8] Amphiphilic polymers and copolymers play an important role in the dispersion, formation, and stabilization of colloidal solutions, emulsions, and gels.[9–10] Poloxamers, where the hydrophobic blocks are isolated (separated) by hydrophilic blocks, are well-established systems.[11] In recent years, polymer-dispersed liquid crystals in which droplets or nanoparticles of liquid crystalline (LC) substances are dispersed into polymer matrices have attracted growing attention.[12–13] The unique behavior of these systems relies not only on the LC structure and characteristics but also on the polymer matrix. In such a system, the change in the orientation of LC molecules with an applied electric field is controlled by the presence of hydrophobic-hydrophilic groups in the polymer matrix, and therefore all LC characteristics (transmitted light, etc.) are tuned accordingly.

On the other hand, the reaction of maleic anhydride with aniline results in the formation of maleanilic acid (**I**) and N-phenylmaleimide (**II**) depending on the reaction conditions.[14] It is obvious that maleanilic acid (**I**) monomer contains hydrophilic carboxylic (−COOH) and hydrophobic (−CONHPh) functionalities. These groups characterize the surface properties, hydrodynamics, and morphology of their polymers and copolymers. This monomer has several inherent advantages. First is the presence of hydrophobic-hydrophilic groups in close proximity. Second, the presence of a pendent carboxylic group (−COOH) allows this monomer or its polymer/copolymers to encapsulate organic, inorganic, and organic-inorganic hybrid nanoparticles. Third, the aniline functionality can be further oxidatively polymerized with excess aniline to form a grafted polyaniline on the backbone of the maleanilic acid polymer and its copolymers. In this article, we describe the synthesis, characterization, and reactivity ratio, *Q*-*e*, scheme for amphiphilic (maleanilic acid-*ran*-styrene) copolymers shown in Scheme 1(III).

EXPERIMENTAL SECTION

Materials and Measurements

Aniline (Aldrich) was distilled before use. All other chemicals and solvents are reagent grade (maleic anhydride (Scharlau), styrene



Scheme 1.

(Aldrich)) and used as received without further purification. Thermogravimetric analysis (TGA) was performed on Shimadzu TGA-50 (Japan) in the temperature range of 25°–500°C under N_2 atmosphere at a heating rate of 10°C/min unless otherwise stated. The Fourier transform-infrared (FT-IR) spectra were recorded on a Nicolet (Avator-360, USA) in the range of $4000–400\,\mathrm{cm}^{-1}$ as KBr pellets. X-ray diffraction (XRD) was obtained using a Philips-Holland diffractometer (PW 1729) using copper, $K\alpha$ radiation ($\lambda = 1.5406$ Å) generated at 30 kV, 40 mA, and 2θ range of 5° and 100°. Scanning electron microscopy (SEM) was obtained using a DSM 950 (Zeiss). The SEM samples were coated with gold by sputtering method (Polaron E6100). The weight average molecular weight (M_w) was measured using light-scattering technique.[15]

Preparation of (Maleanilic acid-*ran*-styrene) Copolymers

Maleanilic acid monomer was prepared according to the literature procedure by reacting equimolar quantities of maleic anhydride and aniline at about 50°C.[14] A creamy solid immediately forms, which is then washed with ether and dried under vacuum. The isolated maleanilic acid product

Table I. The physical data for amphiphilic (maleanilic acid-*ran*-styrene) copolymers

Maleanilic acid/ styrene molar ratio	Yield (%)[a]	m.p (°C)	M_w^b (g/mol)
0.33	40	155–157	142,000
0.5	57	158–178	25,000
1.0	79	160–177	20,000
2.0	77	176–181	167,000
3.0	77	178–184	334,000

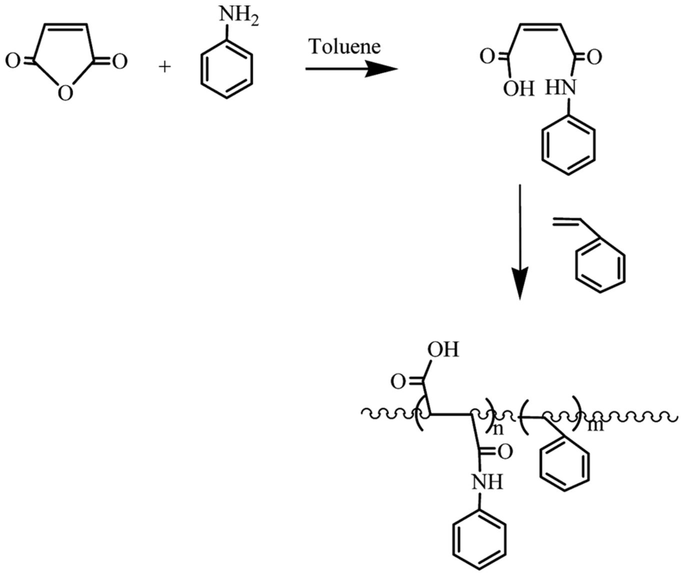
[a] Calculated based on the feed amounts of the monomers.
[b] Determine by light-scattering method.

was characterized by FT-IR and melting point (m.p. = 201°–205°C). The obtained monomer was mechanically crushed into fine particles using an electrical mill, suspended in xylene, and then subjected to sonication for about 1 h, during which maleanilic acid monomer dissolves with the removal of oxygen from the reaction system. Different feed ratios of styrene were added to the maleanilic acid solutions as shown in Table I. The reaction mixture was warmed to 60°–65°C followed by addition of small amounts of radical initiator (benzoyl peroxide) under continuous sonication for 2–3 h and left overnight. The resulting creamy hard solids were filtered off and washed with toluene to remove polystyrene and with chloroform to remove polymaleanilic acid homopolymers.

RESULTS AND DISCUSSION

Synthesis and Characterization

Maleanilic acid was prepared according to the literature procedure by mixing equimolar quantities of maleic anhydride and aniline in toluene. The air-stable creamy monomer is soluble in common organic solvents (tetrahydrofurane (THF), acetonitrile, chloroform, and dimethyl sulfoxide (DMSO)). Melting point and FT-IR spectroscopic analysis of this monomer indicated that the obtained monomer is consistent with that of maleanilic acid (**I**). Our interest in this monomer lies in the fact that it has a hydrophobic aniline group as well as a hydrophilic carboxylic acid group. The xylene solution of this monomer is copolymerized with different molar ratios of styrene in a sonicating bath at ~60°C, as shown in Scheme 2. Caution was taken to remove the formed homopolymers using chloroform and toluene. The percentage yield, melting point, and weight average molecular weight (M_w) of the obtained copolymers are



Scheme 2. Reaction scheme for the formation of (maleanilic acid-*ran*-styrene) copolymer.

listed in Table I. In fact, the low percentage yield in the case of excess styrene can be explained by the formation of substantial amounts of polystyrene homopolymers in the copolymerization mixture. Close inspection of the melting point data shows that the melting point of these copolymers gradually increases with increasing maleanilic acid in the feed ratio, therefore suggesting the carboxylic acid group involvement in the conformation and packing of the copolymer chains. Furthermore, the presence of small melting point range in the 0.33 (155°–157°C) and 3 (178°–184°C) molar ratios is apparent when either styrene or maleanilic acid monomer is in excess over the other.

The weight average molecular weight (M_w) was determined from light scattering[15] and was found to range from 20,000 to 334,000 g/mol mol depending upon the molar feed ratio of these monomers. It is evident that the highest M_w of 334,000 g/mol was obtained when maleanilic acid was predominant over styrene in the feed ratio.

Infrared Spectroscopy (FT-IR)

The FT-IR spectra for the obtained amphiphilic (maleanilic acid-*ran*-styrene) copolymers were recorded in 4000–400 cm^{-1} region as KBr pellets. Figure 1 displays a typical FT-IR spectrum obtained for these

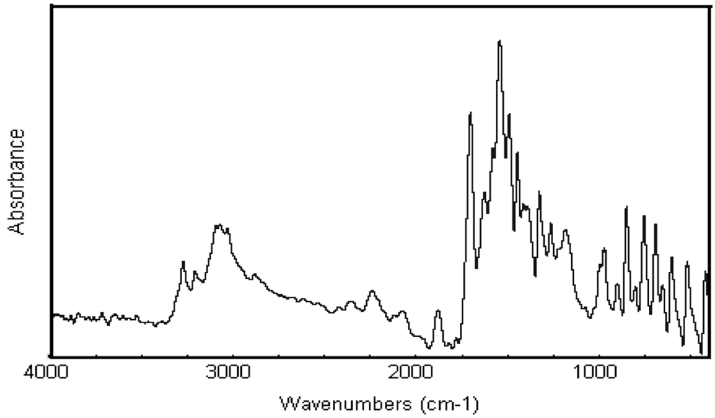


Figure 1. FT-IR spectrum of molar ratio = 1.0 of amphiphilic (maleanilic acid-*ran*-styrene) copolymer.

copolymers. Typical characteristic bands due to the stretching frequencies of ν_{O-H} (3280, 3210 cm^{-1}), ν_{N-H} (3080, 3030 cm^{-1}), ν_{C-H} (2885 cm^{-1}, aliphatic H of styrene group), $\nu_{C=O}$ (1712 cm^{-1}, carboxylic group), $\nu_{C=O}$ (1548 cm^{-1}, amide of the maleanilic acid group), $\nu_{\bar{C}OO}$(1591 cm^{-1}, asymmetric), and $\nu_{\bar{C}OO}$(1400 cm^{-1}, symmetric) are observed. Interestingly, the presence of two well-resolved sharp peaks for ν_{O-H} of the maleanilic carboxylic acid group indicates that –COOH group is confined in two slightly different environments with medium-strong H-bonding. Similarly, the ν_{N-H} of the aniline moiety exhibits two poorly resolved peaks in accordance with the above conclusion.

Thermogravimetric Analysis (TGA)

The thermal behavior of the obtained copolymers was investigated by TGA under N_2 atmosphere in the temperature range of 25°–500°C (heating rate = 10°C/min). The TGA data are summarized in Table II. It is obvious from the degradation data that the decomposition of the maleanilic acid in the copolymer occurs in the 197°–204°C range, which is very close to that of the poly(maleanilic acid) homopolymer. However, styrene degrades between 397° and 403°C, slightly higher than the pure polystyrene. Furthermore, the percentage mass loss results indicate that the maleanilic acid content in the copolymers samples is larger than the styrene content. Although the molar feed ratios were in the range of 0.33–3.0, it was found their molar ratios in the copolymers are in the range of 1.4–3.7. This observation confirms that the maleanilic acid monomer prefers interacting with itself rather than interacting with styrene.

Table II. Decomposition temperatures for the different molar feed ratios of amphiphilic (maleanilic acid-*ran*-styrene) copolymers at a heating rate of 10°C/min

Maleanilic acid/styrene molar feed ratio	Degradation temperature, °C (% mass loss)[a]		Maleanilic/styrene	
	Maleanilic acid	Styrene	Molar ratio in copolymers[b]	Carbonaceous residue (%)[c]
0.33	197 (61)	389 (23)	1.69	16
0.5	201 (63)	397 (24)	1.67	13
1.0	204 (64)	403 (28)	1.40	8
2.0	201 (68)	399 (21)	2.10	11
3.0	202 (76)	397 (13)	3.70	11
Polystyrene	—	387 (99)	—	~1
Poly(maleanilic acid)	204 (99)	—	—	~1

[a] Decomposition temperature as deduced from the first derivative of TGA profile.
[b] Calculated from mass loss % and molecular mass of styrene and maleanilic acid units.
[c] Carbonaceous residue at ~500°C.

This assumption is supported by the observation of the large amount of pure polystyrene homopolymer that was removed when the (maleanilic acid-*ran*-styrene) copolymers were washed continuously with toluene. This is further supported by Kelen-Tudos plot, which also indicates random arrangement of styrene and maleanilic acid in the backbone of the copolymer (see reactivity ratio and Kelen-Tudos section).

Kinetic Parameters of Amphiphilic (Maleanilic acid-*ran*-styrene) Copolymers

Figure 2 displays the degradation kinetic plots of the molar feed ratio of 1.0 at different heating rates of 5, 10, 20, and 40°C/min. The results in Table III show that the degradation temperature of the styrene and maleanilic acid in the copolymer increases with increasing heating rate. According to Ozawa,[16] a plot of the logarithm of the heating rate (log B) versus the reciprocal of the corresponding decomposition temperature ($1/T_{\text{decomposition}}$) is linear like that of the Arrhenius plot. Figure 3(a) and (b) depicts two linear plots for log B versus $1/T_{\text{decomposition}}$ of the maleanilic acid (196°–226°C) and styrene (386°–424°C) fractions, respectively. The corresponding activation energies for the degradation process ($E_{a,d}$) for maleanilic acid and styrene fraction in the copolymer were found to be 57.1 and 89.5 kJ/mol, respectively. These values are in agreement with

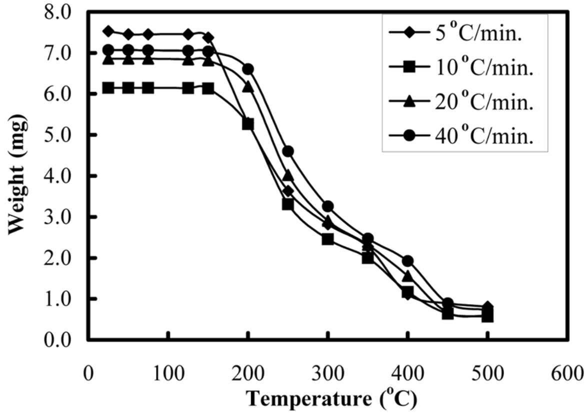


Figure 2. TGA plot of molar feed ratio = 1.0 of amphiphilic (maleanilic acid-*ran*-styrene) copolymer at different heating rates.

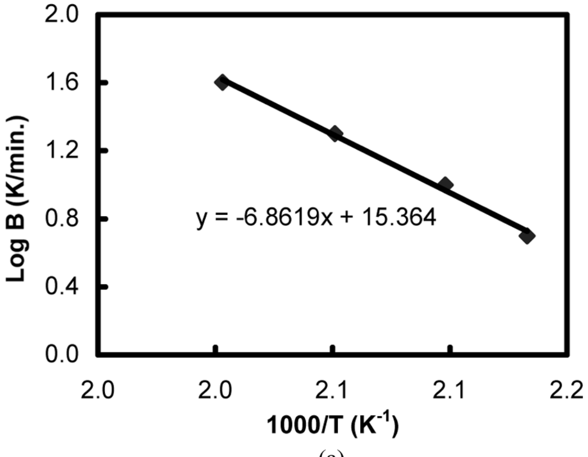
the *Q* values of the constituting monomers where maleanilic acid shows a higher reactivity (higher *Q* value) than styrene (see section on reactivity).

Furthermore, from the weight average molecular weight values of the copolymers from Table I, it can be noted that as molar feed ratios increase from 1.0 to 2.0 and then to 3.0 (i.e., increase in maleanilic acid monomer content) the molecular weight increases from 20,000 to 167,000 to 334,000 g/mol, whereas as molar feed ratio changes from 1.0 to 0.5 and then to 0.33 (i.e., increase in styrene monomer content), the molecular weight increases from 20,000 to 25,000 to 142,000 g/mol. Obviously, for this fixed time polymerization process, the entrance rate of maleanilic acid monomer into the chain is faster than that of styrene monomer, which is then detected through the large jump of molecular weight values as the molar feed ratio increases from 1.0 to 3.0, whereas the increase in molecular

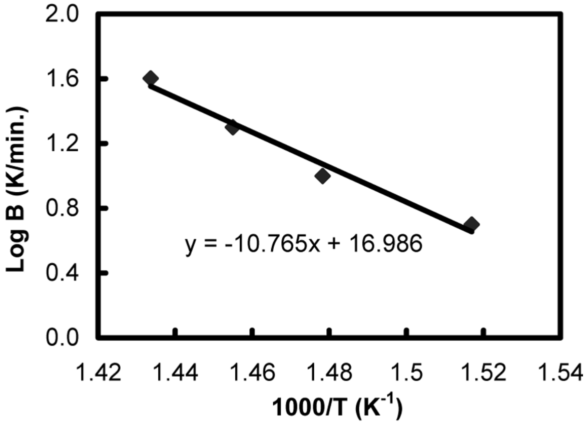
Table III. Decomposition temperatures for molar feed ratio = 1.0 of amphiphilic (maleanilic acid-*ran*-styrene) copolymer as a function of heating rates

Heating rate (°C/min)	$T_{decomp.}$ (°C) (maleanilic acid)[a]	$T_{decomp.}$ (°C) (styrene)[a]
5	196	386
10	204	403
20	215	414
40	226	424

[a] Decomposition temperature was measured from the first derivative of the TGA profile.



(a)



(b)

Figure 3. Plots of log (heating rate) vs. $1/T_{decomposition}$ for (a) maleanilic acid and (b) styrene fractions in the copolymer.

weight values was relatively small when molar feed ratio changes from 1.0 to 0.33. This finding is in accordance with activation energy values, which confirms larger activation energy value for styrene than maleanilic acid monomer.

Reactivity Ratios

The Kelen-Tudos technique (Equation (1)) was used to calculate the reactivity ratios (r_1 and r_2) for styrene and maleanilic acid monomers in the prepared amphiphilic (maleanilic acid-*ran*-styrene) copolymer[17]:

$$\eta = \left(r_1 + \frac{r_2}{\alpha}\right)\xi - \frac{r_2}{\alpha} \tag{1}$$

where

$$\eta = \frac{G}{F+\alpha}, \quad \xi = \frac{F}{F+\alpha}, \quad G = \frac{X(Y-1)}{Y}, \quad F = \frac{X^2}{Y}$$

and $\alpha = (F_m F_M)^{1/2}$, where F_m and F_M are lowest and highest F values, X = molar ratio in the feed, and Y = molar ratio in the copolymer.

The maleanilic acid/styrene molar ratios in the reaction feed (X) are compared to their molar ratios in the copolymer (Y). The molar ratios in the copolymer (Y) values were determined from the FT-IR data of the absorbance of $\upsilon_{C=O}$ of the carboxylic group of maleanilic acid unit located at 1706 cm^{-1} to that of aliphatic υ_{C-H} of styrene segments located at 2885 cm^{-1}; X values are given in Table I. Interestingly, the Y values obtained from FT-IR data are comparable with those calculated from the TGA. Figure 4 shows the Kelen-Tudos plot of η versus ξ used for the determination of the reactivity ratios for both styrene and maleanilic acid monomers. The r_1 and r_2 values were found to be 0.82 and 0.86 respectively. Given that $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$, it can be clearly seen that the rate constants of k_{11}, k_{12}, k_{21}, and k_{22} are very close to each other. This proximity reflects that the rate of the addition of M_1 and M_2 monomers to the macro-radical ($M_nM_1^\bullet$) chain is similar and the rate of the addition of M_2 and M_1 monomers to the macro-radical ($M_nM_2^\bullet$) to the chain is also similar.

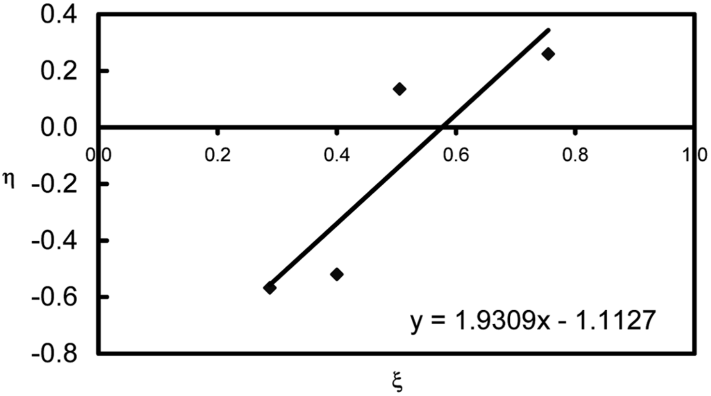


Figure 4. Kelen-Tudos plot of the amphiphilic (maleanilic acid-*ran*-styrene) copolymer.

This result indicates no favoring of the macro-radicals ($M_nM_1^{\bullet}$ or $M_nM_2^{\bullet}$) toward M_1 or M_2 monomers, and, consequently, the formed copolymer will be in *random* sequence arrangement. Furthermore, the ($r_1 \times r_2$) product is less than 1 (i.e., 0.71), which further indicates that the copolymerization process of maleanilic acid and styrene tends to form random copolymers.

Q-e Scheme

The Q and e parameters for any novel monomer find increasing interest due to their significance in determining respectively reactivity and polarity relative to known Q and e values of another monomer. In our case, maleanilic acid monomer Q_2 and e_2 values are determined using the reported values for styrene monomer ($Q_1 = 1.0$ and $e_1 = -0.8$) as shown by the Alfrey-Price equation (Equation (2). The $r_1 \cdot r_2$ product is used to determine e_2, which is then used to calculate Q_2 as in Equation (3)[18]:

$$r_1 \cdot r_2 = \exp[-(e_1 - e_2)^2] \tag{2}$$

$$Q_2 = Q_1/r_1 \exp[-e_1(e_1 - e_2)] \tag{3}$$

It is important to note that the Q-e values represent the reactivity and polarity parameters, respectively. The higher Q value for maleanilic acid compared to styrene implies that maleanilic is more reactive than styrene. This may be explained by invoking the notion of resonance structures in maleanilic acid and styrene where the former resonance structure involves six π-bonds compared to four π-bonds in styrene, and hence greater resonance stability in maleanilic acid. However, the lower e value of maleanilic acid monomer than styrene monomer indicates higher electron-releasing power of the substituents on the vinyl monomer, and consequently maleanilic acid monomer becomes less polar than that in styrene. Table IV summarizes the kinetic parameters obtained for the obtained amphiphilic (maleanilic acid-*ran*-styrene) copolymer. In this context, it is important to note that maleic anhydride and styrene form a typical alternating copolymer (i.e., $r_1 = 0.0$, $r_2 = 0.02$).[4,19] This fact can be utilized to prepare alternating

Table IV. Reactivity ratios (r_1 and r_2) and Q-e scheme parameters for amphiphilic (maleanilic acid-*ran*- styrene) copolymers

r_1(styrene)	r_2 (maleanilic acid)	$r_1 \times r_2$	Q_2	e_2
0.82	0.86	0.71	1.28	−1.15

(maleanilic acid-*alt*-styrene) copolymers by first preparing (maleic acid-*alt*-styrene) followed by reaction with aniline.

Structural Properties of Amphiphilic (Maleanilic acid-*ran*-styrene) Copolymers

Crystalline Structure

Powder X-ray diffraction was performed on the different molar feed ratios of the obtained amphiphilic (maleanilic acid-*ran*-styrene) copolymers. Figure 5 displays the XRD patterns of the prepared copolymers.

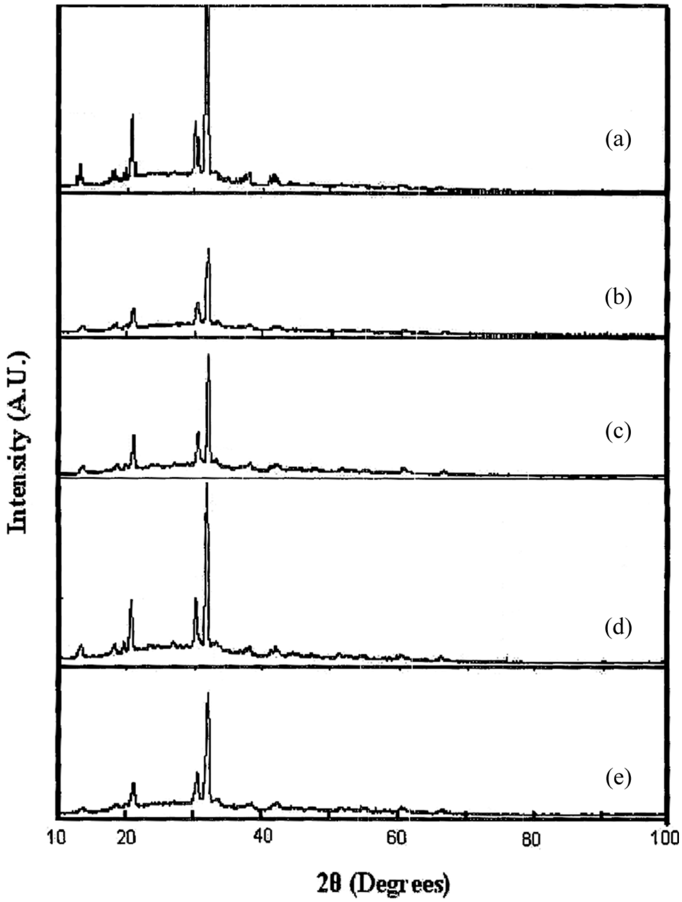
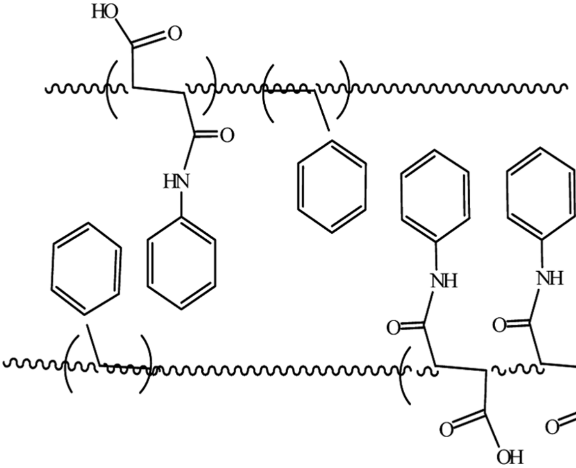


Figure 5. XRD patterns for (maleanilic acid-*ran*-styrene) copolymer with molar feed ratios of (a) 1.0, (b) 0.5, (c) 0.33, (d) 2.0, and (e) 3.0.

The XRD profiles consist of six sharp diffraction peaks superimposed on a broad diffraction feature in the range of $2\theta = 10$–40°. The position of the sharp diffraction peaks due to the crystalline regions in the polymer lattice appears to be unchanged with different molar feed ratios of the constituting monomers. This observation suggests that these copolymers have relatively similar crystal lattice packing and macro conformation. In fact, the presence of aromatic groups on both monomers may cause similar crystal packing characteristics. Recall that pure polystyrene shows 100% amorphous polymer,[20] which can be attributed to the free rotation of the pendant phenyl groups thus preventing/weakening π-π stacking interactions. This demonstrates that the major contributing groups to the observed crystallinity regions are due to maleanilic acid pendant groups (i.e., $-$COOH and $-$CONHPh), which are the main constituents of the copolymer backbone, as the TGA data in Table II suggests. Scheme 3 displays expected modes H-bonding and π-π stacking interactions due to intra- and intermolecular chain interactions, which eventually lead to crystalline regions regardless of the molar feed ratio of the constituting maleanilic acid and styrene monomers.

The diffraction peak at $2\theta = 13.44^\circ$ is strongly dependent on the length of the lateral groups and is therefore associated to intermolecular vectors (d_i-spacing). However, the peak at $2\theta = 31.86^\circ$ is related to the intramolecular average distance along the backbone chain (d_0-spacing). Using Bragg's law of diffraction ($n\lambda = 2d \sin \theta$), d_i and d_0 were found to be 6.6 Å and 2.8 Å, respectively. Interestingly, the relative diffraction peak intensity due to d_0 spacing to d_i spacing were found to be equal



Scheme 3. Possible modes of interaction in (maleanilic acid-*ran*-styrene) copolymer.

to 6 (i.e., $I_{d0}/I_{di} = 6.0$) for all the samples. It is known that H-bonding interaction shows a d-spacing value around 3.0 Å, whereas the π-π stacking interaction gives a d-spacing value around 6.0 Å for maleimide-containing polymers as reported in the literature.[21,22] Thus the d_0 and d_i spacings in our samples represent H-bonding and π-π stacking interactions, respectively. The relative intensity ratio of d_0 spacing to d_i spacing of ~6.0 reflects the contribution of each interaction in the formation of crystalline regions. These findings imply that in addition to π-π stacking, H-bonding interactions play a crucial role in formation of crystalline regions. Obviously, the *trans* configuration of the –COOH and –CONHPh in the maleanilic acid repeating unit is much more stable than the *cis* form. This observation is in accordance with the presence of two resolved peaks ($\nu_{O-H} = 3280$ and $3210\,cm^{-1}$) in the FT-IR spectra of these copolymers that were attributed to symmetric and asymmetric OH stretching frequencies, which indicate medium-strong H-bonding.

Close inspection of the relative intensities of the sharp diffraction peaks in Figure 5 shows that high intensity peaks are observed in the case of molar feed ratio = 1.0 copolymer. The percentage crystallinity in these copolymers can be estimated from the relative areas under the sharp peaks compared to the corresponding areas under the background curve. The calculated crystalline percentages for all the prepared copolymers are recorded in Table V.

In fact, the crystallinity percentage is highest (33.7%) in the case of molar feed ratio = 1.0 (i.e., maleanilic acid/styrene ratio) copolymers, whereas it is least (18.4%) for molar feed ratio = 0.5. Comparison between the crystallinity data in these copolymers clearly suggests that maleanilic acid contributes to copolymer crystallinity more than styrene.

Table V. Change of % crystallinity as maleanilic acid/styrene molar ratios change in the amphiphilic (maleanilic acid-*ran*-styrene) copolymers

Maleanilic acid/ styrene feed molar ratios	Maleanilic acid/ styrene molar ratios in the copolymer[a]	% Crystallinity
1.0 (a)	1.40	33.7
0.5 (b)	1.67	18.4
0.33 (c)	1.69	22.8
2.0 (d)	2.10	30.9
3.0 (e)	3.70	28.5

[a] From Table II.

Morphological Texture

The morphology of the obtained (maleanilic acid-*ran*-styrene) copolymers was studied using scanning electron microscopy (SEM); see Figure 6. The SEM micrographs reveal that these copolymers consist of irregularly shaped agglomerates of different particle sizes. This observation implies that similar textural compactness exists regardless of the different styrene/maleanilic acid ratios in the copolymers. This may be attributed to the similarity in structure of the pendent phenyl group of the styrene units and the aniline group of the maleanilic acid and to the similarity of maleanilic acid/styrene ratios in all the samples, as Table II suggests.

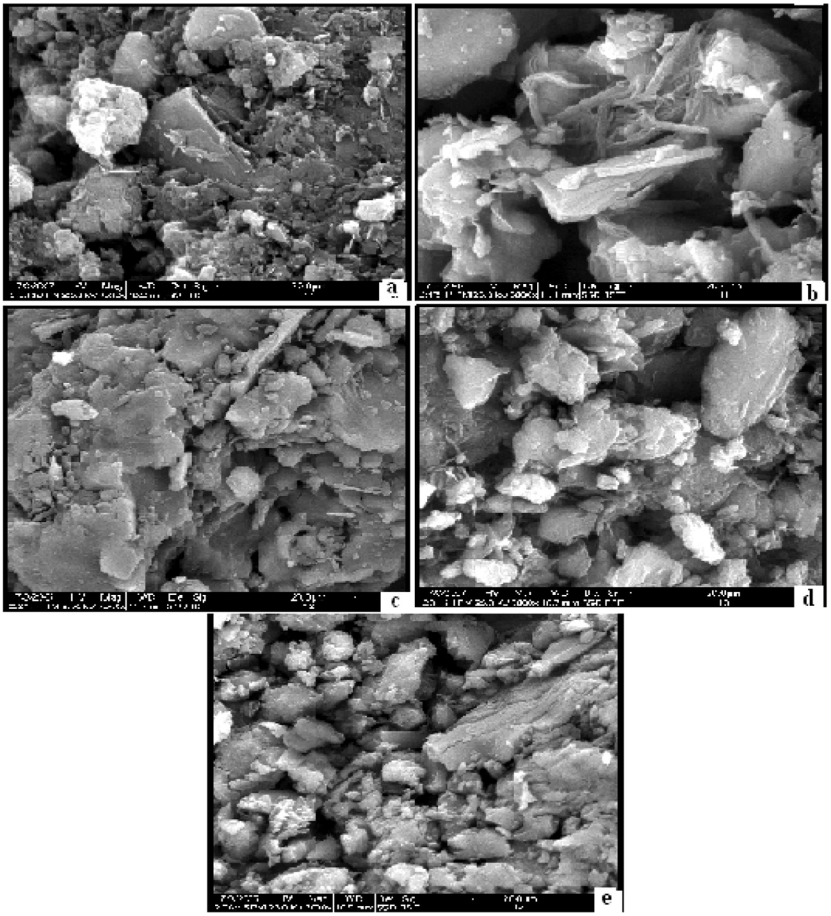


Figure 6. SEM micrographs of (maleanilic acid-*ran*-styrene) copolymer with molar feed ratios of (a) 1.0, (b) 0.5, (c) 0.33, (d) 2.0, and (e) 3.0.

Furthermore, the morphology suggests that in all cases these copolymers exhibit low dimensional textural structures. In fact, different morphologies may be seen when one of the monomers is dominant over the other (>10-fold).

However, close examination of the SEM micrograph in Figure 6(c) (molar feed ratio $= 0.33$) and that in Figure 6(e) (molar feed ratio $= 3.0$) shows that when the maleanilic acid is present in excess (Figure 6(e)) the texture of the copolymer is less compact than that when styrene is dominant in the copolymer.

It is important to note that amphiphilic monomers, which consist of hydrophobic and hydrophilic functionalities, form a highly ordered self-assembly structure. This allows the hydrophobic and hydrophilic segments to orient on opposite sides, permitting the formation of bilayer structures. This case is of particular importance in thin-film casting from organic solvents where the polarity and structure of the solvent are crucial.

CONCLUSION

Maleanilic acid is a versatile monomer that can be used in the preparation of a wide range of copolymers. In this work, random (maleanilic acid-ran-styrene) copolymers show a relatively high tendency towards the formation of crystalline amphiphilic copolymers. However, by adopting a different synthetic procedure alternating amphiphilic (maleanilic acid-*alt*-styrene) can be prepared from the reaction of aniline with (maleic anhydride-*alt*-styrene) copolymers. Comparison between the structural characteristics of resulting amphiphilic random and alternating forms on their overall morphology, surface properties, and dispersion properties is of high value to several industries including cosmetics, protective and decorative coating, and other industries. Furthermore, maleanilic acid has two reactive functional groups ($-COOH$ and $-NHC_6H_5$) that can be further utilized in grafting procedures. Interestingly, the pendent aniline can be involved in oxidative coupling reaction with excess aniline to afford grafted polyaniline onto the backbone of these copolymers. The resulting grafted terpolymers exhibit interesting electrical, morphological, and other structural characteristics that are of potential value to polyaniline chemistry and its applications.

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