

Copolymerization of N-Vinyl pyrrolidone with methyl methacrylate by Ti(III)-DMG redox initiator

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Received: 11.11.2011

Redox copolymerization of N-vinyl-2-pyrrolidone (NVP) with methyl methacrylate (MMA) was carried out using titanium(III)-dimethylglyoxime [Ti(III)-DMG] redox initiator in aqueous sulfuric acid-alcohol media. The resulting copolymer was characterized by FTIR, ¹H-NMR, and ¹³C-NMR spectroscopic methods and elemental analysis. Thermal properties of the copolymer were determined by differential scanning calorimetric technique and thermogravimetric analysis. The reactivity ratios of the monomers were computed by Fineman-Ross, Kelen-Tudos, and extended Kelen-Tudos methods at lower conversion. The reactivity ratios obtained r_1 (MMA) 1.69 and r_2 (NVP) 0.03 showed richer content of MMA than NVP in the copolymer having extreme ideal behavior. The distribution of monomer sequence along the copolymer chain was calculated using a statistical method based on reactivity ratios. Ti(III)-DMG redox initiator showed increased addition of NVP to MMA during copolymerization.

Key Words: Redox initiator, copolymerization, reactivity ratios

Introduction

Copolymerization is an excellent method to prepare macromolecules with specific chemical structures and for the control of properties such as solubility, polarity, and hydrophilic/hydrophobic balance.^{1,2} The chemical structure of a copolymer depends on the 2-monomer units and on sequential distribution of monomer units along the copolymer chain.

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N-vinyl-2-pyrrolidone (NVP) monomer is attracting much attention in various fields due to its good biocompatibility, low toxicity, good film forming, and adhesive characteristics.³⁻¹¹ NVP-based polymers find applications in plasma substitutes, soluble drug carriers, and UV-curable bioadhesives.^{12,13} NVP monomer contains a highly polar amide group, which confirms its hydrophilic and polar properties, while the methylene and methane groups in the main and side chain confirm its hydrophobic property, which helps in the preparation of surface active polymers.^{14,15}

In our previous research, we established the reduction kinetics of oximes by titanium(III).¹⁶ The redox reactions of titanium(III) with oximes often generate free radicals as transient intermediates, which induce redox polymerization with various vinyl monomers.¹⁷⁻²⁰ The redox initiators are widely accepted for free radical polymerization processes in industries due to their lower activation energy over a very wide range of temperature (0-50 °C).^{21,22} There are no reports on copolymer synthesis by using titanium(III)-oxime redox initiator so far.

Various methods of copolymerization reactions have been reported for MMA-co-NVP pair;²³⁻³⁰ hitherto there were no reports on redox copolymerization for MMA-co-NVP pair. One of the earlier reports where benzoyl peroxide was used as initiator for MMA-co-NVP copolymerization showed much lower incorporation of NVP during copolymerization.³¹ In the present work, by considering the versatile use of NVP, we have for the first time introduced titanium(III)-dimethylglyoxime redox initiator to synthesize a copolymer of NVP with MMA. The main focus of the present work was to understand the statistical monomer sequence distribution and to know the percentage of NVP incorporation in synthesized copolymer.

Experimental

Materials and methods

NVP (98%), obtained from Merck, Germany, and MMA (CDH) were distilled under reduced pressure, washed with dilute alkali followed by distilled water and dried over anhydrous sodium sulfate and stored below 5 °C. The titanium dioxide (s.d.fine India), DMG (s.d.fine India), benzene (Merck, Germany), hexane (Merck, Germany), acetone (Nice, India), chloroform (Universal Laboratories, India), methanol (s.d.fine, India), and diethyl ether (Loba Chemie, India) used were of analytical grade. Doubly distilled water was used throughout the experiments. A stock solution of titanium(III)sulfate solution was prepared by electrolytic reduction of an appropriate titanium solution and was standardized against ferric ammonium sulfate.³²

Copolymer synthesis

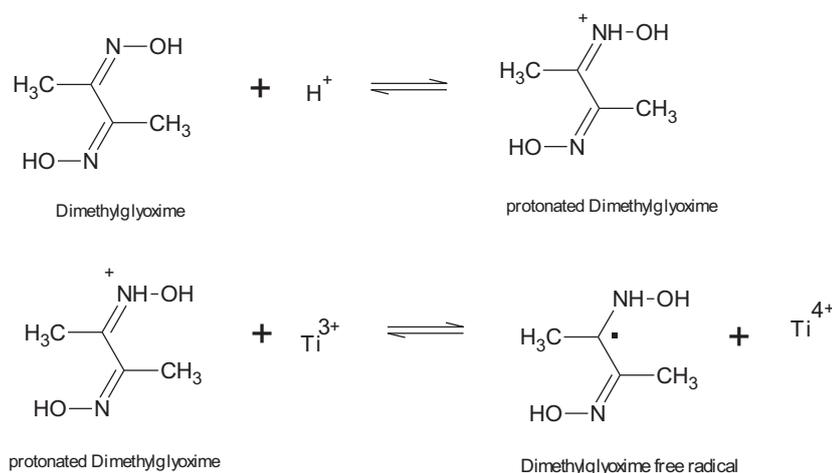
Copolymerization was carried out in a 3-necked 100 mL round bottom flask by taking required amounts of alcoholic DMG, NVP, MMA, Ti(III), Con.H₂SO₄, and water in nitrogen atmosphere at room temperature up to 15% conversion. The reaction was stopped by rapid cooling of the reaction mixture with ice cubes. The obtained solid was washed with water and benzene to remove residual monomers and homopolymers. The sample was dried in a vacuum until constant weight was obtained. The solubility studies were carried out in various polar and non-polar organic solvents by adding 5-10 mg of sample to 5 mL of solvent in a standard test tube and were kept overnight. The solubility was observed after 24 h.

Copolymer characterization

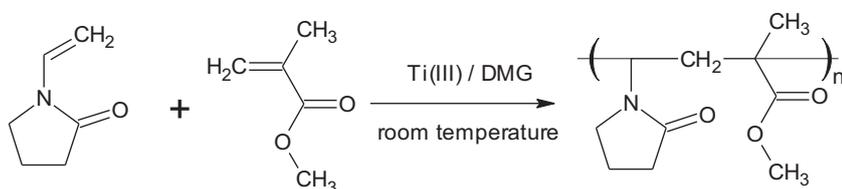
The synthesized copolymers were characterized using $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, and FTIR techniques and elemental analysis (SAIF, STIC, CUSAT, Cochin, Kerala, India). $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ techniques were carried out in deuterated acetone as solvent using a Bruker NRC spectrometer (IISc, Bangalore, India). FTIR spectra were recorded in KBr pellets using a Shimadzu-8400S spectrometer in the range $400\text{-}4000\text{ cm}^{-1}$. Thermal properties were determined by TGA and DSC (NITK, Surathkal, Karnataka, India).

Results and discussion

Redox polymerization involves redox initiation, known as reduction-oxidation or redox catalysis. In the redox initiation system, free radicals are produced by oxidation of the substrate, which in turn initiate polymerization and the plausible mechanism for copolymer formation shown in Schemes 1 and 2.



Scheme 1. Free radical generation in the redox initiation system.



Scheme 2. Synthesis of NVP/MMA copolymer.

Copolymer characterization

Five N-vinyl pyrrolidone-methyl methacrylate copolymers with different compositions were prepared as per the experimental details given in Table 1, using a Ti(III)-DMG redox system in aqueous sulfuric acid-alcoholic media under inert atmosphere.

Figure 1 shows the FTIR spectrum of the copolymer, where a strong absorption peak is at 1728 cm^{-1} for the ester group of the MMA unit and the peak at 1631 cm^{-1} is due to the C=O of the NVP unit. The absorption peak at 1386 cm^{-1} is due to C-N-C of the imide in the NVP unit and the peaks at 2950 and 2842 cm^{-1} are attributed to asymmetric and symmetric C-H stretching of MMA, respectively. The peaks at 3468 cm^{-1} (N-H and O-H stretching) and 1631 cm^{-1} (N-H bending and C=N stretching) indicate the DMG moiety as an end group of the copolymer. The combined FTIR spectrum of copolymer at different compositions is given in Figure 2.

Table 1. FTIR data of NVP/MMA copolymer.

Sample	Feed mole fraction of MMA (M_1)	% Conversion (for 15 min)	N% by Elemental analysis	Integral value		Mole fraction Of MMA in copolymer (m_1) by FTIR	Mole fraction of MMA in copolymer (m_1) by elemental analysis
				Intensity Of Methyl -CH ₃ in MMA	Intensity of Imide C-N-C in NVP		
V-75	0.25	1.4	5	9.3015	5.8900	0.6368	0.6429
V-60	0.40	3.7	4.1	12.943	4.9220	0.7082	0.7071
V-50	0.50	8.0	3.1	15.051	5.0680	0.7672	0.7786
V-40	0.60	8.4	2.4	15.500	3.6898	0.8235	0.8286
V-25	0.75	9.3	2.1	15.712	3.0560	0.8510	0.8500

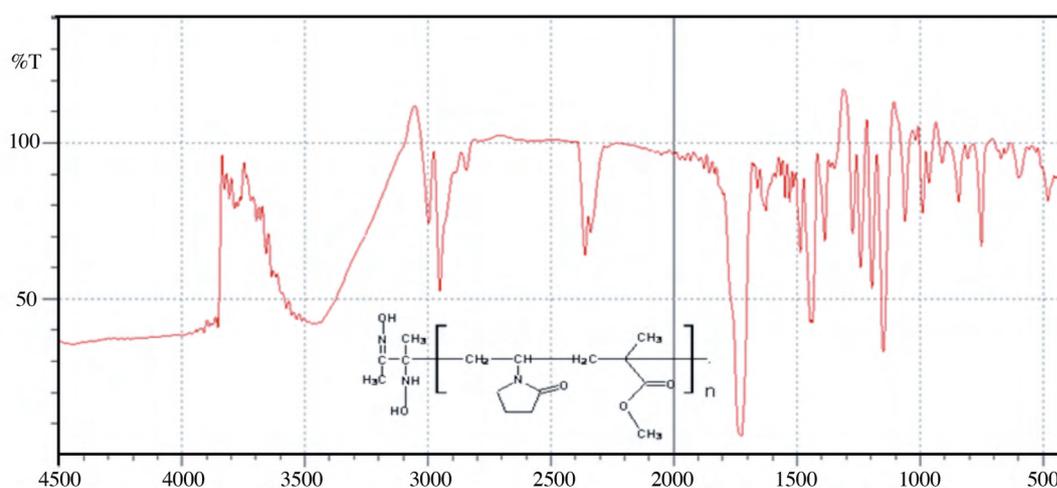


Figure 1. FTIR spectrum of NVP/MMA copolymer.

Figure 3 shows the $^1\text{H-NMR}$ spectrum of the NVP/MMA copolymer where proton signals for the main chain methylene protons of both NVP and MMA unit are at δ 2.23-2.90, which overlap with a different type of compositional configurational sequences. Similarly, signals for methyl ($^7\text{CH}_3$, $^8\text{CH}_3$, and $^{10}\text{CH}_3$) protons of copolymer moiety appear at δ 0.85-1.33, which overlap with each other. Signals for CH of NVP (^1CH) appear at δ 4.67. The ring methylene protons in NVP signals can be assigned at δ 3.5 ($^3\text{CH}_2$), δ 2.2 ($^5\text{CH}_2$), δ 1.94 for ($^4\text{CH}_2$), and δ 2.07 for ($^6\text{CH}_2$) respectively. The signals at δ 5.55 for OH and δ 6.14 for NH are assigned to the DMG moiety.

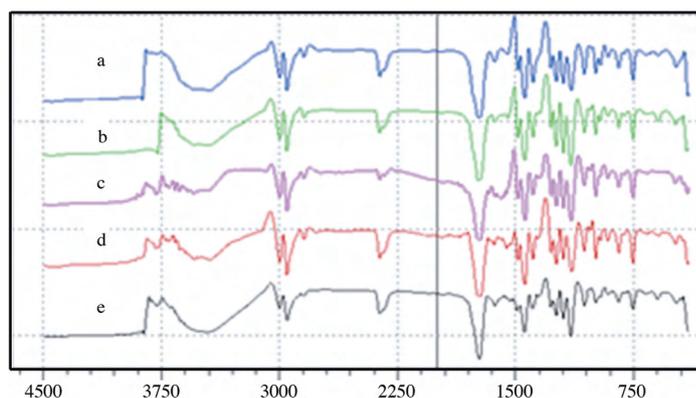


Figure 2. FTIR spectra of NVP/MMA copolymer prepared in various monomer feeds (NVP/MMA): (a) 75:25, (b) 60:40, (c) 50:50, (d) 40: 60, (e) 25:75.

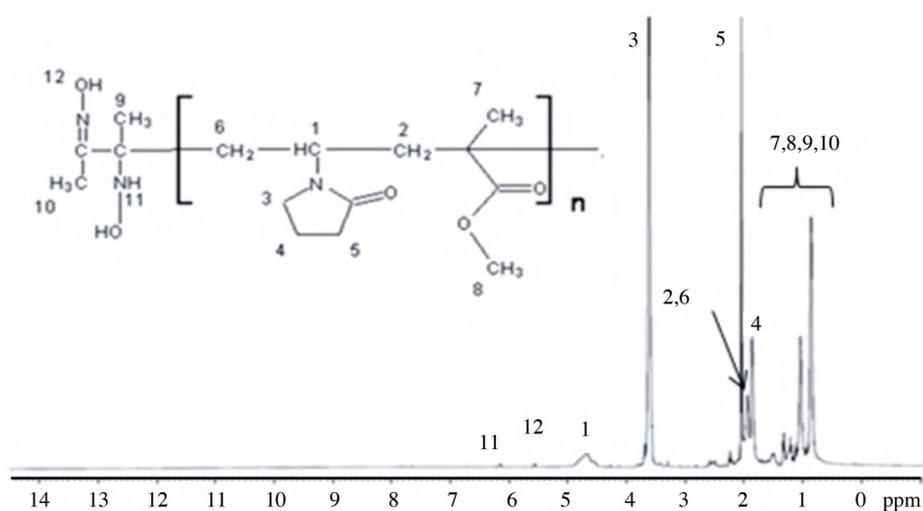


Figure 3. ^1H -NMR spectra of NVP/MMA copolymer.

The ^{13}C -NMR spectrum of NVP/MMA copolymer is shown in Figure 4. The carbonyl carbon ($>\text{C}=\text{O}$) signals of both NVP and MMA units appear between δ 177.28 and 178.49. The spectral region around δ 17.14-55.23 is assigned to aliphatic carbon resonance in the back and side chain of NVP/MMA copolymer. The side chain ring methylene carbon signal is assigned at δ 55.23 ($^6\text{CH}_2$), δ 45.64 ($^4\text{CH}_2$), and δ 29.22 ($^5\text{CH}_2$). The signal at δ 52.05 indicates the methyl carbon of MMA ($^{11}\text{CH}_3$). The carbon (^1CH) signal overlaps with the δ value of $^4\text{CH}_2$.

Copolymer composition

The composition of monomers in copolymer was determined by FTIR through recorded individual absorption peaks of comonomers. The peak corresponding to the imide group of NVP (1386 cm^{-1}) and methylene group

of MMA (2950 cm^{-1}) as per Figure 1 was considered for calculation. The compositions obtained by the FTIR method are listed in Table 1.

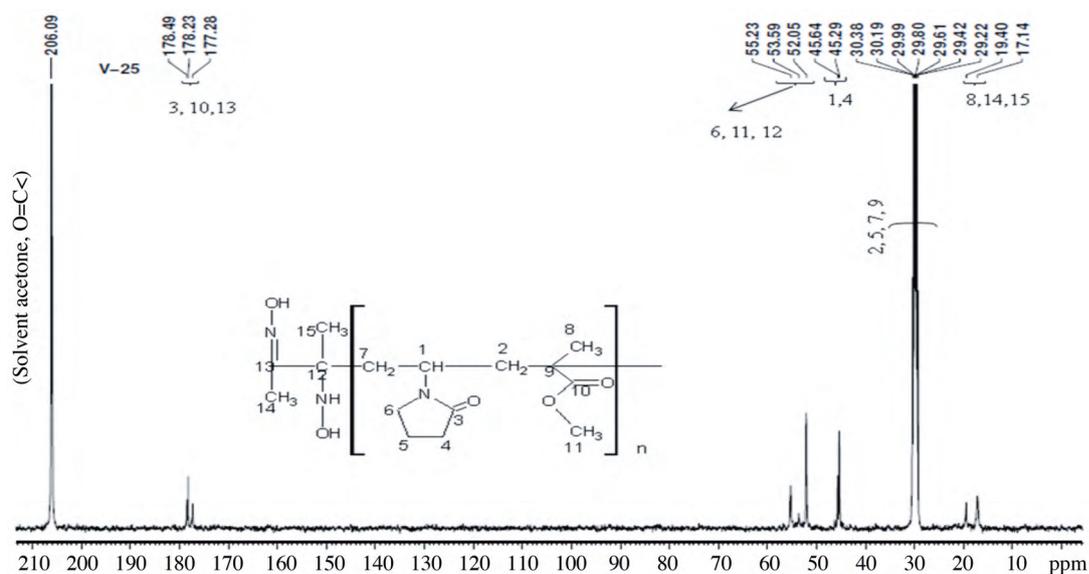


Figure 4. ^{13}C -NMR spectra of NVP/MMA copolymer.

Monomer reactivity ratios

The comonomers' composition sequence is one of the main factors that influence copolymer behavior and properties. Copolymer composition depends on the monomer feed composition and on the relative monomer reactivity. Therefore, it is very important to study the comonomers' reactivity in this system.³³

Copolymer reactivity ratio of NVP and MMA is determined by the Fineman-Ross (F-R), Kelen-Tudos (K-T), and extended Kelen-Tudos (EK-T) methods using the data obtained by FTIR spectroscopy and elemental analysis. The equations used for F-R and K-T are

$$G = r_1 F - r_2 (F - R \text{ equation}) \quad (1)$$

$$\eta = (r_1 + r_2/\alpha)\xi - r_2/\alpha(K - T \text{ equation}) \quad (2)$$

where r_1 and r_2 are the reactivity ratios relating to the monomer MMA and NVP, respectively. The plot of G vs. F will give a straight line, the slope of the straight line gives r_1 , and the intercept gives $-r_2$ (Figure 5a). η , ξ , and α are the mathematical functions of G and F as indicated and presented in Table 2 and Table 3 for the K-T method. The K-T plot of ξ vs. η is shown in Figure 5b using FTIR data and elemental analysis data. From the calculation the reactivity ratios obtained are r_1 1.69 and r_2 0.03.

The EK-T method, another linear least-square method, considers the drift of comonomers and copolymer composition with conversion. The partial molar conversion of NVP is defined as

$$\xi_{NVP} = \frac{W(\mu + x)}{(\mu + y)} \quad (3)$$

where W is the weight of conversion of polymerization and μ is the molecular weight of NVP to that of MMA. The partial molar conversion of MMA is

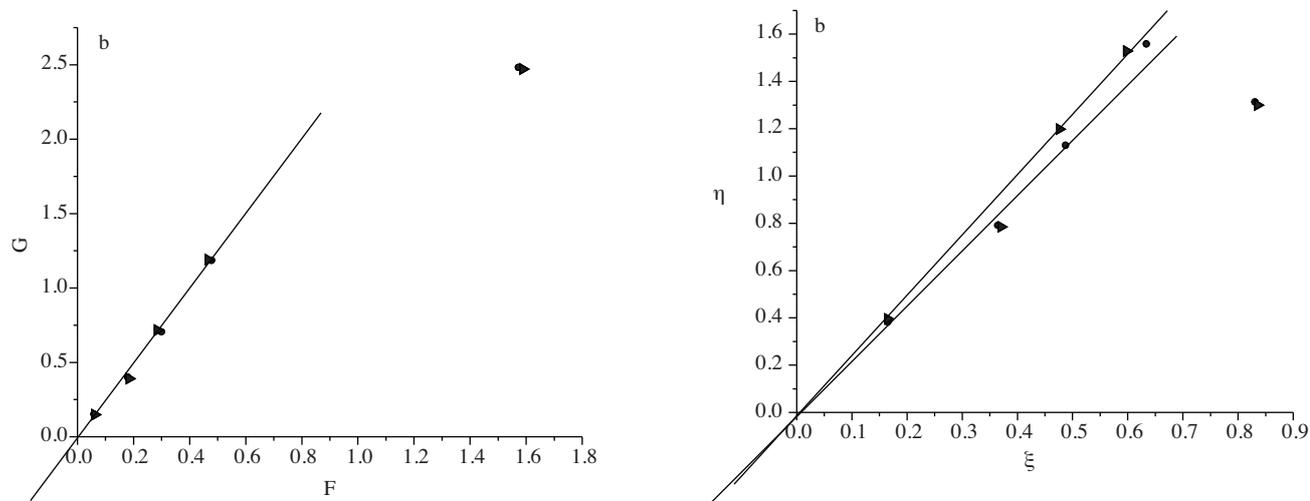


Figure 5. FTIR data (●) and elemental analysis (▲) of (A) F-R plot of G vs. F ; (B) K-T plot of η vs. ξ .

Table 2. F-R and K-T parameters for NVP/MMA copolymer by FTIR data.

Sample	$x = M_1/M_2$	$y = m_1/m_2$	$G = x(y - 1)/y$	$F = x^2/y$	$\eta = G/(\alpha + F)$	$\xi = F/(\alpha + F)$
V-75	0.3333	1.7533	0.1432	0.0634	0.3769	0.1671
V-60	0.6666	2.4278	0.3920	0.1830	0.7855	0.3667
V-50	1.0000	3.2969	0.6966	0.3033	1.1248	0.4897
V-40	1.5000	4.6657	1.1785	0.4822	1.5543	0.6359
V-25	3.0000	5.7114	2.4747	1.5757	1.3081	0.8329

$$\alpha = (F_{min} \cdot F_{max})^{1/2} = 0.3160$$

Table 3. F-R and K-T parameters for NVP/MMA copolymer by elemental analysis data.

Sample	$x = M_1/M_2$	$y = m_1/m_2$	$G = x(y - 1)/y$	$F = x^2/y$	$\eta = G/(\alpha + F)$	$\xi = F/(\alpha + F)$
V-75	0.3333	1.800	0.1481	0.0617	0.3951	0.1646
V-60	0.6666	2.414	0.3905	0.1841	0.7854	0.3703
V-50	1.0000	3.5167	0.7156	0.2844	1.1977	0.4759
V-40	1.5000	4.8343	1.1897	0.4654	1.5282	0.5978
V-25	3.0000	5.666	2.4705	1.5884	1.2995	0.8353

$$\alpha = (F_{min} \cdot F_{max})^{1/2} = 0.3131$$

$$\xi_{MMA} = \xi_{NVP} \frac{Y}{X} \tag{4}$$

Then

$$Z = \frac{\log(1 - \xi_{MMA})}{\log(1 - \xi_{NVP})} \quad (5)$$

where EK-T parameters, $\eta = G/(\alpha + F)$; $G = (y - 1)/Z$; and $F = y/Z^2$ are calculated using FTIR spectroscopy and elemental analysis. The data are provided in Tables 4 and 5. The EK-T plot for copolymer samples is given in Figure 6 and Table 6 shows the reactivity ratios of the monomers calculated from FTIR spectroscopy and elemental analysis. Since r_1 values are greater than one and r_2 values are less than one ($r_1 > 1$, and $r_2 < 1$) the copolymer is richer in MMA than in NVP, which indicates extreme ideal behavior. For this copolymer system, reactivity ratio r_2 increased from 0.004 to 0.03 compared to previous reports,³¹ which indicates that the selected redox initiated system helps to incorporate more NVP content in MMA/NVP copolymer. Hence the proposed redox system can be effectively used for copolymerization of MMA and NVP.

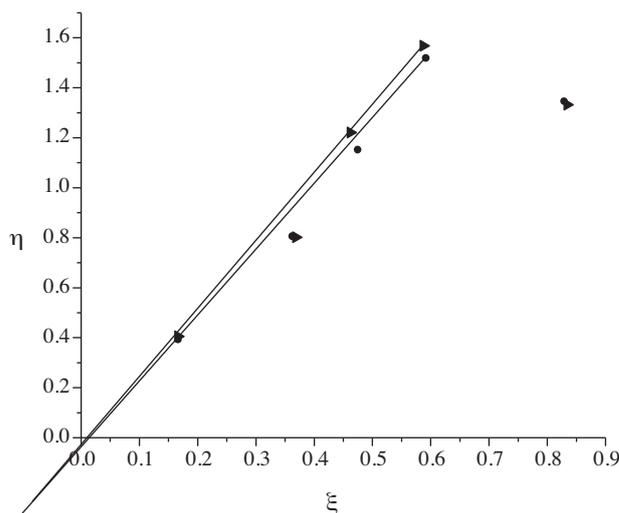


Figure 6. FTIR (●) and elemental analysis (▲) data of EK-T plot of η vs. ξ .

Table 4. EK-T parameters for NVP/MMA copolymer by FTIR data.

Sample	ξ_{vp}	ξ_{MMA}	Z	G	F	η	ξ
V-75	0.0076	0.0399	5.3372	0.1411	0.0615	0.3872	0.1687
V-60	0.0186	0.0677	3.7337	0.3824	0.1741	0.8016	0.3645
V-50	0.0383	0.1262	3.4544	0.6649	0.2763	1.1479	0.4770
V-40	0.0379	0.1178	3.2456	1.1294	0.4429	1.5143	0.5938
V-25	0.0560	0.1066	1.9564	2.4081	1.4922	1.3414	0.8312

$$\alpha = (F_{min} \cdot F_{max})^{1/2} = 0.3029$$

Copolymer microstructure

Statistical distributions of the pair monomer sequence 1-1, 2-2, 1-2 are calculated using the following relations:³⁴

$$S_{(1-1)} = m_1 - \frac{2m_1m_1}{1 + [(2m_1 - 1)^2 + 4r_1r_2m_1m_2]^{1/2}} \quad (6)$$

$$S_{(2-2)} = m_2 - \frac{2m_1m_1}{1 + [(2m_1 - 1)^2 + 4r_1r_2m_1m_2]^{1/2}} \quad (7)$$

$$S_{(1-2)} = \frac{4m_1m_1}{1 + [(2m_1 - 1)^2 + 4r_1r_2m_1m_2]^{1/2}} \quad (8)$$

where r_1 and r_2 are the average reactivity ratios obtained by the linear methods. m_1 and m_2 are the mole fractions of the MMA and NVP in the copolymer obtained from FTIR data and elemental analysis data. The structural data given in Table 7 suggest that the mole fractions of S_{1-1} and S_{1-2} indicate an increasing tendency of MMA towards NVP. The sequence S_{2-2} indicates a very negligible interaction between NVP homo monomers; hence there is much less chance of NVP homo polymerization.

Table 5. EK-T parameters for NVP/MMA copolymer by elemental analysis data.

Sample	ξ_{vp}	ξ_{MMA}	Z	G	F	η	ξ
V-75	0.0069	0.0372	5.4842	0.1459	0.0598	0.4054	0.1662
V-60	0.0186	0.0674	3.7615	0.3805	0.1748	0.8012	0.3681
V-50	0.0365	0.1284	3.6959	0.6809	0.2575	1.2211	0.4618
V-40	0.0368	0.1186	3.3670	1.1388	0.4264	1.5675	0.5869
V-25	0.0564	0.1065	1.9397	2.4055	1.5059	1.3319	0.8338

Table 6. Monomer reactivity ratios for NVP/MMA copolymer.

Reactivity ratios		F-R method	K-T method	EK-T method	Average
By FTIR spectroscopy	r_1	2.25	2.6	2.6	2.5
	r_2	0.04	0.02	0.02	0.03
By elemental analysis	r_1	2.25	2.9	2.8	2.65
	r_2	0.04	0.02	0.02	0.03

Table 7. Structural data for the copolymers of MMA (1) with NVP (2).

Sample	Composition (mole fraction)		Blockness (mole fraction)		Alternation (mole fraction)
	m_1	m_2	S_{1-1}	S_{2-2}	S_{1-2}
V-75	0.6368	0.3632	0.3016	0.0279	0.6705
V-60	0.7082	0.2917	0.4300	0.0135	0.5564
V-50	0.7672	0.2327	0.5416	0.0071	0.4513
V-40	0.8235	0.1765	0.6505	0.0035	0.3461
V-25	0.8510	0.1490	0.7043	0.0023	0.2934

Simona et al.³⁵ calculated the copolymer microstructure and sequence distribution of monomers in the formation of the copolymer and herein we have attempted to calculate the sequence distribution of the resulting copolymer. The probabilities are calculated by the following equations:

$$P_{11} = \frac{r_1}{r_1 + \{[M_2]/[m_1]\}} \quad (9)$$

$$P_{12} = \frac{[M_2]}{r_1[M_1] + [M_2]} \quad (10)$$

$$P_{21} = \frac{M_1}{r_2[M_2] + [M_1]} \quad (11)$$

$$P_{22} = \frac{r_2[M_2]}{r_2[M_2] + [M_1]} \quad (12)$$

The number average sequence length \bar{n}_1 of the monomer M_1 and \bar{n}_2 of the monomer M_2 is calculated as follows:

$$\bar{n}_1 = \frac{r_1[M_1] + [M_2]}{[M_2]} \quad (13)$$

$$\bar{n}_2 = \frac{r_2[M_2] + [M_1]}{[M_1]} \quad (14)$$

The number average sequence lengths \bar{n}_1 and \bar{n}_2 of the monomers M_1 and M_2 are given in Table 8. In this case we observed that the NVP/MMA copolymer contains predominantly a sequence of MMA, which is in agreement with the higher reactivity of MMA.

Table 8. Statistical data for the NVP/MMA copolymer.

Sample	p ₁₁	p ₁₂	p ₂₁	p ₂₂	\bar{n}_1	\bar{n}_2
V-75	0.4545	0.5454	0.9174	0.0826	1.8334	1.0900
V-60	0.6250	0.3750	0.9569	0.0431	2.6667	1.0450
V-50	0.7143	0.2857	0.9709	0.0291	3.5000	1.0300
V-40	0.7895	0.2105	0.9804	0.0196	4.7500	1.0200
V-25	0.8824	0.1176	0.9901	0.0100	8.5000	1.0100

Thermal properties

The thermal property of copolymer is studied by TGA and DSC. TGA is carried out in the temperature range of 0 °C to 550 °C under inert nitrogen atmosphere. Figure 7 shows the TGA graph of MMA-NVP copolymer with initial thermal decomposition at 230 °C. Figure 8 shows the DSC thermogram of MMA-NVP copolymer indicating T_g 130 °C, which is higher than T_g of Poly (MMA) 116 °C³⁶ and lower than T_g of Poly (NVP) 148 °C.³⁷ This result indicates an incorporation of NVP monomer in MMA-NVP copolymer.

Solubility

Solubility of the copolymer samples is examined in different solvents. The copolymers are completely soluble in solvents like acetone, chloroform, methanol, diethyl ether, and ethyl acetate and insoluble in solvents like hexane and benzene.

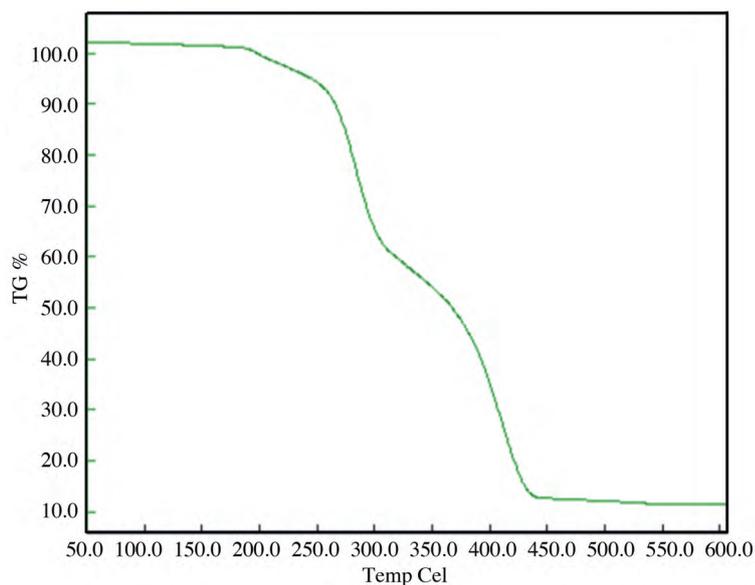


Figure 7. TGA thermogram of NVP/MMA copolymer.

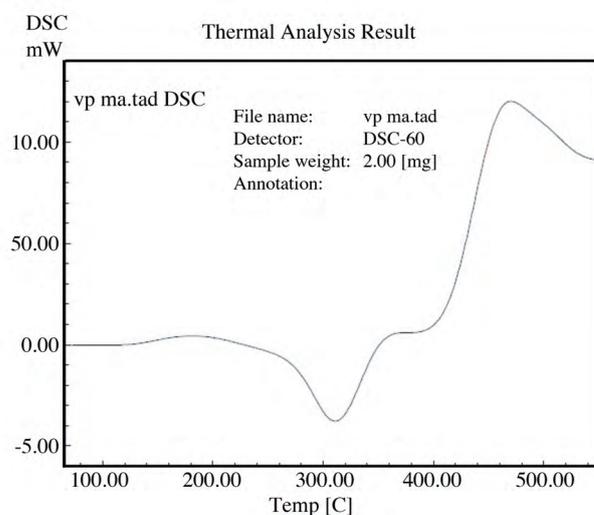


Figure 8. DSC thermogram of NVP/MMA copolymer.

Conclusion

Copolymers of MMA-NVP were prepared in aqueous sulfuric acid-alcoholic media for the first time using Ti(III)-DMG redox initiator system. The obtained copolymer showed excellent solubility in polar solvents and was insoluble in water. The DSC thermogram showed higher T_g for MMA-NVP copolymer as compared to homopolymer PMMA. The reactivity ratios r_1 1.69 and r_2 0.03 calculated by FR, K-T, and EK-T methods using FTIR and elemental analysis data showed ideal copolymer formation between MMA and NVP monomers. Copolymer microstructure calculation indicated higher MMA content along with NVP monomer unit. The

approached redox initiator pair favors the incorporation of NVP content into the copolymer compared to previous reports (r_2 - 0.004 to 0.03).

Acknowledgements

The financial support given by Syndicate Bank, Pariyaram Branch, Kannur, Kerala, India, is gratefully acknowledged.

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