

Synthesis and monomer reactivity ratios of acrylamide with 3-(trimethoxysilyl)propyl methacrylate and tris(methoxyethoxy)vinylsilane copolymers

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Abstract: Copolymers of acrylamide (AM) with 3-(trimethoxysilyl)propyl methacrylate (TMSPMA) and tris(methoxyethoxy)vinylsilane (TMEVS) with different compositions were synthesized at low conversion by free radical polymerization in dimethylformamide (DMF) using benzoyl peroxide (BPO) as an initiator. The copolymers were characterized by Fourier transform infrared spectroscopy (FT-IR), and their thermal properties were studied by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The copolymers composition was determined by elemental analysis. The monomer reactivity ratios were estimated by linearization methods proposed by Fineman-Ross and Kelen-Tudos, the intersection method proposed by Mayo-Lewis and nonlinear method proposed by curve fitting procedure. The derived reactivity ratios (r_1 , r_2) are: 1.87, 0.80 for TMSPMA-co-AM and 0.22, 1.21 for TMEVS-co-AM. Both copolymers formed blocks of one of the monomer units. The microstructure of copolymers and sequence distribution of monomers in the copolymers were calculated by statistical method based on the average reactivity ratios and found that these values are in agreement with the derived reactivity ratios.

Keywords: vinylsilane monomers, acrylamide, reactivity ratios, sequence distribution.

Współczynniki reaktywności monomerów w syntezie kopolimerów akryloamidu, metakrylanu 3-(trimetoksylilo)propylu i tris(metoksyetoksy)winylosilanu

Streszczenie: Kopolimery akryloamidu (AM) z metakrylanem 3-(trimetoksylilo)propylu (TMSPMA) i tris(metoksyetoksy)winylosilanem (TMEVS), o różnych składach, zsyntetyzowano w warunkach małej konwersji metodą wolnorodnikowej polimeryzacji w dimetyloformamidzie (DMF), z zastosowaniem nadtlenu benzoilu (BPO) jako inicjatora. Otrzymane kopolimery charakteryzowano za pomocą spektroskopii w podczerwieni z transformacją Fouriera (FT-IR), różnicowej kalorymetrii skaningowej (DSC) oraz analizy termogravimetrycznej (TGA). Skład kopolimerów ustalono metodą analizy elementarnej. Współczynniki reaktywności monomerów oszacowano metodami linearyzacji zaproponowanymi przez: Finemana-Rossa, Kelena-Tudosa, Mayo-Lewisa i metodą nieliniową z zastosowaniem procedury dopasowania krzywej. Otrzymane współczynniki reaktywności (r_1 , r_2) wynosiły: 1,87 i 0,80 dla TMSPMA-co-AM oraz 1,21 i 0,22 dla TMEVS-co-AM. Oba kopolimery miały budowę złożoną z bloków utworzonych z jednostek monomerów składowych. Mikrostrukturę oraz sekwencję monomerów w kopolimerach wyznaczono metodą statystyczną na podstawie średnich współczynników reaktywności. Stwierdzono zgodność obliczeń z wartościami otrzymanymi doświadczalnie.

Słowa kluczowe: monomery winylosilanowe, akryloamid, współczynniki reaktywności, sekwencja monomerów.

Copolymerization is the best technique for effecting systematic changes in polymer properties [1]. Reactivity ratios are among the most vital parameters for a composition equation of copolymers. Determination of the comonomers

reactivity ratios requires the mathematical treatment on the monomers feed mixtures and compositions of copolymers. In order to estimate the amount of the comonomer incorporated into the copolymer, different analytical methods should be used, nitrogen analysis, proton and carbon nuclear magnetic resonance, and Fourier transform infrared spectroscopy [2–4].

The interests in polymers which contain silicon atom have been expanding because of their hydrophobicity and wide applications as semiconductor and optical ma-

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terials. In radical copolymerization of vinylsilane monomers with different other comonomers, the reactivity of vinylsilane monomers is strongly depending on the position of the silicon atom in respect to the vinyl group [5, 6], the reactivity of these monomers is very low if the silicon atom is near the vinyl group as a result of $d\pi-p\pi$ interactions between the Si atom and the vinyl group. On the other hand, it should be possible to enhance the reactivity of vinylsilane monomers by copolymerization with comonomers do not have high reactivity with themselves. In addition, if the Si atom is away from the vinyl group, the $d\pi-p\pi$ interactions will be absent and this leads to enhance the reactivity of vinylsilane monomers. Vinylsilane monomers have been successfully copolymerized with *N*-vinylpyrrolidone, 2-vinylpyridine, styrene, acrylonitrile, butyl acrylate, methacrylic acid, methyl methacrylate, vinylsulfonate esters, and other monomers [7–13]. In addition, the reactivity ratios of these monomers have been determined, but no study has been reported on the copolymerization and reactivity relationships of vinylsilane monomers with acrylamide.

The aim of this work is the copolymerization of TMEVS and TMSPPMA, a hydrophobic monomers with AM, a hydrophilic monomer, and to study the best synthetic conditions and characterization of the copolymers. This study also determines the reactivity ratios of TMEVS, TMSPPMA, and AM. From these parameters, a specific comonomer distribution is estimated.

EXPERIMENTAL PART

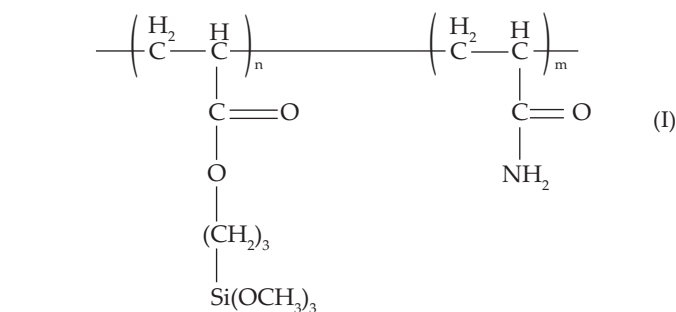
Materials

Commercial samples of monomers TMEVS and TMSPPMA from Aldrich chemical were distilled under vacuum before copolymerization. The monomer AM was purified by recrystallization from methanol and dried in a vacuum. The initiator BPO was recrystallized from chloroform and dried in a vacuum.

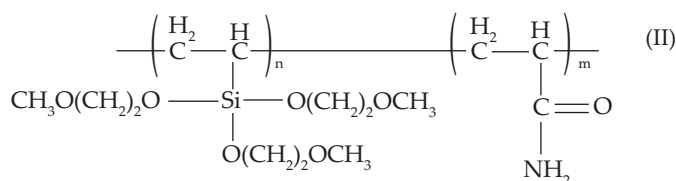
Synthesis of copolymers

Copolymerization of AM with TMEVS and TMSPPMA was carried out by using $1 \cdot 10^{-3}$ mol/dm³ BPO as initiator and DMF as solvent at 60 °C in a glass tube. The total molar composition of the monomers mixture was maintained at 1 mol/dm³ while the monomer feed ratio was varied in a series of copolymerization of AM with TMEVS and TMSPPMA (AM-*co*-TMSPPMA) and (AM-*co*-TMEVS). Nitrogen gas was bubbled through the mixture for 15 minutes prior to the reaction in order to remove all oxygen. Copolymerization time was controlled to obtain low conversion (below 10 %). The copolymers were isolated by precipitation in ethanol. The precipitates were filtered off and purified by washing many times with ethanol. Copolymers were dried in vacuum at 40 °C until constant weight. The structures of copolymers were given in the following formulas [Formulas (I) and (II)]:

lymers were given in the following formulas [Formulas (I) and (II)]:



TMSPPMA-*co*-AM



TMEVS-*co*-AM

Methods of testing

– Perkin Elmer-1650 spectrometer was used to record FT-IR spectra of the copolymers on KBr pellets in the range 280–4000 cm⁻¹.

– Copolymer compositions were determined by elemental analysis following the variation of nitrogen content arising from acrylamide comonomers units.

– Thermal degradability of the polymer was studied by TGA using Perkin Elmer under nitrogen atmosphere at a heating rate of 10 °C/min from 0 to 800 °C and glass transition temperature (T_g) was determined using a DSC-Mettler calorimetric system.

RESULTS AND DISCUSSION

The structure of the homopolymers and copolymers is confirmed by FT-IR as shown in Fig. 1.

PAM: 3350 cm⁻¹ (amide N-H), 1680 cm⁻¹ (amide C=O); PTMSPPMA: 1725 cm⁻¹ (ester C=O), 1150 (ester C-O), 1045 cm⁻¹ (Si-O); PTMEVS: 1155 cm⁻¹ (ether C-O), 1043 cm⁻¹ (Si-O); TMSPPMA-*co*-AM: 3400 cm⁻¹ (amide N-H), 2902 cm⁻¹ (alkane C-H), the carbonyl absorption of TMSPPMA observed at 1720 cm⁻¹ (ester C=O), 1685 cm⁻¹ (amide C=O), 1241 cm⁻¹ (amide C-N), 1147 cm⁻¹ (ester C-O), 1050 cm⁻¹ (Si-O) and 850 cm⁻¹ (Si-C); TMEVS-*co*-AM: 3355 cm⁻¹ (amide N-H), 2920 cm⁻¹ (alkane C-H), 1638 cm⁻¹ (amide C=O), 1248 cm⁻¹ (amide C-N), 1142 cm⁻¹ (ether C-O), 1045 cm⁻¹ (Si-O), and 820 cm⁻¹ (Si-C).

Copolymer composition

The composition of the copolymer depends on the monomer feed composition. Thus, it is very important to study the monomer reactivity in the copolymer system.

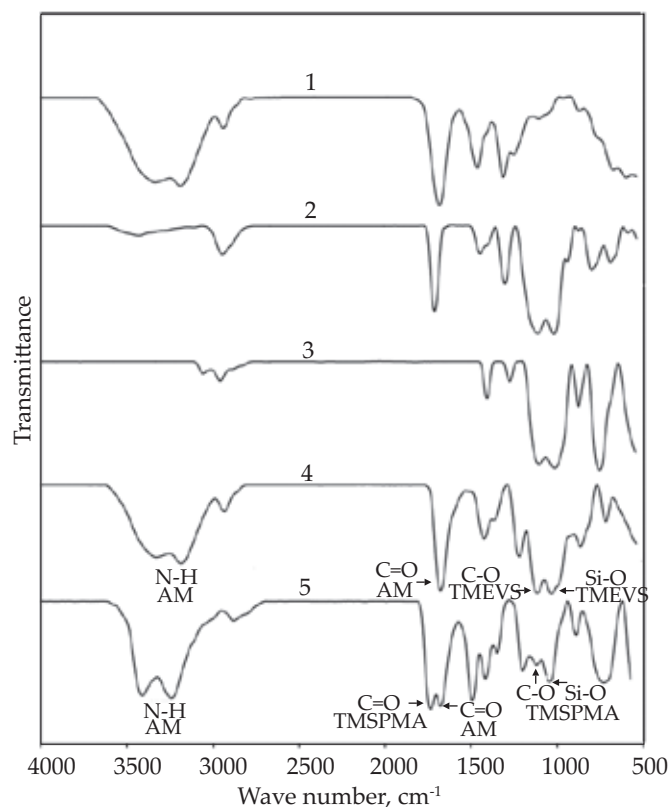


Fig. 1. FT-IR of: 1 – PAM, 2 – PTMSPMA, 3 – PTMEVS, 4 – TMEVS/AM copolymer, 5 – TMSPMA/AM copolymer

In TMEVS/AM and TMSPMA/AM copolymers, composition of the monomer in the copolymer was estimated by determination N % in the copolymers and this ratio indirectly gave the mole fraction of AM in the copolymer. The monomer composition and the results of compositions are listed in Table 1.

The plots of mole fraction of TMSPMA and TMEVS in the feed (f_1) vs. that of mole fraction of TMSPMA and TMEVS in the copolymer (F_1) are shown in Fig. 2. In this

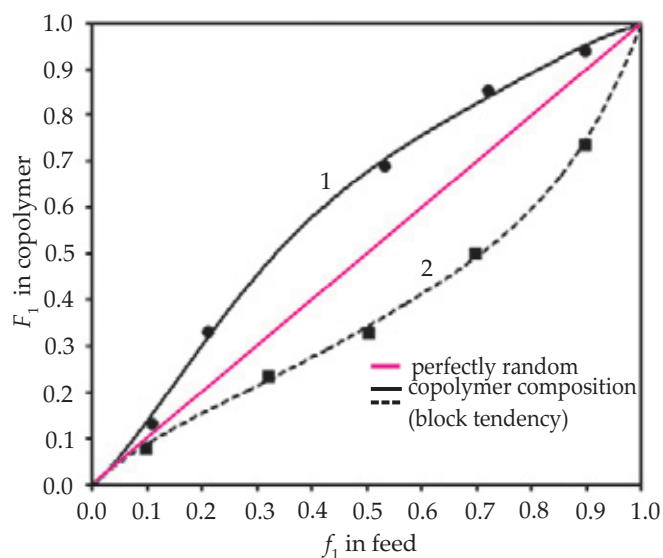


Fig. 2. Variation of copolymer composition F_1 (TMSPMA) and F_1 (TMEVS) with feed composition f_1 (TMSPMA) and f_1 (TMEVS) for: 1 – TMSPMA/AM, 2 – TMEVS/AM copolymers

Table 1. Feed and copolymer compositions, conversion and nitrogen analysis of TMSPMA/AM and TMEVS/AM copolymers

Sample code	f_1 (feed)	Conversion %	N %	F_1 (copolymer)
TMSPMA/AM-1	0.108	7.7	12.81	0.131
TMSPMA/AM-2	0.209	8.1	7.177	0.333
TMSPMA/AM-3	0.533	8.5	2.238	0.691
TMSPMA/AM-4	0.721	9.1	0.934	0.857
TMSPMA/AM-5	0.898	9.6	0.371	0.941
TMEVS/AM-1	0.098	9.8	14.44	0.081
TMEVS/AM-2	0.320	9.5	8.861	0.237
TMEVS/AM-3	0.503	8.9	6.721	0.328
TMEVS/AM-4	0.696	8.2	3.948	0.503
TMEVS/AM-5	0.898	7.8	1.621	0.739

f_1 – the mole fraction of monomer-1 (TMEVS, TMSPMA) in the initial feed; $f_2 = 1 - f_1$.

F_1 – the mole fraction of monomer-1 (TMEVS, TMSPMA) in the copolymer; $F_2 = 1 - F_1$.

figure a high amount of incorporation of TMSPMA monomer in TMSPMA-co-AM and a low amount of incorporation of TMEVS monomer in TMEVS-co-AM can be clearly observed. This can be interpreted in terms of the effect of the carbonyl group of TMSPMA on its corresponding growing radical in the propagation step, in this way; the positive charge density generated on the carbonyl carbon atom can favor a significant electron attraction in the TMSPMA radicals. At the same time, carbonyl groups can induce electronic delocalization, over these radicals, another factor contributing to stabilization. Both factors enhance the reactivity of the corresponding monomers. Thus, high incorporation of TMSPMA in the copolymer is obtained.

Reactivity ratio

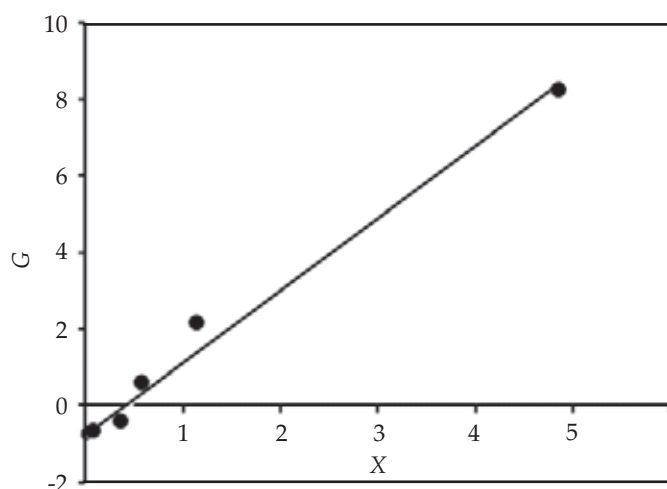
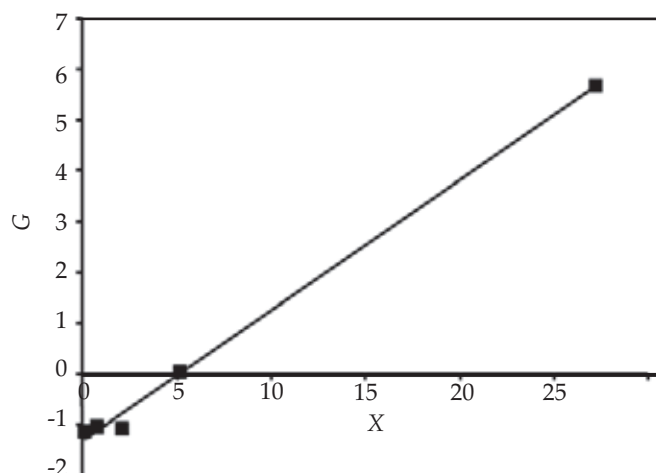
The most widely mathematical model of copolymerization is based on finding the relationship between the composition of the monomer feed and the composition of copolymers in which the monomer reactivity ratios are the parameters to be determined [14]. In our investigation several methods have been proposed for the best fitting of r_1 and r_2 pair from a set of $[M_1]$, $[M_2]$, $d[M_1]$ and $d[M_2]$ pair, using linearization methods proposed by Fineman-Ross [15], Kelen-Tudos [16], Mayo-Lewis [17], and with the nonlinear method proposed by curve-fitting [18] procedure. The equation used for Fineman-Ross is:

$$G = X \cdot r_1 - r_2 \quad (1)$$

By plotting $G = f \cdot (F - 1)/F$ as ordinate versus the $X = f_2/F$ as abscissa, one will obtain a straight line, where the slope is the value of r_1 and the intercept is the value of

Table 2. Fineman-Ross, Kelen-Tudos, and Mayo-Lewis parameters of TMSPMA/AM and TMEVS/AM copolymers

Sample code	f_1	G	X	η	ζ	f	$1/F$
TMSPMA/AM-1	0.108	-0.685	0.097	-0.874	0.123	0.121	6.661
TMSPMA/AM-2	0.209	-0.427	0.363	-0.402	0.346	0.426	2.001
TMSPMA/AM-3	0.533	0.233	1.035	0.458	0.499	1.141	0.795
TMSPMA/AM-4	0.721	2.141	1.142	1.171	0.624	2.584	0.171
TMSPMA/AM-5	0.898	8.252	4.861	1.487	0.876	8.803	0.062
TMEVS/AM-1	0.098	-1.141	0.127	-0.571	0.063	0.108	12.34
TMEVS/AM-2	0.321	-1.046	0.709	-0.411	0.276	0.474	3.225
TMEVS/AM-3	0.503	-1.061	2.098	-0.262	0.531	1.012	2.048
TMEVS/AM-4	0.696	0.027	5.177	0.003	0.734	2.289	0.988
TMEVS/AM-5	0.898	5.692	27.19	0.195	0.935	8.803	0.353

**Fig. 3.** Fineman-Ross plot of TMSPMA/AM copolymer**Fig. 4.** Fineman-Ross plot of TMEVS/AM copolymer

$-r_2$. The values are represented in Table 2 and showed in Fig. 3 and Fig. 4.

For Kelen-Tudos method, the equation used is:

$$\eta = r_1 \cdot \zeta - \frac{r_2}{\alpha} (1 - \zeta) \quad (2)$$

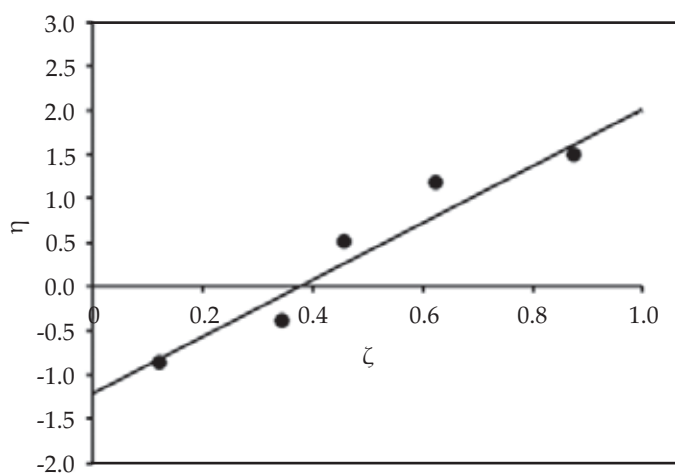
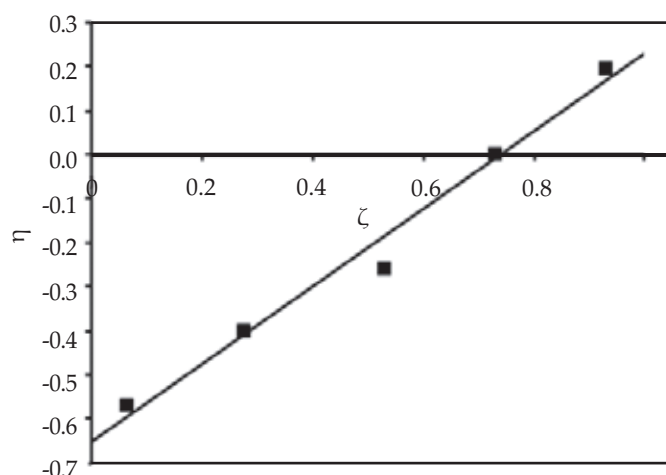
where: $\eta = G/(\alpha + X)$, $\zeta = X/(\alpha + X)$, $\alpha = (X_{min} \cdot X_{max})^{1/2}$.

By plotting η versus ζ a straight line is produced that gives $-r_2/\alpha$ and r_1 as the intercepts on extrapolation to

$\zeta = 0$ and $\zeta = 1$, respectively. The values are represented in Table 2 and showed in Figs. 5 and 6. For Mayo-Lewis method, a plot can be produced for a set of experiments using equation:

$$r_2 = f \left[\frac{1}{F} (1 + r_1 f) - 1 \right] \quad (3)$$

The straight lines that are produced on the plot for each experiment, where assumed r_1 represents the ab-

**Fig. 5.** Kelen-Tudos plot of TMSPMA/AM copolymer**Fig. 6.** Kelen-Tudos plot of TMEVS/AM copolymer

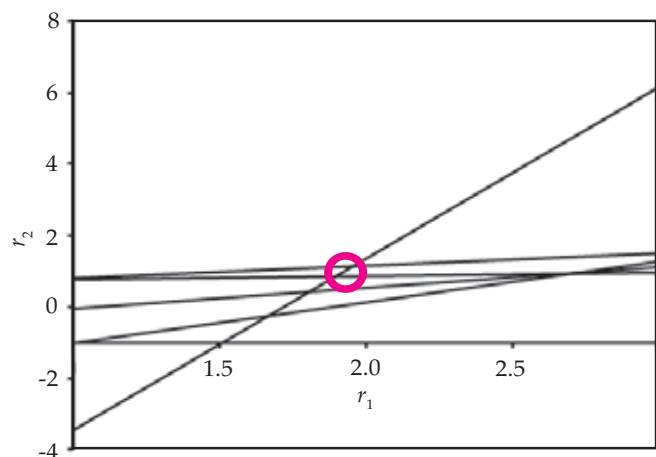


Fig. 7. Mayo-Lewis plot of TMSPMA/AM copolymer

scissa and r_2 represents the ordinate, intersect at a point on the r_2 vs. r_1 plot. The point where these lines meet is taken to be r_1 and r_2 . The values of $f = [M_1]/[M_2]$ and $1/F = d[M_2]/d[M_1]$ are represented in Table 2 and showed in Figs. 7 and 8.

Curve-fitting method is based on equation:

$$F = f \frac{r_1 f + 1}{r_2 + f} \quad (4)$$

Table 3. Theoretical parameters with values $r_1 = 1.885$, $r_2 = 0.779$ of TMSPMA/AM and $r_1 = 0.226$, $r_2 = 1.255$ of TMEVS/AM copolymers

Sample code	$[M_1]/[M_2]$	$d[M_1]/d[M_2]$	f_2	F_2
TMSPMA/AM-1	0.1	0.078	0.909	0.927
TMSPMA/AM-2	0.5	0.321	0.766	0.737
TMSPMA/AM-3	1.0	0.554	0.500	0.643
TMSPMA/AM-4	2.0	0.911	0.333	0.526
TMSPMA/AM-5	4.0	1.443	0.200	0.408
TMEVS/AM-1	0.1	0.125	0.909	0.888
TMEVS/AM-2	0.5	0.722	0.766	0.580
TMEVS/AM-3	1.0	1.567	0.500	0.389
TMEVS/AM-4	2.0	3.368	0.333	0.228
TMEVS/AM-5	4.0	7.092	0.200	0.171

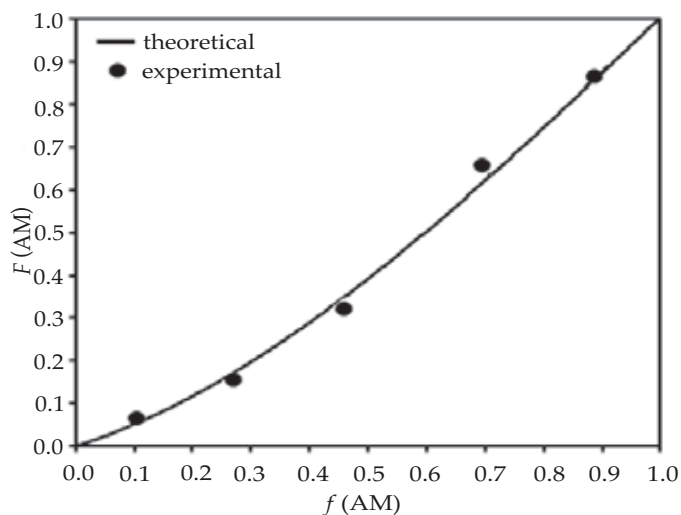


Fig. 9. Curve fitting plot of TMSPMA/AM copolymer

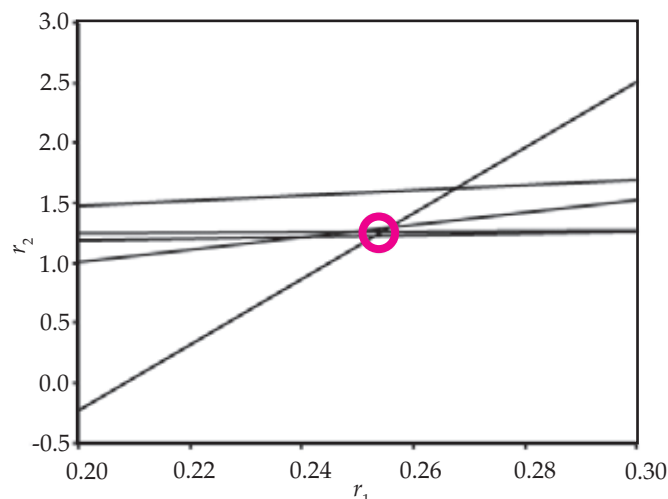


Fig. 8. Mayo-Lewis plot of TMEVS/AM copolymer

where: $F = d[M_1]/d[M_2]$ and $f = [M_1]/[M_2]$.

With selected values of r_1 and r_2 and with series values of $[M_1]/[M_2]$ and the corresponding values of $d[M_1]/d[M_2]$, the validity of the chosen r_1, r_2 can be checked by changing the reactivity ratios until the theoretical curve satisfactorily approximated the experimental curve. The variation of the instantaneous mole fraction F_2 of AM in copolymer with the mole fraction f_2 in the initial feed

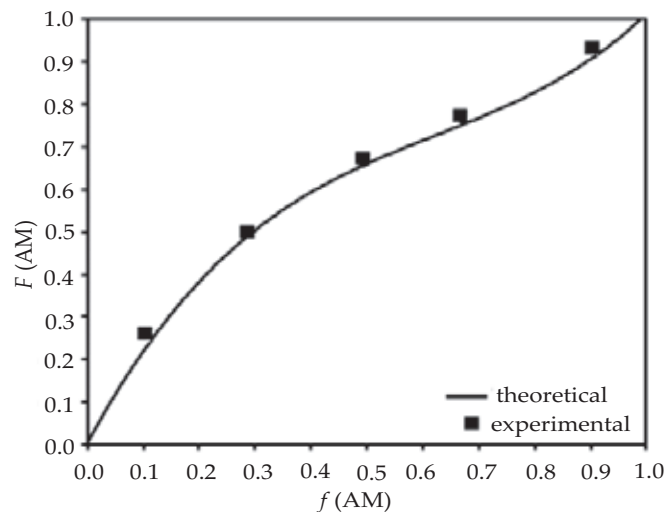


Fig. 10. Curve fitting plot of TMEVS/AM copolymer

Table 4. Monomer reactivity ratios of TMSPMA/AM and TMEVS/AM copolymers

Copolymer	Procedure	r_1	r_2 (AM)
TMSPMA/AM	Fineman-Ross	1.91	0.85
	Kelen-Tudos	1.89	0.80
	Mayo-Lewis	1.80	0.79
	Curve fitting	1.88	0.77
	Average values	1.87	0.80
TMEVS/AM	Fineman-Ross	0.22	1.25
	Kelen-Tudos	0.25	1.21
	Mayo-Lewis	0.21	1.19
	Curve fitting	0.23	1.22
	Average values	0.22	1.21

could be calculated as: $f_2 = 1/f + 1$, $F_2 = 1/F + 1$. The values of the co-ordinates for the theoretical curve, F_2 and f_2 are represented in Table 3 and showed in Figs. 9 and 10.

The values of reactivity ratios by various methods are listed in Table 4. The values r_1 , r_2 from the various procedures are very close, even those obtained by the inverse Fineman-Ross graph.

It is possible to observe that the reactivity of TMSPMA in TMSPMA/AM copolymer is higher than the reactivity of TMEVS in TMEVS/AM copolymer. The electronic stabilization effect exerted by the carbonyl group of the ester group adjoining the carbon carrying the radical electron over the TMSPMA radical on the propagation step, allows explanation of the high reactivity of this monomer. In addition, the spacing out of the trimethoxysilane group of the main chain by means of a carbonyl group increases the reactivity of TMSPMA. A similar behavior was described earlier by Rao and Babu [7] when TMSPMA was copolymerized with methylmethacrylate ($r_{\text{TMSPMA}} = 1.33$, $r_{\text{MMA}} = 0.74$). On the other hand, for TMEVS/AM copolymer, the silicon atom is close to the vinyl group causing steric hindrance by $d\pi$ - $p\pi$ interactions. Moreover, the stabilization of TMEVS growing radical is weak due to absent the resonance of its structure. Thus, r_{TMEVS} is low (0.22). This fact was discussed previously by Gatica *et al.* [19] for other copolymer systems involving vinylsilane

comonomers, for instance, vinyltriethoxysilane-*co*-vinylpyrrolidone ($r_{\text{VTES}} = 0.2$, $r_{\text{NVP}} = 0.6$).

An azeotropic composition is possible when r_1 and r_2 are both greater than 1 and less than 1. This condition is not fulfilled in TMSPMA/AM and TMEVS/AM systems since $r_1 > 1$, $r_2 < 1$ and $r_1 < 1$, $r_2 > 1$, respectively. This fact can be clearly observed in Fig. 2 (copolymer composition curve), which shows no azeotropic composition. The azeotropic feed composition $f_1(\text{az.})$ is given by:

$$f_1(\text{az.}) = \frac{(1 - r_2)}{(2 - r_1 - r_2)} \quad (5)$$

Copolymer microstructure

The statistical distribution of the monomers in the copolymer 1-1, 2-2, and 1-2 are calculated using the following relations [20, 21] and listed in Table 5.

$$S_{1-1} = m_1 - \frac{2m_1m_2}{1 + \left[(2m_1 - 1)^2 + 4r_1r_2m_1m_2 \right]^{1/2}} \quad (6)$$

$$S_{2-2} = m_2 - \frac{2m_1m_2}{1 + \left[(2m_1 - 1)^2 + 4r_1r_2m_1m_2 \right]^{1/2}} \quad (7)$$

Table 5. Structural data of TMSPMA/AM and TMEVS/AM copolymers

Sample code	Copolymer		Blockness (mol %)		Alternation (mol %)
	F_1	F_2	$[M_1]-[M_1]$	$[M_2]-[M_2]$	$[M_1]-[M_2]$
TMSPMA/AM-1	0.131	0.869	0.017	0.754	0.229
TMSPMA/AM-2	0.333	0.667	0.132	0.466	0.402
TMSPMA/AM-3	0.691	0.309	0.336	0.222	0.442
TMSPMA/AM-4	0.857	0.143	0.741	0.027	0.232
TMSPMA/AM-5	0.941	0.059	0.887	0.005	0.108
TMEVS/AM-1	0.081	0.919	0.005	0.840	0.155
TMEVS/AM-2	0.237	0.763	0.023	0.547	0.430
TMEVS/AM-3	0.328	0.672	0.052	0.394	0.554
TMEVS/AM-4	0.503	0.497	0.171	0.168	0.661
TMEVS/AM-5	0.739	0.261	0.499	0.036	0.465

Table 6. Statistical data of TMSPMA/AM and TMEVS/AM copolymers

Sample code	Sequence probability				Sequence length	
	PAA	PBB	PAB	PBA	μ_1	μ_2
TMSPMA/AM-1	0.186	0.868	0.813	0.131	1.23	7.63
TMSPMA/AM-2	0.361	0.728	0.638	0.271	1.56	3.68
TMSPMA/AM-3	0.684	0.411	0.315	0.588	3.17	1.70
TMSPMA/AM-4	0.830	0.236	0.168	0.763	5.81	1.31
TMSPMA/AM-5	0.943	0.082	0.056	0.917	17.8	1.08
TMEVS/AM-1	0.023	0.917	0.977	0.083	1.02	11.9
TMEVS/AM-2	0.093	0.718	0.906	0.281	1.10	3.55
TMEVS/AM-3	0.182	0.542	0.818	0.457	1.22	2.18
TMEVS/AM-4	0.335	0.344	0.665	0.656	1.50	1.52
TMEVS/AM-5	0.660	0.120	0.341	0.880	2.93	1.13

$$S_{1-2} = \frac{4m_1m_2}{1 + \left[(2m_1 - 1)^2 + 4r_1r_2m_1m_2 \right]^{1/2}} \quad (8)$$

where: m_1 (TMSPMA or TMEVS) and m_2 (AM) – the mole fractions in the copolymer, S_{1-1} , S_{2-2} , and S_{1-2} – the mole fractions of 1-1, 2-2, and 1-2 sequences, respectively, r_1 and r_2 – the reactivity ratios.

The probabilities of finding the sequence of TMSPMA, TMEVS, and AM units are calculated as follows and listed in Table 6.

$$PAA = \frac{r_1[A]}{(r_1[A] + [B])} \quad (9)$$

$$PBB = \frac{r_2[B]}{(r_2[B] + [A])} \quad (10)$$

$$PAB = \frac{[B]}{(r_1[A] + [B])} \quad (11)$$

$$PBA = \frac{[A]}{(r_2[B] + [A])} \quad (12)$$

where: PAA, PBB, PAB, and PBA – the probability of a TMSPMA or TMEVS or AM unit to be followed by TMSPMA or TMEVS or AM unit. In these equations A (TMSPMA or TMEVS) and B (AM) are the mole fractions in the feed. The average length sequences of TMSPMA, TMEVS, and AM are listed in Table 6 and calculated using the following equations [3]:

$$\mu_1 = \frac{1}{PAB} \quad (13)$$

$$\mu_2 = \frac{1}{PBA} \quad (14)$$

For TMSPMA/AM copolymer $[M_1]$ - $[M_1]$, PAA and μ_1 increase as TMSPMA increases. At the same time, these values are higher than $[M_2]$ - $[M_2]$ and $[M_1]$ - $[M_2]$, PBB and μ_2 , respectively. On the other hand, in the case of TMEVS/

AM copolymer $[M_2]$ - $[M_2]$, PBB and μ_2 increase as AM increases and higher than $[M_1]$ - $[M_1]$ and $[M_1]$ - $[M_2]$, PAA and μ_1 . From these results, both TMSPMA in TMSPMA/AM copolymer and AM in TMEVS/AM copolymer have a tendency to react with themselves in the growing chain to form block copolymers and these results are in agreement with the values of r_{TMSPMA} (1.87) > 1, r_{AM} (0.80) < 1 and r_{TMEVS} (0.22) < 1, r_{AM} (1.21) > 1.

Thermal properties

The glass transition temperature (T_g) of the copolymers was determined by DSC under nitrogen atmosphere. The homopolymer of AM showed the T_g around 163 °C, whereas TMSPMA/AM-1 copolymer the T_g value observed around 153 °C, and no T_g was observed in case of TMEVS/AM till starts degradation. It is found that by increasing the amount TMSPMA content in the copolymers result in decreased T_g . This may be due to the presence of propyl group in TMSPMA side chain and the free rotation of methoxy groups bonded to silyl groups. TGA was carried out under nitrogen atmosphere in the temperature range of 0–800 °C and is presented in Fig. 11. The

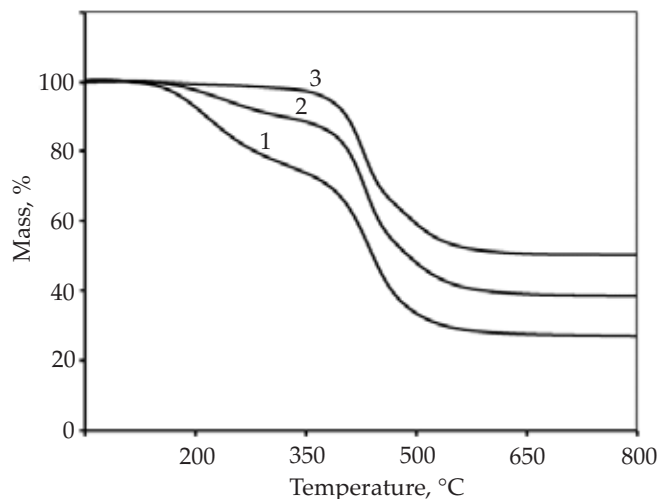


Fig. 11. TGA thermogram of: 1 – PAM, 2 – TMSPMA-co-AM, 3 – TMEVS-co-AM

Table 7. Thermal data of PAM, TMSPMA-co-AM, and TMEVS-co-AM

Samples	T_g , °C	$T_{10\%}$, °C	$T_{50\%}$, °C	Residual at 800 °C, wt %
PAM	163	250	450	28
TMSPMA/AM-1	153	350	500	45
TMEVS/AM-1	–	380	–	52

copolymers are more stable than the homopolymer of AM with 10 % weight loss at about 380 °C of TMEVS/AM-1 and 350 °C of TMSPMA/AM-1 which are higher than 250 °C of PAM 50 % weight loss and residual at 800 °C is given in Table 7.

CONCLUSIONS

TMSPMA/AM and TMEVS/AM copolymers were synthesized by free radical polymerization. The structure of copolymers was confirmed by FT-IR technique. Copolymer compositions were determined by elemental analysis. The reactivity ratios were obtained by different methods: Fineman-Ross, Kelen-Tudos, Mayo-Lewis, and curve fitting procedure and a good agreement was observed between the various methods. TMSPMA-co-AM tend to be block with TMSPMA ($r_1 = 1.87$, $r_2 = 0.80$) and TMEVS/AM is block with AM ($r_1 = 0.22$, $r_2 = 1.21$). The microstructure and sequence distribution of monomers are in agreement with the values of reactivity ratios.

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