Copolymerization of N-Vinyl Pyrrolidone with Functionalized Vinyl Monomers: Synthesis, Characterization and Reactivity Relationships

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Abstract: Copolymers of N-vinylpyrrolidone (NVP) comonomer with styrene (St), hydroxypropyl methacrylate (HPMA) and carboxyphenyl maleimide (CPMI) were synthesized by free radical polymerization using 2,2'-azobisisobutyronitrile (AIBN) initiator in 1,4-dioxane solvent. The copolymers formed were characterized by FTIR, ^{1}H NMR and ^{13}C NMR techniques and their thermal properties were studied by DSC and TGA. Copolymer composition was determined by ^{1}H NMR and/or by elemental analysis and monomer reactivity ratios (MRR) were estimated by the linear methods of Kelen-Tudos (K-T) and extended Kelen-Tudos (EK-T) and the non-linear approach. Copolymers of St and HPMA with NVP formed blocks of one of the monomer units, whereas alternating copolymers were obtained in CPMI-NVP, depending upon the side chain substitution. The MRR values are discussed in terms of monomer structural properties such as electronegativity and electron delocalization. The sequence distribution of monomers in the copolymers was studied by statistical method based on the average reactivity ratios obtained by EK-T method.

Keywords: N-vinyl-2-pyrrolidone, functionalized vinyl copolymers, reactivity ratios, Sequence distribution.

Introduction

N-Vinylpyrrolidone (NVP) has been widely investigated for applications in various fields,[1-5] since these are known to exhibit good biocompatibility due to their hydrophilic nature and have low cytotoxicity.[6-8] The amide group of NVP has high binding affinity for several small and large molecules that are known to be good hydrogen-bond acceptors and has been copolymerized with a variety of monomers.[9-13] However, the copolymer composition is important in evaluating its utility. The copolymer composition and its distribution are dependent on it reactivity ratios, this can be evaluated by employing linear and nonlinear methods or by using other copolymer composition equations.[14-16] In radical copolymerization, the reactivity of a free radical depends upon the electronic delocalization, polarity and volume nature of the side groups linked to the radical carbon. All these factors can be studied by analyzing the reaction between function-

alized monomers to obtain the corresponding functionalized copolymers.

The present work is a continuation of our ongoing research on the synthesis and characterization of NVP-based copolymers.[17] The aim of this work is to study the influence of side group substituent on the reactivity ratio by copolymerize NVP, a hydrophilic monomer with styrene (St), hydroxypropyl methacrylate (HPMA) and carboxyphenyl maleimide (CPMI). The reactivity of NVP with St, HPMA and CPMI during the copolymerization reaction was quantified by estimating the monomer reactivity ratios by both Linear methods such as K-T[18] and EK-T[19] method and the non-linear method; reactivity ratios in error-variable model (RREVM).[20] The reactivity of comonomers was discussed in terms of their electronic delocalization and volume of the side groups. From these parameters, a specific comonomer distribution was postulated to study the effect of chemical structure on reactivity of this kind of functional monomers. The prepared copolymers were characterized by FTIR, ^{1}H NMR, ^{13}C NMR DSC and TGA. Compositions of the copolymers prepared at low conversions were determined by ^{1}H NMR and/or elemental

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analysis. Distribution of the monomer sequences along the copolymer chain was determined by the statistical method based on the reactivity ratios obtained by EK-T method.

Experimental

Materials. Commercial grade samples of NVP, HPMA and 2,2'-azobis isobutyronitrile (AIBN) were all purchased from Aldrich Chemicals, Milwaukee, WI, USA. NVP and HPMA were distilled under vacuum and stored below -5 °C, whereas St was washed with aqueous alkali followed by distilled water and stored below 0 °C. AIBN was recrystallized twice from methanol and dried in vacuum. Maleic anhydride, *p*-aminobenzoic acid, acetic anhydride and other solvents of 99% purity grade were used as received. The monomer CPMI was synthesized using the method reported by Reo, *et al.*.[21]

Synthesis of Copolymer. Copolymerization was carried out in 1,4-dioxane solvent at 70 °C under inert nitrogen atmosphere. Known amounts of monomer M_1, M_2, 0.5% AIBN and 1,4-dioxane were taken in a three-necked 100 mL round bottom flask placed in an oil bath maintained at 70 °C. Copolymerization was continued up to low conversion (less than 10%) and polymerization was ceased by rapid cooling of the reaction mixture to ambient temperature (30 °C). Copolymers of St-NVP and HPMA-NVP were isolated by precipitation in diethyl ether, purified by redissolving and reprecipitating in 1,4-dioxane/diethyl ether mixture. The copolymer CPMI-NVP was then isolated by filtration followed by repeated washings with ethyl acetate and reprecipitation in DMF/ethyl acetate mixture to ensure complete removal of residual monomers. The samples were dried in vacuum at 40 °C until attainment of constant weight. The structure of copolymers were given in Scheme I.

Solubility Studies. Solubility of the polymers was tested in various polar and non-polar organic solvents. To a 5 mL solvent in a standard test tube, about 5-10 mg of polymer was added and kept overnight. The solubility of the polymers was observed after 24 h.

Copolymer Characterization. FTIR spectra of the copolymers were recorded using Shimadzu-1800S spectrometer on KBr pellets in the range of 4000-400 cm⁻¹. The ¹H NMR and ¹³C NMR (Bruker AMX-400, at Indian Institute of Science, Bangalore, India) spectra of the copolymers were
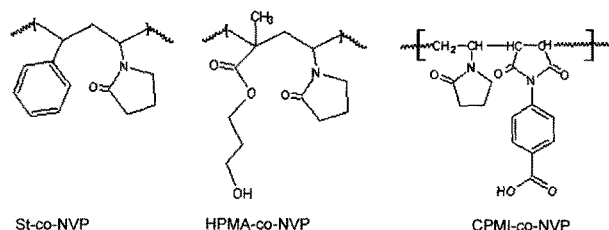
recorded in $CDCl_3$ and deuterated DMSO using tetramethylsilane (TMS) as an internal standard. Mole fraction of the monomers in the copolymer was determined by elemental analysis and/or ¹H NMR. The glass transition temperature (T_g) of the copolymer was analyzed by using a DSC-Mettler Calorimetric system and thermal degradability of the copolymer were studied by TGA using a Perkin-Elmer Thermal analyzer under a stream of nitrogen at a heating rate of 10 °C/min.

Copolymer Composition. Copolymer compositions of St-NVP and HPMA-NVP were determined by elemental analysis by estimating nitrogen content of the copolymers. In case of CPMI-NVP system, both the monomers contain nitrogen and hence, the composition was determined by ¹H NMR spectra by measuring intensities of the chemical shifts produced by the aromatic protons present in CPMI units and methine proton of NVP of the copolymer.

Results and Discussion

Synthesis of Copolymers. Copolymers with different compositions of St-NVP, HPMA-NVP and CPMI-NVP were prepared as per experimental details given in Table I using AIBN initiator in 1,4-dioxane solvent under inert nitrogen atmosphere. The copolymers of St-NVP and HPMA-NVP are soluble in polar solvents like tetrahydrofuran (THF), dimethylsulfoxide (DMSO), dimethyl formamide (DMF), dimethyl acetamide, ethyl acetate, isobutyl acetate, and chloroform and 1,4-dioxane. CPMI-NVP copolymer showed a very limited solubility and is soluble in highly polar solvents like DMSO, DMF and THF, this is due to the presence of rigid imide group in the polymer. All the copolymers were insoluble in nonpolar solvents like *n*-hexane, cyclohexane, carbon tetrachloride, diethyl ether, and benzene.

Copolymer Characterization. Structures of all the copolymers were confirmed by FTIR (Fig. not shown), ¹H NMR (Figure 1) and by ¹³C NMR (Figure 2) spectroscopy. Thermal properties of the copolymer were studied by using DSC and TGA.

Fourier Transform Infrared Spectra (FTIR). The peaks at 1672, 1386 and 1424 cm⁻¹ in St-NVP and HPMA-NVP are due to C=O, C-N-C imide and C-N stretches from NVP unit. In case of St-NVP copolymer, St shows a peak at 3076 cm⁻¹ (aromatic C-H stretch), 2954 and 2879 cm⁻¹ (asymmetric and symmetric C-H stretch), 1561 (aromatic C=C stretch) and 696 cm⁻¹ (aromatic C-H out of plane bending). The peaks at 1146, 1727 and 3100-3400 cm⁻¹ are due to C-O, C=O of the ester and OH stretching, respectively from HPMA-NVP copolymer. In case of CPMI-NVP, the carbonyl absorption of CPMI observed at 1711 cm⁻¹, which is merged with that of NVP at 1682 cm⁻¹ to form a single peak at 1710 cm⁻¹. A shoulder peak at 1776 cm⁻¹ is attributed to symmetric stretching of the carbonyl group in the imide ring. The peaks at
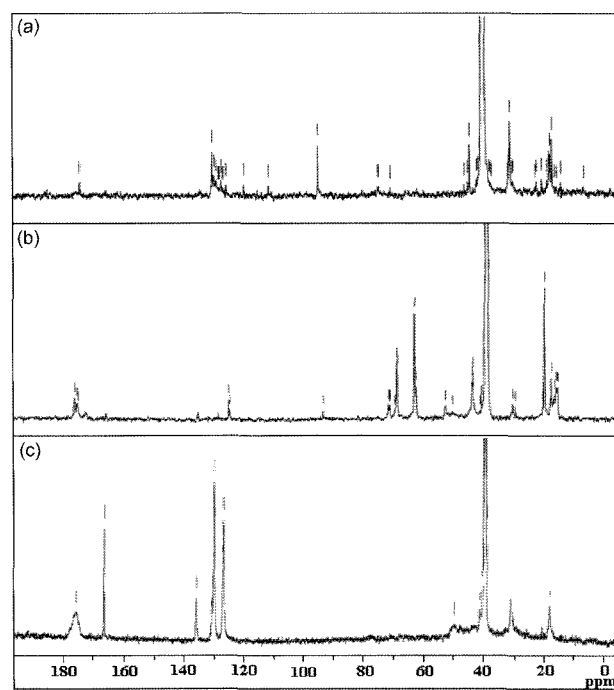

St-co-NVP   HPMA-co-NVP   CPMI-co-NVP

Scheme I. Structure of the copolymers.

Table I. Reaction Conditions for St-NVP, HPMA-NVP and CPMI-NVP Copolymer and Composition from Elemental Analysis/ ¹H NMR Data

Sample Code	M_1 in Feed	% Weight Conversion	N% by Elemental Analysis			m_1 in Copolymer
St-NVP-1	0.10	2.5	9.95			0.29
St-NVP-2	0.30	3.7	2.66			0.81
St-NVP-3	0.50	6.8	1.12			0.92
St-NVP-4	0.70	7.5	0.70			0.95
St-NVP-5	0.90	9.9	0.14			0.99
HPMA-NVP-1	0.10	6.9	11.62			0.17
HPMA-NVP-2	0.30	7.2	7.14			0.49
HPMA-NVP-3	0.50	8.5	4.06			0.71
HPMA-NVP-4	0.70	9.2	2.11			0.85
HPMA-NVP-5	0.90	9.9	0.56			0.96
			Integral Value			
			I_{ArI}	$I_{(CH)NVP}$	C	
CPMI-NVP-1	0.10	8.7	11.18	5.20	2.15	0.349
CPMI-NVP-2	0.30	9.9	7.70	2.15	3.58	0.472
CPMI-NVP-3	0.50	9.5	6.35	1.65	3.84	0.489
CPMI-NVP-4	0.70	3.8	6.99	1.55	4.51	0.530
CPMI-NVP-5	0.90	3.0	7.07	1.23	5.75	0.589

Solvent: 1,4-Dioxane. Temperature: 65 °C. Initiator AIBN: 0.05% based on the total weight of the monomers and solvent.
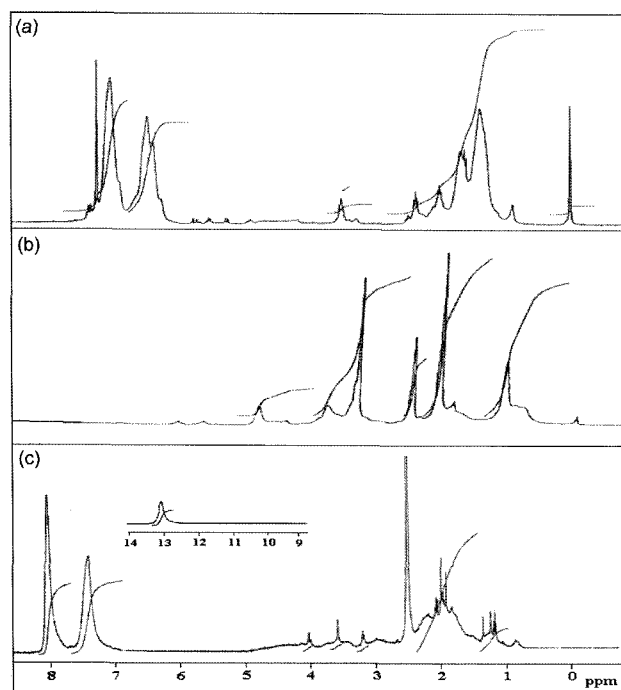
Figure 1. ¹H NMR spectra of (a) St-NVP, (b) HPMA-NVP, and (c) CPMI-NVP copolymer.

Figure 2. ¹³C NMR spectra of (a) St-NVP, (b) HPMA-NVP, and (c) CPMI-NVP copolymer.

1604 and 1513 cm⁻¹ are due to aromatic absorption of CPMI component. A strong absorption at 1385 cm⁻¹ is due to sym-

metric C-N-C stretching of the imide ring of NVP and CPMI components of the copolymer.

Nuclear Magnetic Resonance Spectroscopy (^{1}H NMR δ ppm).

St-NVP in CDCl$_3$: The methine proton in NVP resonates at $\delta = 3.60$, while methylene protons α, β, γ to the carbonyl group of NVP resonate between $\delta = 1.18$-2.28 ppm. In St, the aromatic protons are assigned at $\delta = 7.24$ ppm and methine protons appear at $\delta = 2.79$ ppm.

HPMA-NVP in DMSO d$_6$: Methylene side chain protons of NVP resonate between 1.18 and 2.28 ppm. The methine proton resonates at 3.58 ppm in the NVP unit. Methyl group of HPMA resonates in the range of 0.85-1.35 ppm. The ester group in HPMA resonates at $\delta = 3.90$ and the shift at 4.80 ppm is assigned to OH of HPMA.

CPMI-NVP in DMSO d$_6$: The peak at $\delta = 3.58$ is assigned to methane proton of the NVP unit. The side chain peaks of methylene proton are overlapped with each other and appear between $\delta = 1.18$ and 2.22 ppm in the NVP unit. Aromatic protons of CPMI resonate between $\delta = 7.49$ and 8.14. The peak around $\delta = 13.0$ is due to acidic proton in CPMI.

Nuclear Magnetic Resonance Spectroscopy (^{13}C NMR in DMSO d$_6$ δ ppm).

St-NVP: Aromatic protons of St resonate at 122.12 ppm. Chemical shifts in the range of 17.5-30.14 ppm are due to side chain methylene carbon of NVP. A shift to 172.15 ppm was due to carbonyl carbon of the NVP unit.

HPMA-NVP: The side chain ring and backbone methylene carbons of NVP and HPMA resonate in the range of 30.57-17.86 ppm. The shift at 174.14 ppm is assigned to carbonyl carbons of both NVP and HPMA moieties. Side chain methylene carbons of HPMA are assigned at 65.62-72.23 ppm. Methyl carbon of HPMA resonates at 15.86 ppm.

CPMI-NVP: Broad carbonyl (>C=O) signals of both NVP and CPMI units appear in the range of 173.4-176.8 ppm. The side chain ring of methylene carbon shifts of NVP resonate between 41.43 and 17.86 ppm. Further, the backbone imide carbons of CPMI appear at 49.66 ppm, while the shift around 126.78-135.74 is due to four aromatic carbons of CPMI. Carboxylic carbon resonates at 166.53 ppm.

Monomer Composition. Copolymer composition depends on monomer feed composition as well as relative monomer reactivity. Therefore, it is very important to study the comonomer reactivity in these systems.[15] In St-NVP and HPMA-NVP polymers, composition of the monomer in the copolymer was determined by analyzing N% of the copolymer, which indirectly gave the mole faction of NVP incorporated in the copolymer. The results of elemental analysis and monomer compositions are presented in Table I. In case of CPMI-NVP polymer, both the monomers contain nitrogen and thus, compositions of the monomer were determined by ^{1}H NMR technique. In ^{1}H NMR spectra, the methine proton of NVP and aromatic protons of CPMI are well distinguished; these chemical shift intensities were used to determine the relative mole fraction of both the monomers incorporated in the

copolymer. Assuming m_1 to be the mole fraction of CPMI present in the copolymer chain and $m_2 = (1-m_1)$ that of NVP unit, an equation was derived using the integral values of one methine proton, representing NVP monomer and four aromatic protons, representing CPMI as follows:

$$C = I_{Ar(CPMI)}/I_{CH(NVP)}$$

where $I_{Ar(CPMI)}$ and $I_{CH(NVP)}$ represent intensities of aromatic protons in CPMI and methine proton in NVP, respectively. Table I gives the values of $I_{AR(CPMI)}$, $I_{CH(NVP)}$, C and the corresponding mole fraction of CPMI in the copolymer.

$$C = 4m_1/m_2 = 4m_1/(1-m_1); \quad m_1 = C/4 + C \qquad (2)$$

The plots of mole fraction of St, HPMA and CPMI (M_1) in the feed vs that of mole fraction of St, HPMA and CPMI (m_1) in the copolymer were shown in Figure 4(a, b and c).

In case of St-NVP polymer (Figure 3(a)), a low amount of incorporation of NVP monomer is observed, which is in agreement with the previous report of Huglin, *et al.*,[22] who showed high incorporation of St into the St-NVP copolymer chain. This can be interpreted in terms of the effect of aromatic group of St on its corresponding growing radical chain during the propagation step. Aromatic group induces the electronic delocalization over the radicals, which is more stable than the NVP monomer. Thus, the high incorporation of St in the copolymer is obtained.

When NVP is copolymerized with HPMA (Figure 3(b)), we have observed a greater incorporation of NVP unit compared to St-NVP polymer. In this case, the double bond of HPMA appears to have slightly more positive charge due to the presence of carbonyl ester bond. The charge density generated on carbonyl carbon atom would favor a significant electron attraction in HPMA radicals, which creates a slightly more positive charge on the double bond. Due to electron
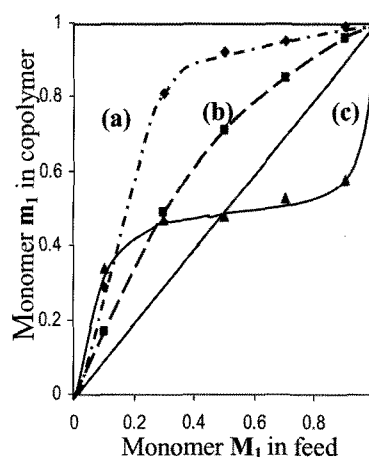

Figure 3. The plots of mole fraction of St, HPMA and CPMI (M_1) in the feed vs that of mole fraction of St, HPMA and CPMI (m_1) in the copolymer. (a) St-NVP, (b) HPMA-NVP and (c) CPMI-NVP copolymer.

deficiency in the double bond of HPMA, the electron-rich NVP is easily involved in copolymerization and hence, higher content of NVP is observed as compared to St-NVP polymer. A similar behavior was observed in our earlier case,[17] wherein NVP was copolymerized with ethoxyethyl methacrylate, which contained similar carbonyl ester bond attached to the double bond. We have found that NVP forms alternates copolymer with CPMI (Figure 3(c)). Here, the presence of two carbonyl and imide groups for each CPMI monomer unit gave rise to a significant attraction of free electron in the double bond and generate a positive charge in the growing polymer chain and stabilization of the corresponding macroradical. Since NVP is electron rich, it forms the bond easily with electron deficient species, thus it easily involved in polymerization. Hence, we have observed a higher content of NVP when copolymerized with CPMI than in St and HPMA copolymers.

Reactivity Ratios. The type of copolymer formed can be best understood from the data of reactivity ratios of the copolymers. Copolymerization reactivity ratios of St, HPMA and CPMI with NVP were determined by K-T, EK-T and RREVM methods using the data obtained by elemental analysis and ^{1}H NMR. Table II shows the comparision of reactivity ratios of the monomers.

Using the RREVM values presented in Table II as a reference, St shows a trend to form blocks in St-NVP polymer, where the reactivity ratio of St is much higher than unity (r_{St} =10.52). The high value obtained for St can be interpreted in terms of the stabilization by the resonance of St radicals. A similar behavior is shown by HPMA monomer, which is having a reactivity higher than unity (r_1=2.63) in HPMA-NVP polymer. Here, the electronic stabilization effect exerted by the carbonyl group of ester adjoined to carbon carrying the radical electron on HPMA radical in the propagation step explains higher reactivity of HPMA than NVP. Both St-NVP and HPMA-NVP polymers have the r_1r_2 values greater than unity, indicating the random distribution with the formation of small blocks richer in one of the monomers.

When the two monomers have the reactivity ratios equal to zero, the corresponding copolymer shows an alternating comonomer distribution.[23] Each monomer suffers a cross

Table II. Monomer Reactivity Ratios for (St-NVP), (HPMA-NVP) and (CPMI-NVP) Copolymer

Copolymer	Method	r_1	r_2 (NVP)	r_1r_2
(St-NVP)	KT	10.31±1.04	0.14±0.02	1.40
	E-KT	11.66±1.50	0.29±0.03	3.33
	RREVM	10.52±0.91	0.20±0.06	2.10
(HPMA-NVP)	KT	2.43±0.34	0.54±0.03	1.32
	E-KT	2.80±0.50	0.55±0.05	1.54
	RREVM	2.63±0.15	0.56±0.03	1.47
(CPMI-NVP)	KT	0.06±0.02	0.086±0.10	0.005
	E-KT	0.06±0.09	0.08±0.05	0.004
	RREVM	0.05±0.05	0.07±0.05	0.003

propagation (i.e., in a growing macroradical, each time one monomer prefers to react with a molecule of other monomer) permits its classification as a copolymer with a high tendency to alternation. In case of CPMI-NVP polymer, the monomer reactivity ratios of both NVP (0.07) and CPMI (0.05) are less than unity and closer to zero, indicating that a monomer in a growing chain prefers to react with other monomer than itself. Hence, we have observed nearly an equal amount of NVP and CPMI incorporation into the copolymer. A similar behavior was observed earlier by Gatica, *et al.*.[24] when NVP was copolymerized with electron deficient vinyl trichlorosilane (VTCS) monomers ($r_{VP} = 0.0$ and $r_{VTCS} = 0.3$).

Copolymer Microstructure. Statistical distributions of the monomer sequences 1-1, 2-2 and 1-2 are calculated using the following relations:[25]

$$S_{1-1} = m_1 - \frac{2m_1m_2}{1+[(2m_1-1)^2+4r_1r_2m_1m_2]^{1/2}} \tag{3}$$

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

$$S_{1-2} = \frac{4m_1m_2}{1+[(2m_1-1)^2+4r_1r_2m_1m_2]^{1/2}} \tag{5}$$

where r_1 and r_2 are the reactivity ratios obtained by EK-T method; m_1 (St or HPMA or CPMI) and m_2 (NVP) are mole fractions in the copolymer. The mole fractions of 1-1, 2-2 and 1-2 sequences are shown by S_{1-1}, S_{2-2} and S_{1-2}, respectively. Structural data are given in Table III. The mole fraction of 1-1 sequences increases as the mole fraction of St or HPMA increases, indicating a higher reactivity and higher incorporation of St or HPMA in the respective copolymers. In case of CPMI-NVP polymer, 1-1 and 2-2 sequences of the monomer shows nearly a constant value with increasing amount of both the monomers. On the other hand, the 1-2 sequence is nearly tending to unity, which indicates both the monomer preference to react with other monomer in the growing chain.

Thermal Properties. The glass transition temperature of the copolymers were determined by DSC under nitrogen atmosphere. The homopolymer of polyNVP showed the glass transition temperature around 148 °C, whereas St-NVP-3 and HPMA-NVP-3 the T_g value observed around 102 °C and 73 °C respectively, and no T_g was observed in case of CPMI-NVP copolymers till starts degradation. It is found that by increasing the amount St or HPMA content in the copolymers result in decreased T_g, the effect is more in case of HPMA-NVP copolymer because of presence of propyl group in HPMA side chain, which significantly lowers the T_g value. The thermal stabilities of all types of copolymers were determined by means of thermogravimetric measurements recorded in nitrogen atmosphere and are presented in Figures 4. It is evident that all the copolymers decompose by a one-stage mechanism.

Table III. Structural Data for the Copolymer St-NVP, HPMA-NVP and CPMI-NVP

Sample Code	Composition[a] (mole fraction)		Blockiness[b] (mole fraction)		Alternation[b] (mole fraction)
	M_1	M_2	S_{1-1}	S_{2-2}	S_{1-2}
St-NVP-1	0.29	0.71	0.138	0.558	0.304
St-NVP-2	0.81	0.19	0.335	0.438	0.227
St-NVP-3	0.92	0.08	0.556	0.316	0.128
St-NVP-4	0.95	0.05	0.730	0.184	0.086
St-NVP-5	0.99	0.01	0.922	0.059	0.019
HPMA-NVP-1	0.17	0.83	0.038	0.302	0.660
HPMA-NVP-2	0.49	0.51	0.316	0.265	0.419
HPMA-NVP-3	0.71	0.29	0.455	0.041	0.504
HPMA-NVP-4	0.85	0.15	0.730	0.035	0.235
HPMA-NVP-5	0.96	0.04	0.923	0.004	0.073
CPMI-NVP-1	0.35	0.65	0.002	0.302	0.696
CPMI-NVP-2	0.47	0.53	0.013	0.067	0.920
CPMI-NVP-3	0.49	0.51	0.021	0.042	0.937
CPMI-NVP-4	0.53	0.47	0.092	0.032	0.876
CPMI-NVP-5	0.59	0.41	0.174	0.014	0.812

[a]From elemental analysis data from elemental analysis data. [b]Statistically calculated using reactivity ratios.
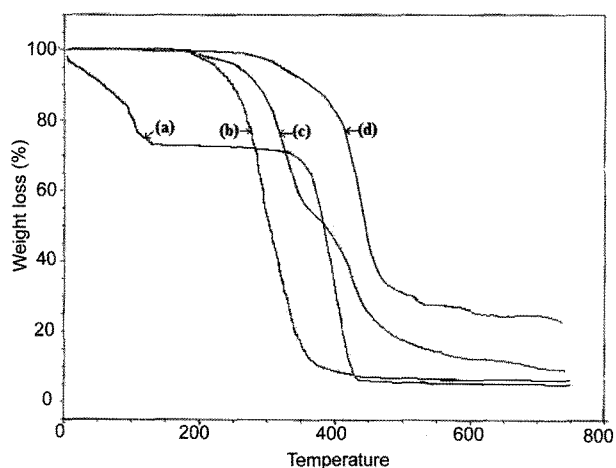

Figure 4. TGA Thermogram of (a) PolyNVP, (b) HPMA-NVP-2 copolymer, (c) St-NVP-2 copolymer, (d) CPMI-NVP-2 copolymer.

As expected, the CPMI-NVP copolymer shown better heat resistant property because of presence of rigid imide group in the backbone, 10% weight loss was observed at around 358 °C which is much higher than polyNVP, St-NVP and HPMA-NVP copolymer. 50% weight loss and residual at 500 °C is given in the Table IV indicates superior thermal properties of the CPMI-NVP copolymers. It's also observed that the % weight loss was decrease against the temperature by increasing amount of CPMI in CPMI-NVP copolymer. The presence aliphatic chain in HPMA-NVP

Table IV. Structural Data for the Copolymer St-NVP, HPMA-NVP and CPMI-NVP

Samples	T_g (°C)	$T_{10\%}$ (°C)	$T_{50\%}$ (°C)	Residual at 500 °C (wt%)
PolyNVP	148	-	403	4
St-NVP-2	107	282	385	16
HPMA-NVP-2	73	263	310	5
CPMI-NVP-2	-	358	448	30

copolymer makes it less thermal resistant which decomposes faster than rest of the copolymers.

Conclusions

Different copolymers were synthesized by free radical polymerization and were characterized by FTIR, ^{1}H NMR and ^{13}C NMR. DSC and TGA data suggest the superior thermal properties of the CPMI-NVP copolymer. The MRR values were obtained for the copolymers using K-T, EK-T and RREVM methods and a good agreement was observed between the different methods. RREVM procedure estimated the values: r_{St}=10.52±0.91 and r_{NVP}=0.20±0.06 (for St-NVP), r_{HPMA}=2.63±0.15 and r_{NVP}=0.56±0.03 (for HPMA-NVP), and r_{CPMI}=0.05±0.05 and r_{NVP}=0.07±0.05 (for CPMI-NVP). The MRR values indicated the presence of zones with a high concentration of St units in the St-NVP polymer, which was interpreted in terms of St block formation. This

copolymer contains some units of NVP in between the blocks of St, to a lesser extent and similarly for HPMA-NVP polymer. In the case of CPMI-NVP polymer, a tendency to form alternating copolymers was observed, as confirmed by determining the sequence distribution of monomers by a statistical method. However, reactivity of the monomer depended on its strength and nature of functional groups present.

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