

Terpolymerization of 2-ethoxy ethylmethacrylate, styrene and maleic anhydride: determination of the reactivity ratios

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Abstract. Terpolymerization of 2-ethoxyethyl methacrylate (2-EOEMA), styrene (St) and maleic anhydride (Ma) initiated by benzoyl peroxide was carried out in acetone as common solvent for three monomers. The structure and composition of terpolymer were determined by FTIR spectroscopy by recording analytical absorption bands for St (3002 cm^{-1}), Ma (1781 cm^{-1}) and 2-EOEMA (1261 cm^{-1}) units, respectively. The reactivity ratios for the monomers were calculated according to the general copolymerization equations following the Fineman–Ross and Kelen–Tudos models. The results show that terpolymerization were carried out through primary “complex” mechanism at near-binary copolymerization of [St...Ma] complex with 2-EOEMA. Structure of the resulting terpolymer illustrated by ¹H-NMR and differential scanning calorimeter showed reduction in T_g value.

Keywords. Terpolymerization; 2-ethoxyethyl methacrylate; reactivity ratio.

1. Introduction

For the last two decades, an acceptor–donor–acceptor (donor) monomer system is an effective method for the synthesis of functional macromolecules with given composition, structure and properties (Triverdi and Culberston 1982; Rzaev 1984). The complex-radical terpolymerization of Ma (acceptor), with vinyl aromatic i.e. St (donor), gives an alternating copolymer, probably through formation of a donor–acceptor complex between St and Ma. Valuable properties can be obtained in terpolymer system in which St along with various functional group monomers such as vinyl acrylate etc (as acceptor or donor), are present besides Ma (Wittmer *et al* 1969; Ham 1983). This type of terpolymer is applied as water-dispersing agent, paint additive, thickening agent and carrier of biologically active substances etc (Florjanczyk and Krawiec 1933).

As a part of our on going studies on free radical polymerization (Sherigara *et al* 1999; Rai *et al* 2000; Yashoda *et al* 2000, 2001; Prashantha *et al* 2002), polymeric blends and surfactants (Prashantha *et al* 2001; Prasanna-kumar *et al* 2003; Sanmathi *et al* 2004), we present here the preliminary data on the radical terpolymerization of the system containing St and Ma complex with 2-ethoxyethyl methacrylate (2-EOEMA). This system was chosen to understand the characteristics of the mechanism of

complex radical terpolymerization involving St and Ma. None of these three monomers homopolymerized under the conditions of the reaction selected.

2. Experimental

2.1 Characterization methods

2.1a Infrared spectra: Infrared spectra of the synthesized terpolymers on KBr pellets were obtained from Shimadzu FTIR 4200 series spectrophotometer.

2.1b ¹H-NMR spectra: The ¹H-NMR spectra of the terpolymer was recorded on a 90 MHz Varian EM-360 spectrometer at room temperature as 10–15 g l⁻¹ solutions, in deuterated chloroform with TMS as internal standard.

2.1c Glass transition temperature: The glass transition temperature was determined on a Mettler TA4000 DSC. Temperature and energy calibrations were carried out with indium. Samples weighing between 12 and 15 mg were used in all cases. The scan rate was 10°/min in air. The glass transition temperature (T_g) was calculated as the inflection point of the jump of heat capacity.

2.2 Materials

Styrene and 2-ethoxyethyl methacrylate (Aldrich) were washed with aqueous sodium hydroxide solution and dis-

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tilled water followed by drying over anhydrous calcium chloride and finally distilled under vacuum for further use. Maleic anhydride (Aldrich) was purified before use by recrystallization from anhydrous benzene and sublimation in vacuum. Benzoyl peroxide of analytical grade (S-d fine), was purified by recrystallization in chloroform methanol mixture. The solvents used, diethyl ether and acetone, were of analytical grade (E-Merck).

2.3 Synthesis

Synthesis of ternary copolymer with different compositions, were carried out in a 100 ml round bottom flask with acetone as solvent and benzoyl peroxide as initiator at 60°C. The reaction flask was purged with nitrogen gas continuously and reactions were continued up to 15% conversion. On completion of reaction, the mixture was cooled to room temperature to terminate polymerization. Cooled mixture was poured into a large volume of diethyl ether to precipitate the terpolymer and was separated by filtration. Obtained terpolymer products were in powder form, which were dried under vacuum at 50°C to constant weight (scheme 1).

3. Results and discussion

3.1 Infrared spectroscopy (IR)

The terpolymers synthesized were characterized by FTIR spectroscopy for the determination of St, Ma and 2-2-EOEMA units. The absorption band value for characteris-

tics groups are, 3100–3000 cm^{-1} (–CH in aromatic fragments), 1225–1200 (asymmetric C–O–C stretching) and 1870–1770 (anhydride groups). Mole fractions (mol%) of commoners units (m_1 , m_2 and m_3) in Ma (M_1)–St–(M_2)–2-2-EOEMA(M_3) terpolymer were obtained by FTIR analysis, and the data were calculated according to the following equations (Rzaev *et al* 2002).

$$m_1 = \frac{A^{1781} / M_{\text{Ma}}}{A^{3002} / M_{\text{St}} + A^{1781} / M_{\text{Ma}} + A^{1261} / M_{2\text{-EOEMA}}} \times 100,$$

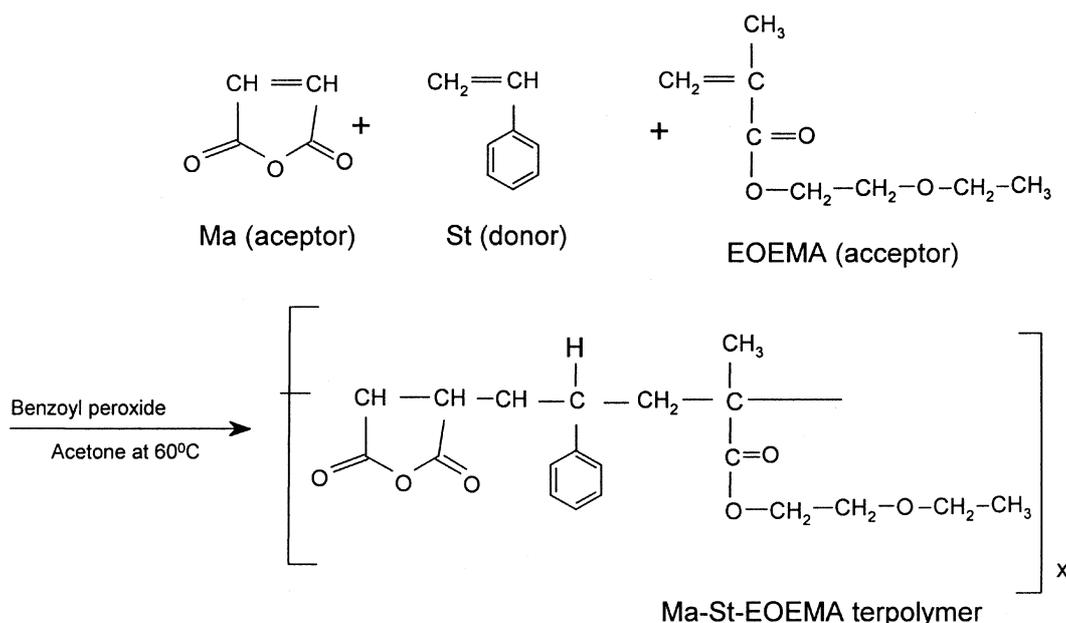
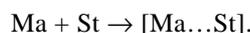
$$m_2 = \frac{A^{3002} / M_{\text{St}}}{A^{3002} / M_{\text{St}} + A^{1781} / M_{\text{Ma}} + A^{1261} / M_{2\text{-EOEMA}}} \times 100,$$

$$m_3 = \frac{A^{1261} / M_{\text{EOEMA}}}{A^{3002} / M_{\text{St}} + A^{1781} / M_{\text{Ma}} + A^{1261} / M_{2\text{-EOEMA}}} \times 100,$$

where $A = \log(1/T)$, A = absorbency and T = % transmittance.

M_{Ma} , M_{St} and $M_{2\text{-EOEMA}}$ are molecular weights of Ma, St and 2-EOEMA monomer units, respectively. The composition of terpolymers obtained by FTIR analysis is presented in figure 1 and table 1.

The donor–acceptor interaction between St and Ma results in equimolar (1 : 1) charge transfer complex (CTC) system and was studied by various methods (Rzaev *et al* 1984).



Scheme 1. Preparation of terpolymer reaction.

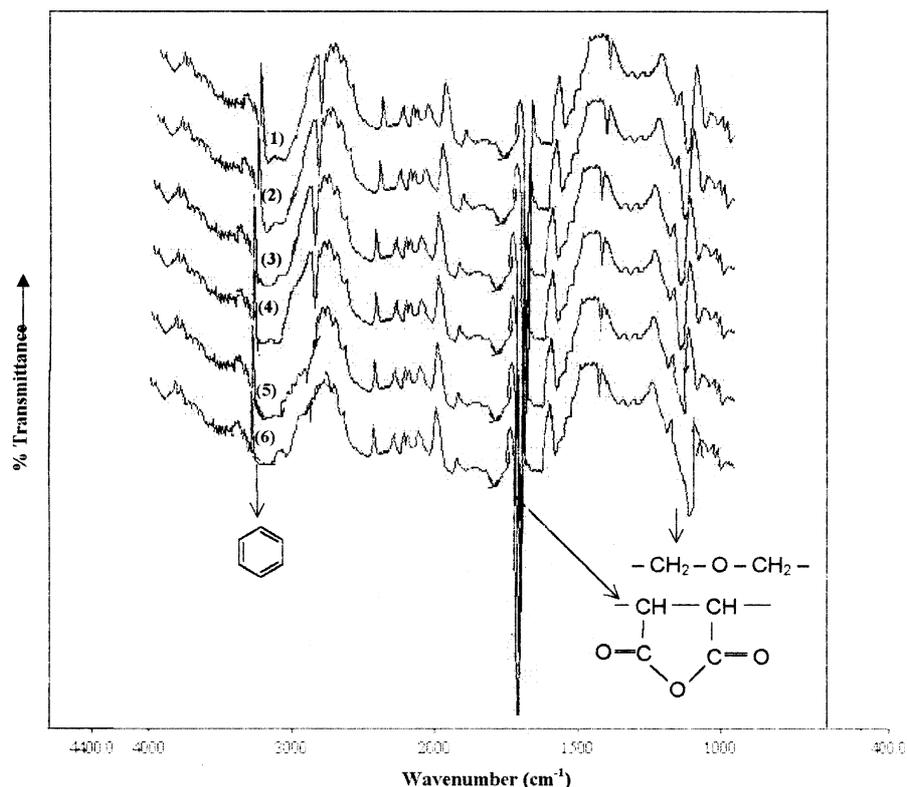


Figure 1. FTIR spectra of Ma-St-2-EOEMA terpolymers prepared in various monomer feeds (Ma: St: 2-EOEMA): (1) 35:50:15, (2) 30:50:20, (3) 35:35:30, (4) 30:30:40, (5) 25:25:50, (6) 20:20:60. (Absorption band value of characteristics groups: 3002 cm^{-1} ($-\text{CH}$ in aromatic fragments); 1261 cm^{-1} (asymmetric C–O–C stretching); 1781 cm^{-1} (anhydride groups)).

Table 1. Analysis of the data for the determination of Ma–St–2-EOEMA terpolymer composition synthesized in the various initial monomers mixtures.

Monomer feed (mol%)			Terpolymer composition (mol%)		
[MA]	[St]	[2-EOEMA]	[MA]	[St]	[2-EOEMA]
35	50	15	28.68	35.4	35.92
30	50	20	36.2	26.4	37.4
35	35	20	25.28	21.57	53.15
30	30	40	28.96	17.03	51.94
25	25	50	22.89	22.01	64.1
20	20	60	21.37	24.8	65.77

The CTC formation constant (K_c) for Ma...St complex was reported earlier by Hanna–Ashbaugh (Hanna *et al* 1964) as $K_c(60^\circ\text{C}) = 0.289$ in deuterated chloroform. The CTC effects in radical terpolymerization with Ma and various donor–donor or donor–acceptor vinyl monomers were clearly illustrated (Rzaev *et al* 1984; Florjanczyle and Krawiec 1989; Yang and Otsa 1992). From these studies it can be suggested that the Ma and St monomer pairs will behave as complexed monomer in radical copolymerization with acrylics. The difference in reactivity

of the Ma...St complex in complex radical copolymerization with different acrylic comonomer causes formation of terpolymer with different ratios of 2-EOEMA units.

The ternary monomer systems studied can be classified as acceptor (Ma) and donor (St) and acceptor (2-EOEMA) which can be characterized as follows (Rzaev 1999):

- (i) The acceptor–donor monomer pair of Ma and St has a tendency to form the complex.

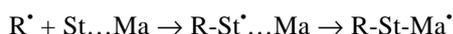
(ii) Neither Ma nor St get homopolymerized in selected conditions of terpolymerization.

(iii) The formation of poly 2-EOEMA fragments in low conversion conditions can be ignored by taking into consideration the high reactivity of the macroradicals towards other monomers.

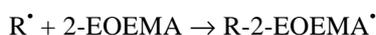
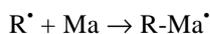
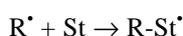
(iv) The formation of 2-EOEMA–St and 2-EOEMA–Ma diad can also take place. While in this case, St and Ma macroradicals have low activity towards 2-EOEMA monomers as compared with Ma and St monomers, respectively.

On the basis of these selective characteristics of the self organized ternary system studied, the elementary stages of propagation reaction can be proposed for participation of both complexed and free monomers in the following preferable initiation and chain growth reactions (Rzaev 1999):

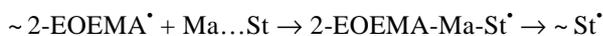
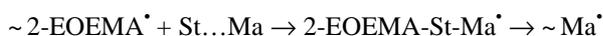
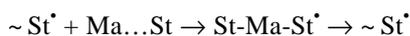
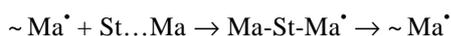
a. Initiation via complex-bond monomers



b. Initiation via free monomers



c. Chain growth via complex-bond monomers



d. Chain growth via free monomers



Monomer–terpolymer composition is given in figure 1 and table 1. As evident from these data, the content of St

and Ma units in the terpolymer having different acceptor monomer ratios are close to equimolar.

The results of FTIR analysis of terpolymer synthesized by using various initial monomer ratios are illustrated in figure 1 and table 1. A diagram of monomer–terpolymer composition is given in figure 2. As evident from these results, the content of St and Ma units in the terpolymer having different acceptor monomer ratios are closest to equimolar. It is also shown that the nature of an acceptor monomer (Ma or 2-EOEMA) as well as the change of monomer composition has strong influence on the character of the diagram point distribution (Rzaev 1999) (figure 2).

These data allow one to determine copolymerization constants (reactivity ratio) $r_1, r_2, r_1(K_c)^{-1}$ and r_2K_c for the St–Ma (M_1) complex and 2-EOEMA (M_2) pairs using the modified terminal model of the Kelen–Tudos (KT) (Kelen 1975) and Fineman–Ross (FR) (Fineman 1950) equation in the following forms.

Fineman–Ross Method:

$$F(f-1)/f = r_1K_cF^2/f - r_2K_c - 1. \quad (1)$$

Kelen–Tudos Method:

$$h = [r_1K_c + r_2K_c^{-1}/a]x - (r_2K_c^{-1})/a, \quad (2)$$

$$h = [(F^2/f)/(F^2/f + a)],$$

$$a = \sqrt{(F^2/f)_{\min} (F^2/f)_{\max}}.$$

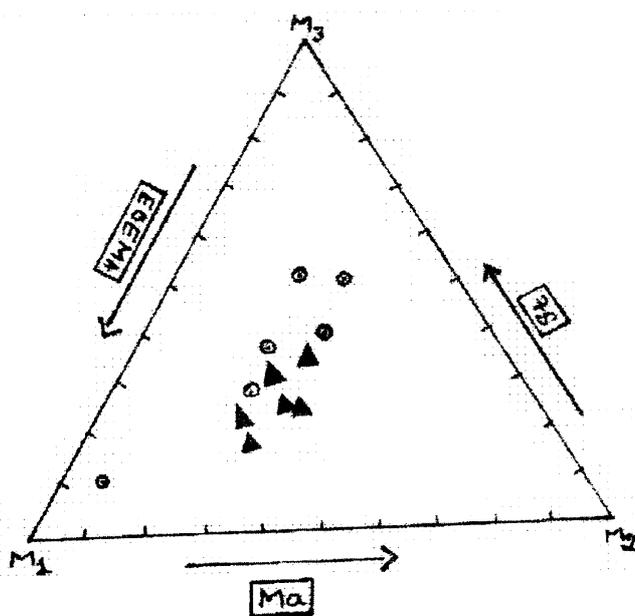
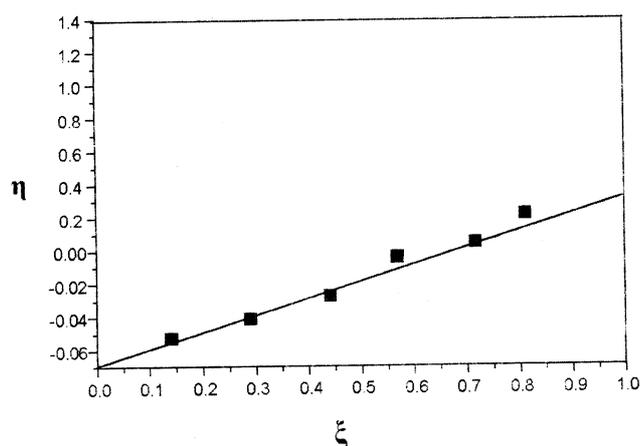
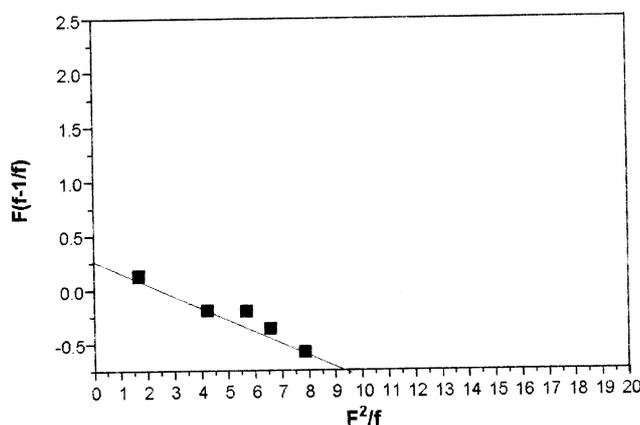


Figure 2. Monomer–terpolymer composition diagram: (○) for monomers, and (▲) for composition of St-2-EOEMA-Ma terpolymers.

Table 2. Experimental data for determining the copolymerization constants (r_1 and r_2) for MA–St (M_1) and 2-EOEMA (M_2) pair in the low conversion condition.

Monomer ratio $F[M_1]/[M_2]$	Monomer unit, $f(m_1/m_1)$	$F(f-1)/f$	F^2/f	$F^2/f + /a$	$h = [(F^2/f)/(F^2/f + /a)]$	$x = [F(f-1)/f/F^2/f + /a]$
5.667	1.7839	2.4902	18.00	21.05	0.1182	0.854
4.000	1.673	1.61	9.563	12.61	0.1276	0.7579
2.333	0.8814	-0.313	6.159	9.212	-0.0339	0.6685
1.500	0.8515	-0.261	2.642	5.695	-0.0458	0.4639
1.000	0.81488	-0.227	1.227	4.28	-0.0530	0.2866
0.667	0.8577	-0.1874	0.518	3.571	-0.0524	0.14505


Figure 3. Kelen–Tudos plots for the copolymerization of St...Ma (M_1) with 2-EOEMA (M_2) in acetone at 60°. $a = r_1K_c + r_2K_c^{-1}/a$ and intercept $-r_2K_c^{-1}/a$.

Figure 4. Fineman–Ross plots for the copolymerization of St...Ma (M_1) with 2-EOEMA (M_2) in acetone at 60°. $a = r_1K_c$ and intercept $-r_2K_c^{-1}$.

K_c = constant of CTC formation for [St...Ma] complex monomer where

$$F = M_1/M_2 = \text{Ma...St}/2\text{-EOEMA},$$

$$f = m_1/m_2.$$

Table 3. Constants of copolymerization for St...MA (M_1) and 2-EOEMA (M_2).

Parameter	KT method	FR method
r_1	0.26	0.2
r_2	0.213	0.117
r_1K_c	0.07	0.056
$r_2K_c^{-1}$	0.76	0.417

By using (1) and (2) and experimental results and values of the KT and FR equation parameters for the calculation of the monomers reactive ratios, r_1 , r_2 , r_1K_c and $r_2K_c^{-1}$ of the monomers obtained by figures 3 and 4 are presented in tables 2 and 3.

The effect of observed K_c on the reactivity of the monomers confirms the fact that chain growth proceeds primarily by addition of CTC to growing macroradicals. By these values it can be concluded that [Ma...St] complexes preferentially add to 2-EOEMA comonomer in the St–Ma–2-EOEMA system, and shows that terpolymerization proceeded mainly through a “complex” mechanism in the state of near binary copolymerization of Ma–St and 2-EOEMA comonomer. Only in the chosen ratios of complexed and free monomers the effects of CTC formation from the kinetic point of view allows one to approximate terpolymerization to binary copolymerization of Ma–St (M_1) and 2-EOEMA (M_2).

3.2 $^1\text{H-NMR}$ spectroscopy

The structure of obtained terpolymer (1 : 1 : 1 monomers concentration) was illustrated by $^1\text{H-NMR}$ spectroscopy and from $^1\text{H-NMR}$ spectra (figure 5) characteristics peak signals corresponding to $d-0.9$ for CH_3 -, $d-3.8$ for $-\text{CH}_2-\text{O}-\text{CH}_2-$ in 2-ethoxyethyl methacrylate and $d-7.3$ for benzene ring of styrene were obtained.

3.3 Glass transition temperature (T_g)

DSC graph (figure 6) shows $T_g = 138^\circ\text{C}$ for terpolymer product, which is less than the T_g of styrene maleic anhydride copolymer.

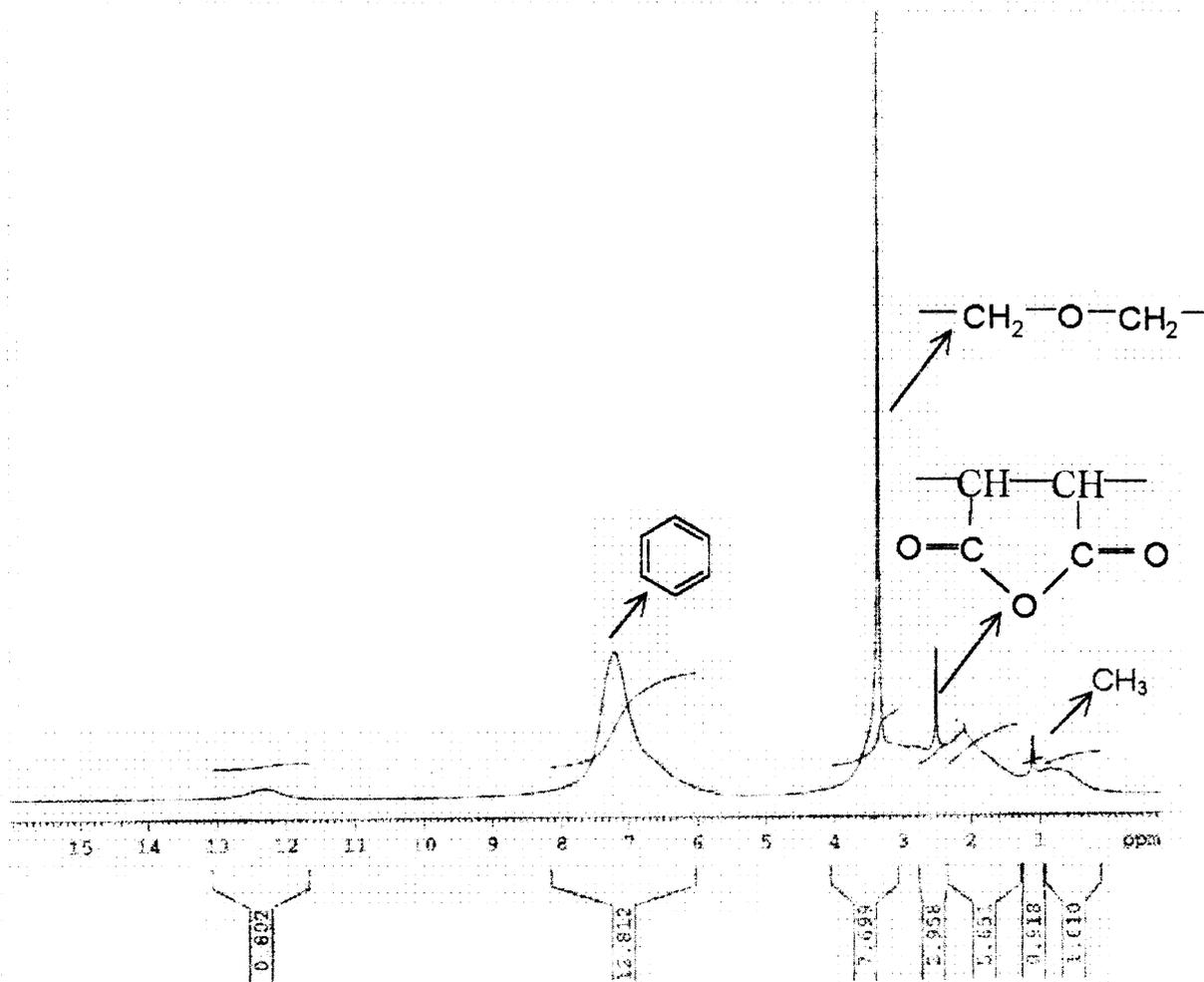


Figure 5. $^1\text{H-NMR}$ spectrum of Ma-St-2-EOEMA terpolymer.

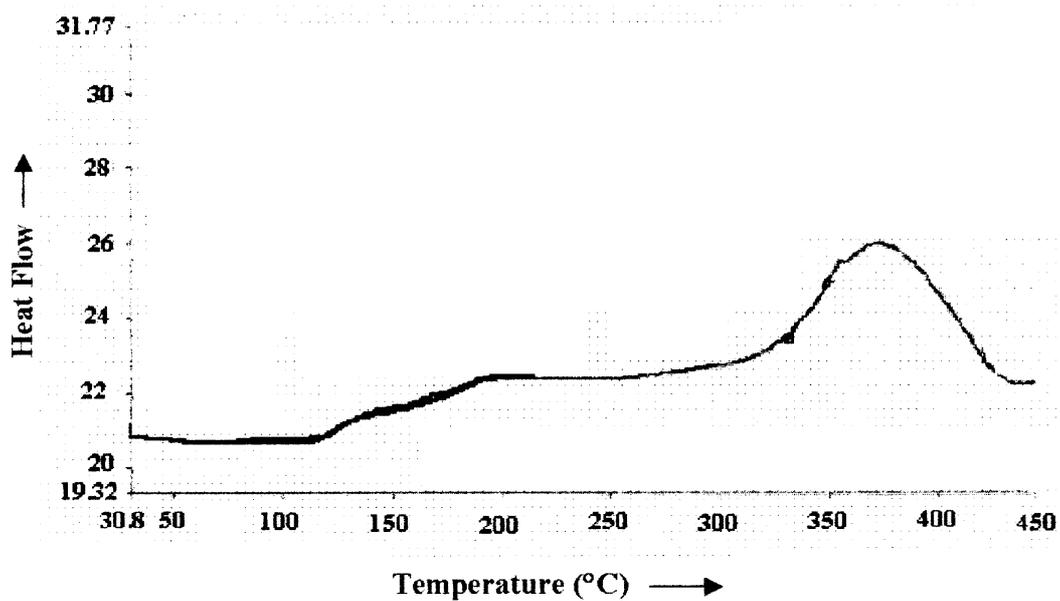


Figure 6. DSC thermograms of Ma-St-2-EOEMA terpolymer, $T_g = 138^\circ\text{C}$.

4. Conclusions

Calculated reactivity ratio from KT and FR method ($r_1 < 1$, $r_2 < 1$) clearly indicates that the terpolymer products based on St...Ma-2-EOEMA system has an alternating pattern.

St...Ma-2-EOEMA terpolymer has a T_g of 138°C which is much lower compared to that of corresponding St...Ma copolymer i.e. 201°C (Hellenne and Bengt 1995). This kind of overall reduction in T_g of the terpolymer may be due to the internal plasticization effect of the 2-EOEMA in the terpolymer product. Obtained reactivity ratio, low T_g value of the terpolymer product and point distribution of three-phase diagram clearly indicates the successful participation of 2-EOEMA as third monomer in terpolymerization process. Further, this type of St...Ma-2-EOEMA terpolymer could be a better candidate as surfactant than the corresponding copolymer already in use, in surface science.

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