Int. J. Chem. Sci.: 14(4), 2016, 2279-2291
ISSN 0972-768X
www.sadgurupublications.com

SYNTHESIS AND MONOMER REACTIVITY RATIOS OF [3-(TRIMETHOXYSILYL) PROPYL METHACRYLATE/N-VINYL PYRROLIDONE] COPOLYMER

AMEEN HADI MOHAMMED[a,b*], MANSOR B. AHMAD[a], NOR AZOWA IBRAHIM[a] and NORHAZLIN ZAINUDDIN[a]

[a]Department of Chemistry, Faculty of Science, Universiti Putra Malaysia,
43400 Serdang, SELANGOR, MALAYSIA
[b]Department of Chemistry, College of Science for Women,
University of Baghdad, 10071 Al Jadria, BAGHDAD, IRAQ

ABSTRACT

Copolymer of 3-(trimethoxysilyl) propyl methacrylate (TMSPM) with N-vinyl pyrrolidone (VP) was synthesized by free radical polymerization in dry benzene using (BPO) as initiator. The copolymer was characterized by FTIR, ^{1}H-NMR. Thermal properties of homopolymers and copolymers were studied by TGA and DSC. The copolymer composition was determined by elemental analysis. The monomer reactivity ratios were estimated by different procedures: Fineman-Ross, Kelen-Tudos, Mayo-Lewis and curve fitting method. The derived reactivity ratios (r_1, r_2) are: (3.722, 0.097), and found that the reactivity of the monomer TMSPM is more than the monomer NVP. The sequence distribution of monomers in the copolymer and the microstructure of copolymer were calculated by statistical method based on the average reactivity ratios.

Key words: 3-(Trimethoxysilyl) propyl methacrylate, N-vinyl pyrrolidone, Reactivity ratios, Sequence distribution, Thermal properties.

INTRODUCTION

Copolymerization is one of the best techniques 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 commonomers 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

---

[*] Author for correspondence; E-mail: ameenhadi80@yahoo.com; Ph.: +6001112311077

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 materials. The reactivity of vinyl silane monomers is basically 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 dπ–pπ interactions between the Si atom and the vinyl group. On the other hand, it should be possible to increase the reactivity of these 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 dπ–pπ interactions will be absent and this leads to enhance the reactivity of vinyl silane monomers. TMSPMA is one of these monomers (vinylsilane derivatives), which can be prepared by the reaction of 3-chloropropyltrimethoxysilane with methacrylic acid. In fact, this monomer and other functional vinyl silane monomers (having the Si atom away from the vinyl group) such as [(2-methacryloyloxy) alkoxy] trialkylsilanes, [(2-methacryloyloxy)propoxy] trialkyl (aryl) silanes and [(2-methacryloyloxy) ethoxy] trimethylsilane have been successfully copolymerized with butyl acrylate, styrene, methyl methacrylate, acrylonitrile, butyl methacrylate, perfluorodecylacrylate and other monomers[7-13], but no study has been reported onthe copolymerization and reactivity relationships of 3-(Trimethoxysilyl)propyl methacrylate (TMSPM) with VP.

The aim of this work is to copolymerize TMSPM, a hydrophobic monomer with VP, a hydrophilic monomer, and to study the best synthetic conditions and characterization of the copolymer. This study also determines the reactivity ratios of TMSPM and VP. From these parameters, a specific comonomer distribution is estimated.

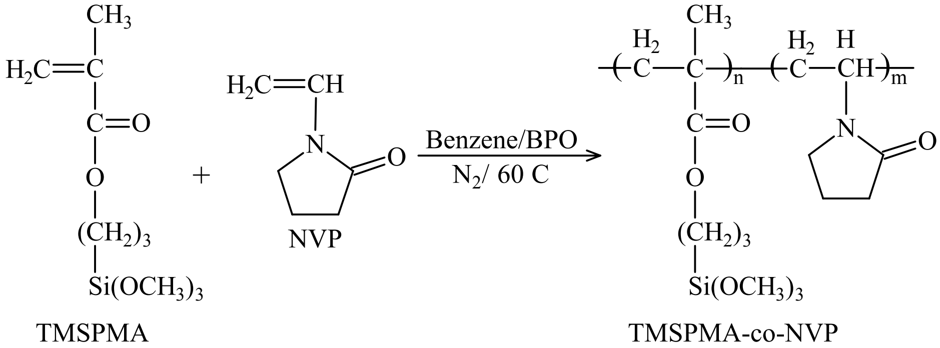
EXPERIMENTAL

Materials

Commercial samples of VP and TMSPM from Aldrich chemical were distilled under vacuum before copolymerization. The initiator Benzoyl peroxide was recrystallized from chloroform and dried in a vacuum. Solvents of 99% purity grade were used as received.

Synthesis of TMSPMA/NVP copolymers

Copolymerization of VP with TMSPM was carried out by using (1×10^{-3} mol/dm^3) BPO as initiator and dry benzene as solvent at 60°C in a glass tube. The total molar composition of the monomers mixture was maintained at (1 mol/dm^3) while the monomer feed ratio was varied in a series of copolymerization of VP and TMSPM (see Table 1). Nitrogen gas was bubbled through the mixture for 15 mins prior to the reaction in order to remove all oxygen. Copolymerization time was controlled in order to obtain low conversion (below 10%). The copolymers were precipitated in diethyl ether. The precipitates were filtered off, purified by redissolving in benzene and precipitated in diethyl ether. Copolymers were dried at 40ºC until constant weight. The reaction of copolymerization is shown in the following scheme (**Scheme 1**).



Scheme 1: The process formation of TMSPM-co-VP from TMSPM and VP as monomers

Characterization

FTIR spectrain KBr were recorded using a Perkin Elmer-1650 spectrometer in the range 400-4000 cm^{-1}. JOEL JMTC-500/54/SS (500 MHz) spectrometer was used to record the ^{1}H-NMR using tetra methyl silane as internal standard and DMSO as solvent. Copolymer compositions were determined by elemental analysis following the variation of the nitrogen content arising from vinyl pyrrolidone comonomers units.

RESULTS AND DISCUSSION

The structures of the PTMSPM, PVP and their copolymer are confirmed by FITR as shown in Fig. 1. The absorption bands which appear in the FTIR spectra of the copolymer Fig. 1 (c) belong to the stretching vibration in different functional groups of corresponding homo polymers Fig. 1 (a,b). The absorption bands of TMSPM/VP copolymer as follows: 2925 (alkane C-H), the carbonyl absorption of TMSPM observed at 1710 (ester C=O), 1650 (tertiary amide C=O), 1270 (amide C-N), 1075 (Si-O), 850 cm^{-1} (Si-C) and (alkane C-H bending vibration) at about1400 cm^{-1}.

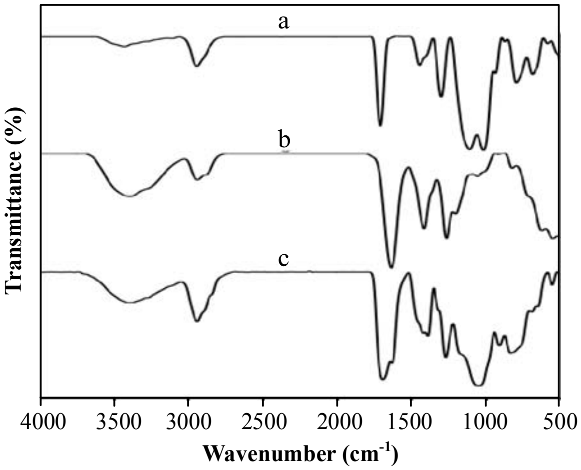


Fig. 1: FTIR of: (a) PTMSPM, (b) PVP, (c) TMSPM-co-VP

Fig. 2 shows ^{1}H-NMR spectrum of the copolymer. Methylene protons in VP ring resonate in 2.5, 3.2 and 4.4 ppm, while CH_2 protons for main chain backbone of monomers resonate at 1.8-2.4 ppm. CH proton main chain backbone of NVP resonates at 4.6 ppm. The signal corresponding to the protons of the methoxy groups linked to the silicon atom in TMSPM at about 3.5 ppm can be clearly observed. The ester and methyl groups in TMSPM resonate at 3.8 and 1.2 ppm, respectively.

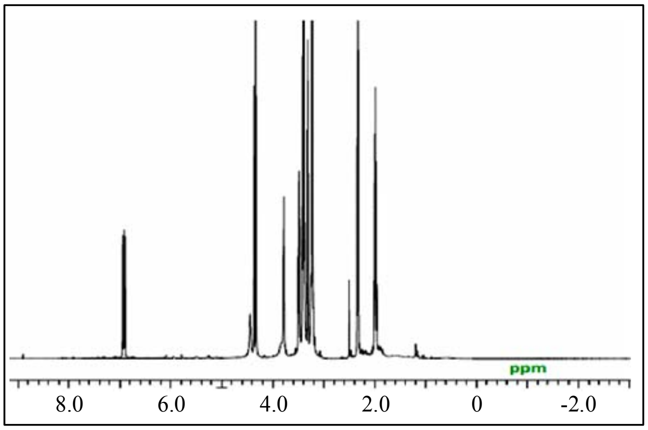


Fig. 2: ^{1}H-NMR of TMSPM/VP copolymer

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. In TMSPM/

VP copolymer, the composition of the two monomers in the copolymer was determined by estimating N% in the copolymers and this ratio indirectly gave the mole fraction of VP in the copolymer. The monomer composition and the results of compositions are listed in Table 1.

Table 1: Feed and copolymer compositions of TMSPM/VP copolymer

Test No.	f_1 (feed)	Conversion%	N%	F_1 (copolymer)
1	0.072	5.1	5.784	0.338
2	0.129	6.7	3.668	0.476
3	0.307	7.8	2.007	0.706
4	0.571	8.5	1.038	0.840
5	0.715	9.5	0.612	0.905
6	0.888	9.3	0.205	0.967

f_1 is the mole fraction of monomer-1 (TMSPM) in the initial feed; $f_2 = 1 - f_1$

F_1 is the mole fraction of monomer-1 (TMSPM) in the copolymer; $F_2 = 1 - F_1$

The plot of mole fraction of TMSPM in the feed (f_1) vs that of mole fraction of TMSPM in the copolymer (F_1) is shown in Fig. 3, a low amount of incorporation of VP monomer is observed.

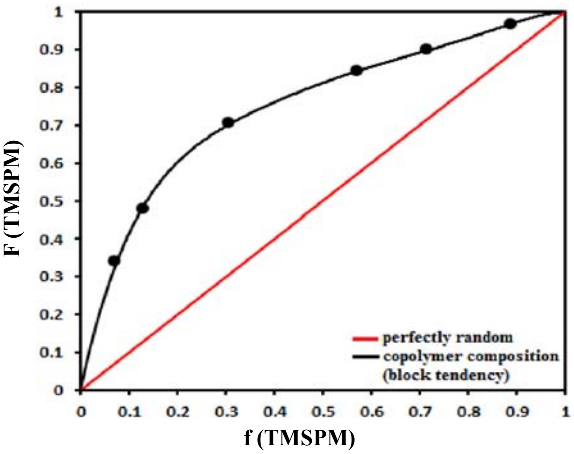


Fig. 3: Variation of copolymer composition F (TMSPM) with feed composition of (TMSPM) for TMSPM/VP copolymer

This can be interpreted in terms of the effect of the carbonyl group of TMSPM on its corresponding growing radical in the propagation step. In this way; the positive charge density generated on the carbonyl carbon atom can favour a significant electron attraction in the TMSPM 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 TMSPM 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 & 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:

$$G = Xr_1 - r_2 \qquad \ldots(1)$$

By plotting $G = f\,(F-1)/F$ as ordinate versus the $X = f^2/F$ as abscissa, one will obtain a straight line where the slope is the value for (r_1) and the intercept is the value for ($-r_2$). The values are represented in Table 2 and showed in Fig. 4. For Kelen-Tudos method, the equation used is:

$$\eta = r_1\,\zeta - \frac{r_2}{\alpha}(1-\zeta) \qquad \ldots(2)$$

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

By plotting ŋ 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 Fig. 5. For Mayo-Lewis method, a plot can be produced for a set of experiments using equation:

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

The straight lines that are produced on the plot for each experiment, where assumed r_1 represents the abscissa 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 Fig. 6. Curve-fitting method is based on the following equation:

$$F = f\,\frac{r_1 f + 1}{r_2 + f} \qquad \ldots(4)$$

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 VP in copolymer with the mole fraction f_2 in the initial feed 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 Fig. 7.

Table 2: Fineman-Ross, Kelen-Tudos, and Mayo-Lewis parameters of TMSPM/VP copolymer

Test No.	G	X	η	ζ	f	1/F
1	-0.074	0.012	-0.441	0.071	0.078	1.952
2	0.014	0.024	-0.081	0.132	0.148	1.100
3	0.258	0.081	1.084	0.340	0.443	0.416
4	1.077	0.337	2.180	0.682	1.331	0.190
5	2.229	0.698	2.611	0.816	2.508	0.111
6	7.505	2.061	3.383	0.929	7.771	0.034
α = 0.157						

Table 3: Theoretical parameters with values $r_1 = 3.756$, $r_2 = 0.092$ of TMSPM/VP

Test No.	f	F	f_2	F_2
1	0.1	0.721	0.909	0.581
2	0.5	2.415	0.666	0.292
3	1.0	4.311	0.500	0.188
4	2.0	8.031	0.333	0.110
5	4.0	15.82	0.200	0.059
6	6.0	22.82	0.142	0.043

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

Table 4: Monomer reactivity ratios of TMSPM/VP copolymer

Procedure	r_1 (TMSPM)	r_2 (VP)
Fineman and Ross	3.714	0.092
Kelen and Tudos	3.688	0.100
Mayo and Lewis	3.731	0.095
Curve fitting	3.756	0.102
Average values	3.722 ± 0.034	0.097 ± 0.005

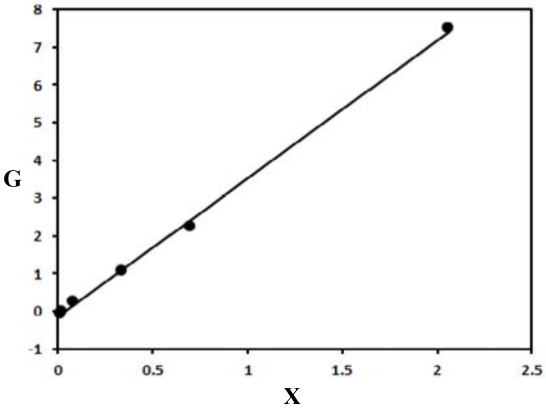


Fig. 4: Fineman-Ross plot of TMSPM/VP copolymer

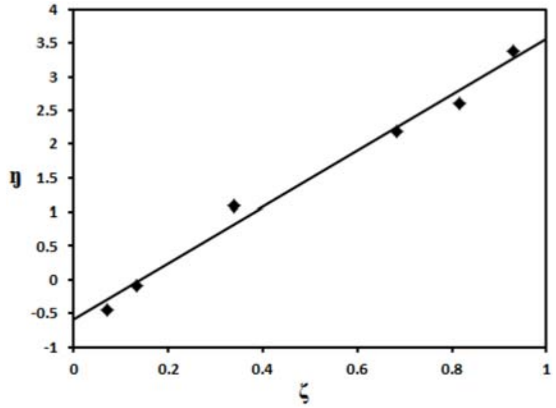


Fig. 5: Kelen-Tudos plot of TMSPM/VP copolymer

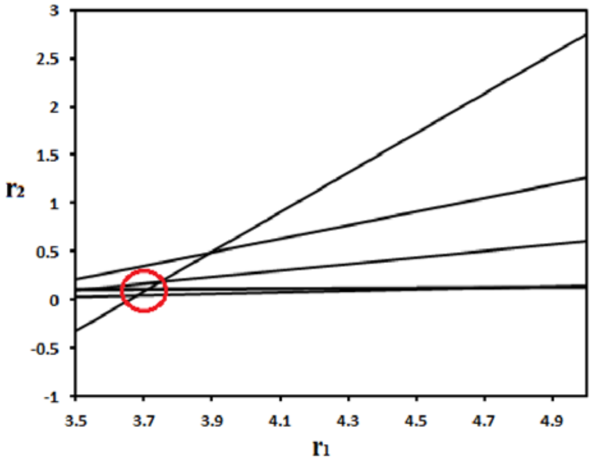


Fig. 6: Mayo-Lewis plot of TMSPM/VP copolymer

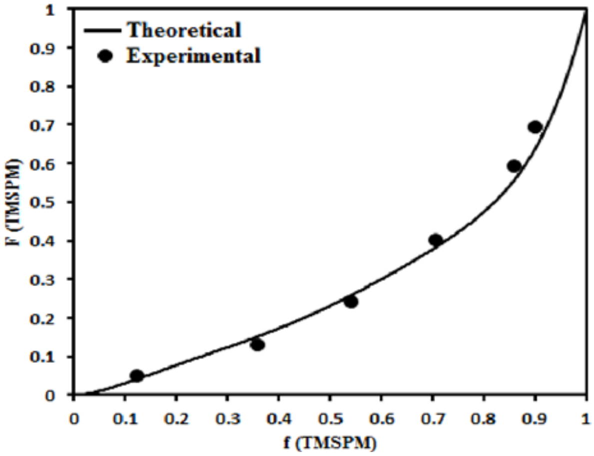


Fig. 7: Curve fitting plot of TMSPM/VP copolymer

It is possible to observe that TMSPM shows a trend towards the formation of blocks (r_{TMSPM} = 3.722) and towards cross-propagation for VP (r_{VP} = 0.097). The electronic stabilization effect exerted by the carbonyl group of the ester group adjoining the carbon carrying the radical electron over the TMSPM radical on the propagation step, allows explanation of the high reactivity of TMSPM in the copolymerization. In addition, the spacing out of the trimethoxysilane group of the main chain by means of a carbonyl group increases the reactivity of TMSPM against VP.

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 (TMSPM/VP) system since $r_1 > 1$ and $r_2 < 1$. This fact can be clearly observed in Fig. 3 (copolymer composition curve), which shows no azeotropic composition. The azeotropic feed composition f_1 (az.) is given by:

$$f_1(az) = (1 - r_2)/(2 - r_1 - r_2) \qquad \ldots(5)$$

$f_1(az)$ = Azeotropic feed composition.

Copolymer microstructure

The distribution of the monomers in the formation of the copolymer 1-1, 2-2 and 1-2 arecalculated using the following relations[19] and listed in Table 5.

$$S_{1\text{-}1} = m_1 - \frac{2\,m_1 m_2}{1 + [(2\,m_1 - 1)^2 + 4\,r_1 r_2\,m_1 m_2]^{1/2}}$$

$$S_{2\text{-}2} = m_2 - \frac{2\,m_1 m_2}{1 + [(2\,m_1 - 1)^2 + 4\,r_1 r_2\,m_1 m_2]^{1/2}} \qquad \ldots(6)$$

$$S_{1\text{-}2} = \frac{4\,m_1 m_2}{1 + [(2\,m_1 - 1)^2 + 4\,r_1 r_2\,m_1 m_2]^{1/2}}$$

Where m_1 and m_2 are the mole fractions of TMSPM and VP in the copolymer, $S_{1\text{-}1}$, $S_{2\text{-}2}$ and $S_{1\text{-}2}$ are the mole fractions of 1-1, 2-2 and 1-2 sequences, respectively, r_1 and r_2 are the reactivity ratios.

The probabilities of finding the sequence of TMSPM and VP units are calculated as follows and listed in Table 5:

$$PAA = r_1\,[A]/(r_1[A] + [B])$$

$$PBB = r_2\,[B]/(r_2[B] + [A]) \qquad \ldots(7)$$

$$PAB = [B]/(r_1[A] + [B])$$

$$PBA = [A]/(r_2[B] + [A])$$

Where, PAA, PBB, PAB and PBA are the probability of a TMSPM or VP unit to be followed by TMSPM or VP unit. In these equations [A] and [B] are the mole fractions of TMSPMA and NVP in the feed. The average length sequences of TMSPM and VP are calculated using the following equations and listed in Table 5:

$$\mu_1 = 1/PAB \quad \ldots(8)$$

$$\mu_2 = 1/PBA$$

Table 5: Statistical data of TMSPM/VP copolymer

Test No.	**Blockness**		**Alternation**	**Sequence probability**				**Sequence length**	
	M_1-M_1	**M_2-M_2**	**M_1-M_2**	**P_{AA}**	**P_{BB}**	**P_{AB}**	**P_{BA}**	**μ_1**	**μ_2**
1	0.065	0.388	0.547	0.223	0.538	0.777	0.464	1.28	2.15
2	0.161	0.208	0.631	0.354	0.378	0.646	0.623	1.54	1.60
3	0.457	0.045	0.498	0.621	0.169	0.379	0.831	2.63	1.20
4	0.691	0.011	0.298	0.831	0.063	0.168	0.937	5.95	1.06
5	0.803	0.003	0.194	0.902	0.034	0.097	0.966	10.31	1.03
6	0.934	0.001	0.065	0.966	0.011	0.033	0.988	30.30	1.01

The mole fraction of 1-1 sequence, PAA sequence and sequence length μ_1 increase as the mole fraction of TMSPM increases. At the same time, these values are much higher than the mole fraction of 2-2 and 1-2 sequences, PBB sequence and sequence length μ_2 respectively, indicating a higher reactivity and higher incorporation of TMSPM in the respective copolymer. In addition, the monomer TMSPM have a tendency to react with itself in the growing chain to form block copolymer and these results are in agreement with the values of $r_1(3.722) > 1$, $r_2(0.097) < 1$. The mean sequence length of TMSPM μ_1 varied from 1.28 to 30.30 for these copolymer compositions, values of μ_2 VP were between 2.15 and 1.01.

Thermal properties

The glass transition temperature (Tg) of the copolymers was determined by DSC under nitrogen atmosphere. The homopolymers of VP and TMSPM showed the Tg around 176°C and 55°C, respectively, whereas TMSPM/VP-3 copolymer the Tg value observed around 110°C. It is found that by increasing the amount TMSPM content in the copolymers result in decreased Tg. This may be due to the presence of propyl group in TMSPM 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. 8. The copolymers are more stable than the homopolymer of VP with 10% weight loss at about 290 of TMSPM-co-VP-3 which are higher than 110 of poly VP. 50% weight loss and residual at 800°C is given in Table 6.

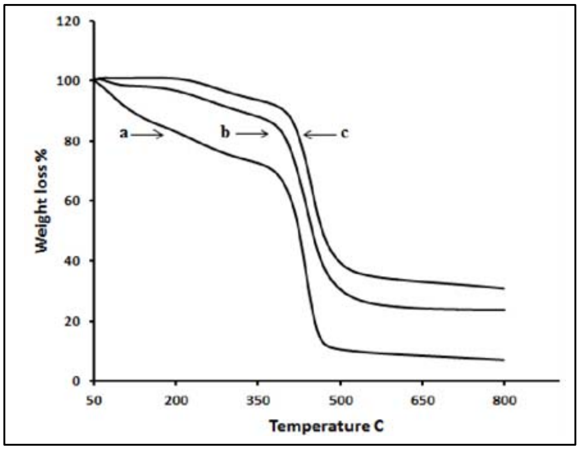


Fig. 8: TGA thermogram of: (a) Poly VP, (b) TMSPM-co-VP-3 (c) Poly TMSPM

Table 6: Thermal data of PolyVP, TMSPM-co-VP-3, and poly TMSPM

Samples	**T_g (°C)**	**T10% (°C)**	**T50% (°C)**	**Residual at 800°C (wt %)**
Poly NVP	176	110	400	7
TMSPM/NVP-3	110	290	460	23
Poly TMSPM	55	360	490	35

CONCLUSION

TMSPM/VP copolymer was synthesized by free radical polymerization. The structure of the synthesized copolymer was confirmed by FTIR and ^{1}H-NMR techniques. Copolymer compositions were obtained by elemental analysis. The reactivity ratios were obtained by Fineman-Ross, Kelen-Tudo, Mayo-Lewis and curve fitting methods and a good agreement was observed between the various methods. The value of $r_{TMSPM} = 3.722$ is higher than $r_{NVP} = 0.097$. This result can be explained in term of the electronic stabilization effect exerted by the carbonyl group of TMSPMA, so this copolymer can be classified as a block copolymer. The microstructure and sequence distribution are in agreement with the values of reactivity ratios.

REFERENCES

1. A. K. Patel, R. J. Patel, K. H. Patel and R. M. Patel, J. Chil. Chem. Soc., **54**, 228-233.2. (2009).

2. S. Ashenagar, F. Ziaee and S. M. Jalilian, Iran. Polym. J., **22**, 635-639 (2013).
3. A. M. Parambil, Y. M. Puttaiahgowda and P. Shankarappa, Turk. J. Chem., **36**, 397-409 (2012).
4. M. G. Patel, H. J. Patel, K. H. Patel and R. M. Patel, MPJ., **3**, 14-26 (2008).
5. N. Gatica, F. R. D´ıaz, L. Gargallo and D. Radi´c, Polym. Bull., **40**, 707-713 (1998).
6. T. M. Stefanac, M. A. Brook and R. Stan, Macromolecules, **29**, 4549-4555 (1996).
7. V. L. Rao and G. N. Babu, Eur. Polym. J., **25**, 605-609 (1989).
8. P. Bajaj and D. C. Gupta, J. Polym. Sci. A Polym. Chem., **21**, 1347-1359 (1983).
9. P. Bajaj, Y. P. Khanna and G. N. Babu, J. Polym. Sci. A Polym. Chem., **14**, 465-474 (1976).
10. P. Bajaj, D. C. Gupta and A. K. Gupta, J. Appl. Polym. Sci., **25**, 1673-1684 (1980).
11. F. Pardol, V. Lapinte and R. J. Jacques, Eur. Polym. J., **45**, 1198-1207 (2009).
12. G. R. Shan, G. Fevotte, N. S. Othman and E. B. Lami, Macromolecules, **41**, 5166-5173 (2008).
13. J. Pu and Y. Chen, Macromolecules, **37**, 6322-6328 (2004).
14. N. Ayaz, F. Bezgin and K. Demırellı,isrn Polymer Sci., **13**, 2012 (2012).
15. M. Fineman and S. D. Ross, J. Polym. Sci. A Polym. Chem., **5**, 259-265 (1950).
16. T. Kelen and F. T¨ud¨os, Pure Appl. Chem., **9**, 1-27 (1975).
17. F. R. Mayo and F. M. Lewis, J. Am. Chem. Soc., **66**, 1594-1601 (1944).
18. T. Alfrey, J. J. Bohrer and H. Mark, Copolymerization, Interscience, NY (1952) pp. 96-103.
19. S. Vijaykumar, S. Prasannkumar and B. S. Sherigara, Macromol. Res., **17**, 1003-1009 (2009).

Revised : 13.08.2016 *Accepted : 16.08.2016*