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Radical copolymerization of 2-vinyl pyridine with functional methacrylates: Monomer reactivity ratios and thermal properties

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ABSTRACT

Statistical copolymers of *2*-vinylpyridine (VP) with 2-diethyl amino ethyl methacrylate (DEAEMA), di (ethylene glycol) methyl ether methacrylate (DEGMA), and 2-butoxyethyl methacrylate (BuOEMA) were prepared by free radical copolymerization. The reactivity ratios of every set of monomers were estimated using the Finemann-Ross, the inverted Finemann-Ross and the Kelen-Tüdos graphical methods. Structural parameters of the copolymers were obtained by calculating the dyad monomer sequence fractions and the mean sequence length. The effect of the chemical nature of the methacrylates on the copolymerization characteristics is discussed. The glass-transition temperature (T_g) values of the VP copolymers with DEAEMA, DEGMA, and BuOEMA were measured and examined by means of several theoretical equations, allowing for the prediction of these T_g values.

KEYWORDS

Statistical copolymers;
Reactivity ratios;
2-Vinylpyridine;
Functional methacrylates;
Thermal analysis.

INTRODUCTION

Functional polymers impact many aspects of polymer science and technology[1]. These macromolecules contain functional groups that have polarity or reactivity differences from backbone chains. Such polymers often show unusual or improved properties by virtue of enhancement in phase separation, reactivity or association. When the formation or dissociation of self-assemblies is triggered by chemical or physical stimuli so called “smart” materials can be obtained[2].

Functional polymers are produced either by chemical modification of preformed nonfunctional polymers or by direct copolymerization of the functional monomers with desired physicochemical properties[1a,3]. In this respect, radical copolymerization of vinyl monomers is very important in determining their structure-property relationship.

Copolymerization is the most successful and powerful method for effecting systematic changes in polymer properties[4]. The incorporation of two different monomers, with diverse physical and/or chemical properties, in the same polymer molecule in varying proportions leads to the formation of new materials with great scientific and commercial importance[5]. The chemical composition of the copolymers depends on the degree of incorporation of the comonomers and the relative reactivity between them. Monomer reactivity ratios are very important parameters for the elucidation of copolymer structure (copolymer composition, monomer sequence distribution) and kinetics (propagation rate coefficients)[6]. The elucidation of copolymer structure (copolymer composition, monomer sequence distribution) and kinetics (propagation rate coefficients) are the major concerns for the prediction of copolymer properties and the correlation between structure and properties.

Copolymerization modulates both the intramolecular and intermolecular forces acting on like and unlike polymer segments and consequently properties such as glass transition temperature, melting point, solubility, crystallinity, permeability, dyeability, adhesion, elasticity and chemical reactivity may vary significantly[7].

Among the various copolymerization reactions, radical copolymerization is the most important since it does not demand rigorous experimental conditions and can be applied to a large variety of monomers, leading to the formation of new materials[8].

In our continuing effort to explore the structure-property relationship exhibited by vinyl monomers[9], in the present study we focus on the radical copolymerization of 2-vinylpyridine (VP) with 2-diethyl amino ethyl methacrylate (DEAEMA), di (ethylene glycol) methyl ether methacrylate (DEGMA), and 2-butoxyethyl methacrylate (BuOEMA). Poly (2-diethyl amino ethyl methacrylate) (PDEAEMA) is insoluble in aqueous solutions at neutral pH. However, it readily dissolves in acidic solutions due to protonation of the tertiary amine residues (pKa=6.9)[10]. Poly[di (ethylene glycol) methyl ether methacrylate] (PDEGMA) is water soluble and thermoresponsive, with a lower critical solution temperature, LCST, equal to 26°C[11]. The LCST can be modulated by copolymerization with other oligo (ethylene glycol) methacrylates. Finally, poly (2-butoxyethyl methacrylate) (PBuOEMA) is not water soluble due to the replacement of one of the oxygen atoms of the ester group with a hydrocarbon moiety. Therefore, these copolymers can be considered as stimuli-responsive polymers, since their properties can be triggered by changes in temperature and pH in aqueous solutions.

EXPERIMENTAL SECTION

Materials

All manipulations were performed using high-vacuum techniques. VP and all three methacrylates: DEAEMA, DEGMA and BuOEMA were purchased from Aldrich. The monomers were vacuum-distilled from calcium hydride in the vacuum line, in order to remove antioxidant inhibitors and humidity and were stored under vacuum at -20°C until polymerization. 2,2'-Azobisisobutyronitrile, AIBN, was purchased from Aldrich. It was recrystallized twice from methanol, filtered and dried under vacuum.

Copolymerization studies

In order to study the copolymerization of VP with DEAEMA, DEGMA and BuOEMA a set of five experiments was conducted for each monomer pair (VP-DEAEMA, VP-DEGMA, VP-BuOEMA). Different feed ratios were employed each time (monomer molar ratios: 20/80, 40/60, 50/50, 60/40 and 80/20), and the copolymerization reactions were quenched at low (<10%) yields. The copolymerization procedure was monitored by size exclusion chromatography, SEC, and UV spectroscopy. The experimental results were processed on the basis of the Finemann-Ross (FR), Inverted Finemann-Ross (IFR) and Kelen-Tüdos (KL) equations.

Copolymerization of VP with DEAEMA or DEGMA

The copolymerization reactions were performed in glass reactors in bulk. AIBN in the concentration of 0.1% wt was the initiator. The mixtures were degassed under high vacuum using three freeze-thaw cycles and the reactors were flame-sealed. The copolymerizations were conducted at 50°C for 6hr. The copolymers were precipitated in methanol, left at -20°C overnight for complete precipitation, filtered, dried, redissolved in chloroform and reprecipitated in methanol once more. The same procedure was repeated as many times as necessary in order to remove all remaining quantities of VP, DEAEMA or DEGMA that were not copolymerized, since these monomers are soluble in methanol. Finally, the copolymers were dried overnight in a vacuum oven.

Copolymerization of VP with BuOEMA

The copolymerizations were performed in glass reactors in bulk, with AIBN in the concentration of 0.1% wt as the initiator, as already described above. The solutions were degassed under high vacuum using three freeze-thaw cycles and the reactors were flame-sealed. In this case, the copolymerizations were conducted at 50°C for three hours. Finally, the copolymer along with the monomer excess was precipitated in heptanes, dried and dissolved again in few mLs of tetrahydrofuran. The excess of VP and BuOEMA was removed by continuous precipitations in heptanes and the pure copolymers were finally dried in a vacuum oven overnight.

Characterization techniques

Size Exclusion Chromatography (SEC) experiments were carried out at 40^{0}C using a modular instrument consisting of a Waters model 510 pump, U6K sample injector, 401 refractometer, 486 UV spectrophotometer, and a set of five μ-Styragel columns with a continuous porosity range from 500 to 10^6 Å. The columns were housed in an oven thermostatted at 40^{0}C. $CHCl_3$ was the carrier solvent at a flow rate of 1 mL/min. The system was calibrated with nine PS standards having molecular weights in the range of 970–600,000.

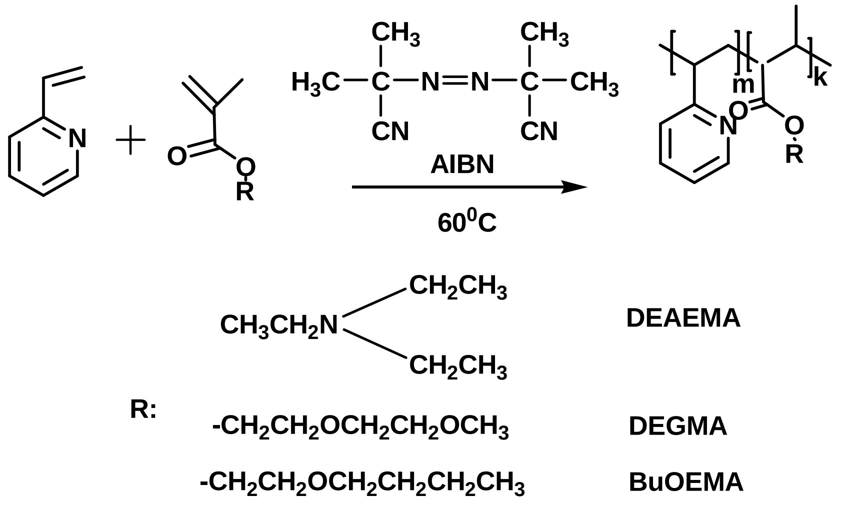
The copolymer compositions were determined by UV analysis using a Lambda 650 Perkin Elmer model UV-Vis spectrophotometer. A calibration curve was constructed using a PVP sample prepared by anionic polymerization (M_w=35,000, M_w/M_n=1.03) and measuring the absorbance at 252 nm.

The glass-transition temperatures were obtained by differential scanning calorimetry (DSC) using a 2910 modulated DSC model from TA instruments. The samples were heated or cooled at a rate of 10^{0}C/min. The second heating results were obtained in all cases.

RESULTS AND DISCUSSION

Statistical copolymers of VP with DEAEMA, DEGMA, and BuOEMA

The free radical copolymerization of VP with functional methacrylates was conducted using AIBN as the initiator (Scheme 1). The copolymerizations were conducted in bulk and the conversion was, in all cases, lower than 10%, satisfying the differential copolymerization equation. The copolymers with DEAEMA and DEGMA were purified by repeated precipitations in methanol, where all three monomers, VP, DEAEMA and DEGMA are soluble. On the other hand, the copolymers with BuOEMA, were purified by repeated precipitations in heptanes. The molecular characteristics of the samples are given in TABLE 1. The molecular weights were measured by SEC using a calibration curve constructed by polystyrene standards. UV analysis at 252 nm, where only PVP has an absorbance band, was employed to measure the composition of the copolymers. Different copolymers are symbolized by the various feed molar ratios of the monomers, e.g. sample VP-DEAEMA 20/80 indicates the PVP-*co*-PDEAEMA copolymer for the synthesis of which 20% VP and 80% DEAEMA was employed as the molar feed composition.



Scheme 1 : Synthesis of the statistical copolymers

Monomer reactivity ratios and statistical analysis of the copolymers

The monomer reactivity ratios were determined using the Finemann-Ross (FR)[12], the inverted Finemann-Ross (IFR)[12] and the Kelen-Tüdos (KT)[13] graphical methods. According to the Finemann-Ross method, the monomer reactivity ratios can be obtained by the equation:

$$G=Hr_{VP}-r_A \quad (1)$$

where, A refers to the comonomers DEAEMA, DEGMA or BuOEMA and the reactivity ratios, r_{VP} and r_A correspond to the VP and DEGMA, DEAEMA or BuOEMA monomers, respectively.

The parameters G and H are defined as follows:

$$G=X(Y-1)/Y \text{ and } H=X^2/Y \quad (2)$$

with $X=M_{VP}/M_A$ and $Y=dM_{VP}/dM_A$ (3)

M_{VP} and M_A are the monomer molar compositions in feed and dM_{VP} and dM_A the copolymer molar compositions.

The inverted Finemann-Ross method is based on the equation:

$$G/H=r_{VP}-(1/H)r_A \quad (4)$$

The plots of the G versus H values and the G/H versus 1/H values yield the reactivity ratios r_{VP} and r_A from the intercept and the slope of the graphs.

Alternatively the reactivity ratios can be obtained using the Kelen-Tüdos method which is based on the equation:

$$\eta=(r_{VP}+r_A/\alpha)\xi-r_A/\alpha \quad (5)$$

where η and ξ are functions of the parameters G and H:

$$\eta=G/(\alpha+H) \text{ and } \xi=H/(\alpha+H) \quad (6)$$

and α a constant which is equal to $(H_{max}H_{min})^{1/2}$, H_{max}, H_{min} being the maximum and the minimum H values, respectively from the series of measurements. From the linear plot of η as a function of ξ the values of η for ξ=0 and ξ=1 are used to calculate the reactivity ratios according to the equations:

$$\xi=0 \Rightarrow \eta=-r_M/\alpha \text{ and } \xi=1 \Rightarrow \eta=r_S \quad (7)$$

The copolymerization data for all systems are provided in TABLE 2. The graphical plots concerning the methods previously reported are given in Figures 1-3, whereas the reactivity ratios are summarized in TABLE 3.

The plots were linear in all cases and for all graphical methods, thus indicating that these copolymerizations follow the conventional copolymerization kinetics and that the reactivity of a polymer radical is determined only by the terminal monomer unit.

According to the data obtained by the Kelen-Tüdos method, r_{VP}=0.95 and r_{DEAEMA}=0.85 for the statistical copolymers P (VP-*co*-DEAEMA). This result implies that the homopolymerization of the two monomers is not favored, or in other words that there is a tendency for the production of an alternating copolymer. However, the probability for the incorporation of VP units is slightly greater than for the incorporation of DEAEMA units ($r_{VP}>r_{DEAEMA}$). This kind of copolymerization is characterized as nonideal azeotropic[8,14].

A different situation was obtained for the other copolymers. The Kelen-Tüdos method revealed that for both cases $r_{VP}>1$ and $r_A<1$. Specifically, r_{VP}=1.57 and r_{DEGMA}=0.92 for the statistical copolymers P (VP-*co*-DEGMA), and r_{VP}=3.04 and r_{BuOEMA}=0.48 for the

TABLE 1 : Molecular characteristics of the statistical copolymers.

Sample	$^aM_n \times 10^{-3}$	$^aI=M_w/M_n$	Conversion %
VP-DEAEMA 20/80	494.0	1.64	7.7
VP-DEAEMA 40/60	149.0	1.28	3.5
VP- DEAEMA 50/50	201.3	1.33	3.9
VP-DEAEMA 60/40	305.0	1.32	6.1
VP-DEAEMA 80/20	254.6	1.29	4.1
VP-DEGMA 20/80	1078.0	1.34	6.8
VP- DEGMA 40/60	1358.0	1.43	6.7
VP-DEGMA 50/50	1182.0	1.41	10.4
VP-DEGMA 60/40	1091.0	1.39	8.6
VP-DEGMA 80/20	695.0	1.36	6.7
VP-BuOEMA 20/80	83.5	1.36	3.7
VP-BuOEMA 40/60	77.2	1.39	3.9
VP-BuOEMA 50/50	65.8	1.73	3.4
VP-BuOEMA 60/40	65.3	1.34	5.9
VP-BuOEMA 80/20	78.4	1.37	3.5

^{a}by SEC in $CHCl_3$

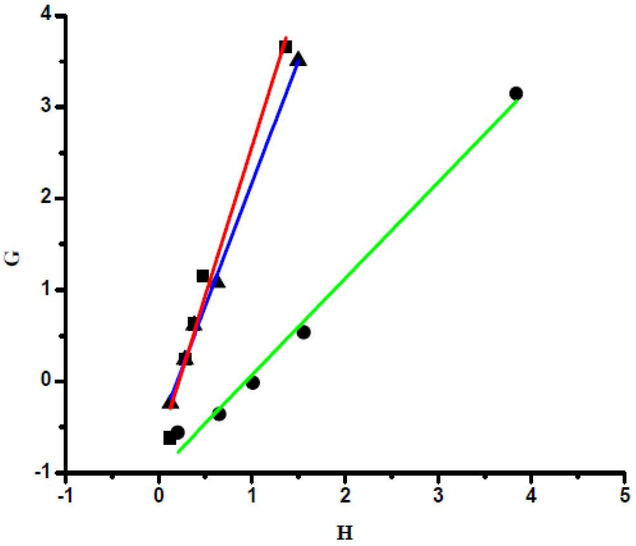


Figure 1 : FR plots of the VP-DEAEMA (●), VP-DEGMA (▲) and VP-BuOEMA (■) statistical copolymers.

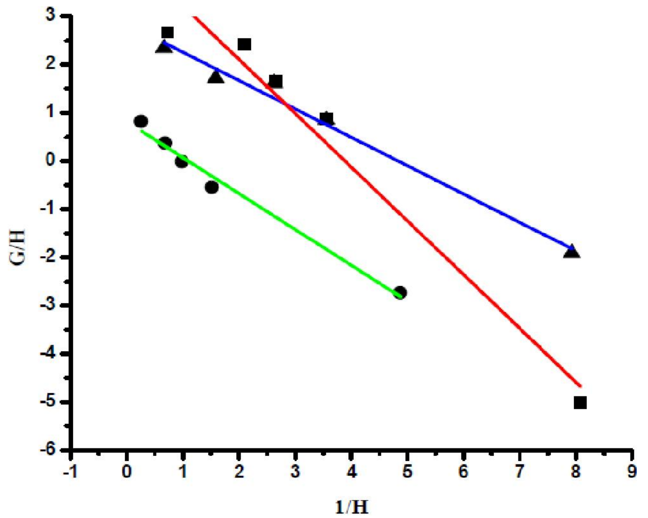


Figure 2 : IFR plots of the VP-DEAEMA (•), VP-DEGMA (▲) and VP-BuOEMA (■) statistical copolymers.

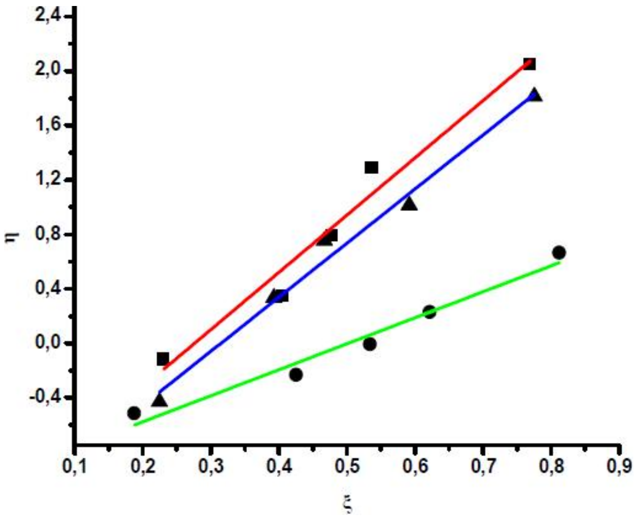


Figure 3 : KT plots of the VP-DEAEMA (•), VP-DEGMA (▲) and VP-BuOEMA (■) statistical copolymers.

TABLE 2 : Copolymerization data for the statistical copolymers.

Sample	M_{VP}	dM_{VP}	X	Y	G	H	1/H	G/H	η	ξ
VP-DEAEMA 20/80	0.201128	0.2360	0.25177	0.30890	-0.56328	0.2052	4.87330	-2.74504	-0.51540	0.18775
VP-DEAEMA 40/60	0.394290	0.3916	0.65096	0.64366	-0.36038	0.6583	1.51910	-0.54744	-0.23310	0.42580
VP- DEAEMA 50/50	0.500175	0.4960	1.00070	0.98413	-0.01587	1.0176	0.98270	-0.01560	-0.00833	0.53410
VP-DEAEMA 60/40	0.599528	0.6055	1.49706	1.53485	0.53485	1.5602	0.68484	0.36628	0.22780	0.62190
VP-DEAEMA 80/20	0.803330	0.8129	4.08487	4.34474	3.14468	3.8405	0.26038	0.81882	0.66509	0.81225
α= 0.8877										
VP-DEGMA 20/80	0.202760	0.3389	0.2543	0.51263	-0.24176	0.12615	7.9271	-1.91645	-0.43081	0.224794
VP- DEGMA 40/60	0.398917	0.6102	0.6636	1.56542	0.239688	0.28131	3.55479	0.85204	0.3346	0.392704
VP-DEGMA 50/50	0.499299	0.7228	0.9972	2.60750	0.61476	0.38136	2.62219	1.61202	0.75302	0.46713
VP-DEGMA 60/40	0.600141	0.7813	1.5008	3.57247	1.080698	0.63049	1.58607	1.71406	1.01424	0.59172
VP-DEGMA 80/20	0.795696	0.9100	3.8947	10.1110	3.509505	1.50022	0.66657	2.3393	1.81347	0.77521
α=0.4350										
VP-BuOEMA 20/80	0.243665	0.4560	0.3222	0.8382	-0.6222	0.1238	8.0762	-5.0258	-0.11604	0.23109
VP-BuOEMA 40/60	0.399168	0.6115	0.6644	1.5740	0.2423	0.2804	3.5662	0.8641	0.34992	0.40500
VP-BuOEMA 50/50	0.500525	0.7273	1.0021	2.6670	0.6263	0.3765	2.6558	1.6635	0.79438	0.47752
VP-BuOEMA 60/40	0.595634	0.8196	1.4730	4.5432	1.1487	0.4776	2.0939	2.4056	1.29142	0.53688
VP-BuOEMA 80/20	0.799790	0.9209	3.9948	11.6422	3.6513	1.3707	0.7296	2.6638	2.04839	0.76890
α=0.4120										

statistical copolymers P (VP-*co*-BuOEMA). These results imply that the homopolymerization of VP is favored over the homopolymerization of the corresponding methacrylate monomers. This case is referred as a nonideal nonazeotropic copolymerization[8,14]. It is not very common in free radical polymerization to have $r_1>1$ and $r_2<1$ and at the same time $r_1.r_2>1$, as confirmed for both systems. However, similar results have been previously reported in the literature[15] and have been attributed to specific interactions called the "bootstrap effect"[16]. This effect may arise from the formation of radical-solvent and monomer-solvent complexes, which do not propagate, thus altering the effective radical or monomer concentration. In the present case, the copolymerization was conducted in bulk, and thus radical-monomer complexes may be responsible for this behavior. Alternatively, the bootstrap effect can be attributed to some bulk preferential sorption of one of the comonomers around the growing polymer chains. It is surprising that such a small change in the chemical struc-

TABLE 3 : Reactivity ratios of the statistical copolymers.

r_{VP}	r_A, A: DEGMA/DEAEMA/ BuOEMA/OEGMA	$r_{VP} \cdot r_A$
VP-DEAEMA		
FR 1.05	0.97	1.02
IFR 0.92	0.75	0.69
KT 0.95	0.85	0.81
VP-DEGMA		
FR 1.52	0.88	1.34
IFR 1.68	0.99	1.66
KT 1.57	0.92	1.44
VP-BuOEMA		
FR 3.02	0.48	1.45
IFR 2.94	0.44	1.29
KT 3.04	0.48	1.46
VP-OEGMA$_{300}$		
FR 0.99	0.16	0.159
IFR 1.13	0.25	0.282
KT 1.08	0.23	0.248
VP-OEGMA$_{1100}$		
FR 1.25	0.13	0.162
IFR 1.15	0.08	0.092
KT 1.20	0.10	0.120

ture of the comonomer (DEGMA instead of BuOEMA) can cause an appreciable change in the copolymerization behavior. It seems that the presence of more oxygen atoms at the side group of DEGMA leads to more stable complexes with VP, thus indirectly increasing the reactivity of the methacrylate monomer compared to BuOEMA.

The results obtained from the P (VP-*co*-DEGMA) copolymers can be compared with those obtained by the free radical copolymerization of VP with oligo[(ethylene glycol) methyl ether methacrylates], $H_2C{=}C\ (CH_3)COO\text{-}(CH_2CH_2O)_nCH_3$ OEGMA$_{300}$ and OEGMA$_{1100}$, with number average molecular weights 300g/mol (n=5) and 1100g/mol (n=23).[9e] For DEGMA n=2. Oligo[(ethylene glycol) methacrylates] represent a very interesting family of monomers, since they are biocompatible and thermoresponsible materials and their solubility in aqueous solutions increases upon increasing the size of the ethylene glycol group.[11] The members of this family bearing longer ethylene glycol chains can be considered as macromonomers bearing a methacrylate end-group. The reactivity ratios of VP and OEGMA$_{300}$ or OEGMA$_{1100}$ are given in TABLE 3. It is obvious that the r_{OEGMA} and the $r_{VP}.r_{OEGMA}$ values (Figure 4) decrease substantially upon increasing the ethylene glycol chain length. This result is in agreement with the reported data regarding the copolymerization behavior of styrene with similar OEGMA monomers[17]. The difference in reactivity of the two methacrylate monomers can be treated considering the reduced reactivity of macromonomers upon increasing their molecular weight.

The statistical distribution of the dyad monomer sequences M_{VP}-M_{VP}, M_A-M_A and M_{VP}-M_A were calculated using the method proposed by Igarashi[18]:

$$X = \phi_{VP} - \frac{2\phi_{VP}(1-\phi_{VP})}{1+\left[(2\phi_{VP}-1)^2+4r_{VP}r_A\phi_{VP}(1-\phi_{VP})\right]^{1/2}} \quad (8)$$

$$Y = (1-\phi_{VP}) - \frac{2\phi_{VP}(1-\phi_{VP})}{1+\left[(2\phi_{VP}-1)^2+4r_{VP}r_A\phi_{VP}(1-\phi_{VP})\right]^{1/2}} \quad (9)$$

$$Z = \frac{4\phi_{VP}(1-\phi_{VP})}{1+\left[(2\phi_{VP}-1)^2+4r_{VP}r_A\phi_S(1-\phi_{VP})\right]^{1/2}} \quad (10)$$

where X, Y and Z are the mole fractions of the M_{VP}-M_{VP}, M_A-M_A and M_{VP}-M_A dyads in the copolymer, respectively, and j_{VP} the VP mole fraction in the copolymer. Mean sequence lengths μ_{VP} and μ_A were also calculated using the following equations[19]:

$$\mu_{VP} = 1 + r_{VP}\frac{[M_{VP}]}{[M_A]} \quad (11)$$

$$\mu_A = 1 + r_A\frac{[M_A]}{[M_{VP}]} \quad (12)$$

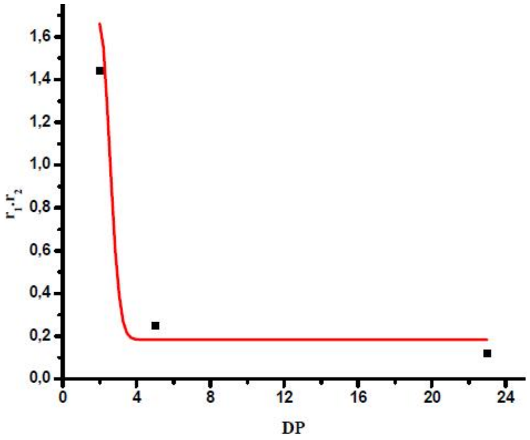


Figure 4 : Reactivity ratios product r_1r_2 vs the degree of polymerization (DP) of the side oligo (ethylene glycol) ester group for the copolymers VP-DEGMA (DP=2), VP-OEGMA$_{300}$ (DP=5) and VP-OEGMA$_{1100}$ (DP=23). The red line serves as a guide.

The data are summarized in TABLE 4, whereas the variation of the dyad fractions with the VP mole fraction in the copolymers is displayed in Figures 5, 6 and 7.

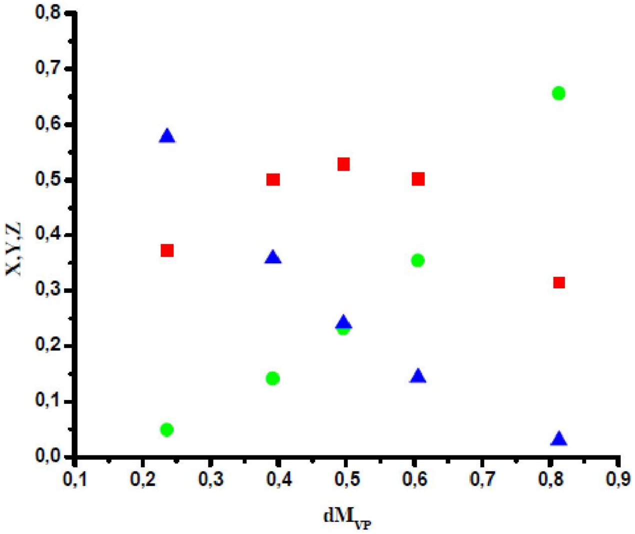


Figure 5 : Dyad monomer sequence fractions vs the VP mole fraction for the VP-DEAEMA copolymers: $X=M_{VP}-M_{VP}$ (●), $Y=M_{DEAEMA}-M_{DEAEMA}$ (▲) and $Z=M_{VP}-M_{DEAEMA}$ (■) dyads, calculated using equations (8)-(10).

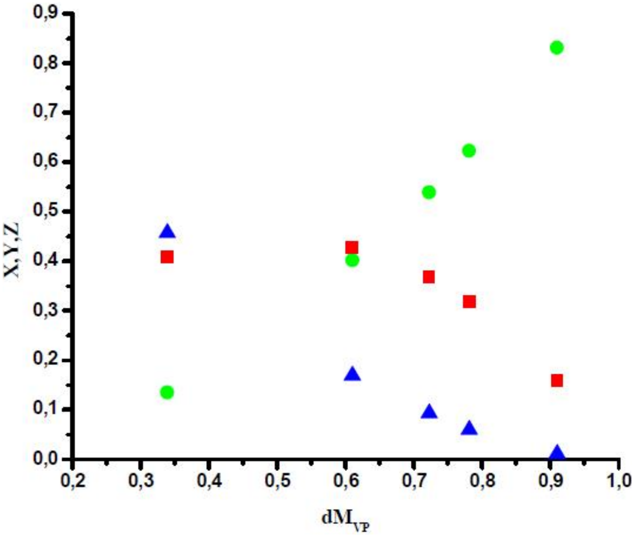


Figure 6 : Dyad monomer sequence fractions vs the VP mole fraction for the VP-DEGMA copolymers: $X=M_{VP}-M_{VP}$ (●), $Y=M_{DEGMA}-M_{DEGMA}$ (▲) and $Z=M_{VP}-M_{DEGMA}$ (■) dyads, calculated using equations (8)-(10).

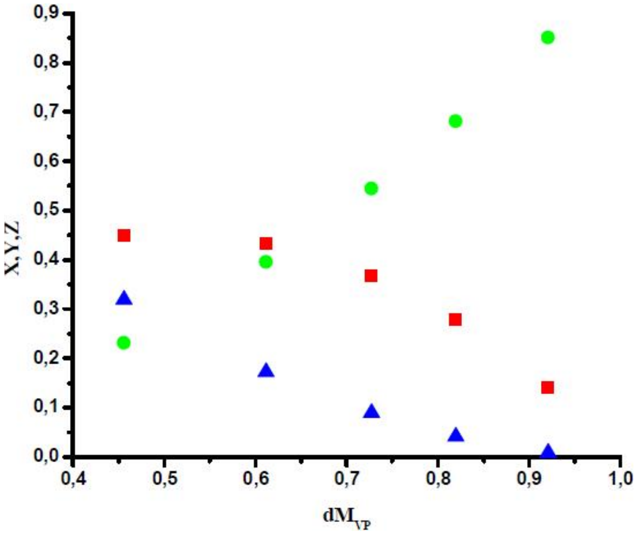


Figure 7 : Dyad monomer sequence fractions vs the VP mole fraction for the VP-BuOEMA copolymers: $X=M_{VP}-M_{VP}$ (●), $Y=M_{DEAEMA}-M_{BuOEMA}$ (▲) and $Z=M_{VP}-M_{BuOEMA}$ (■) dyads, calculated using equations (8)-(10).

TABLE 4 : Structural data for the statistical copolymers.

Sample	X	Y	Z	μ_{vp}	μ_A
VP-DEAEMA 20/80	0.0488	0.5768	0.3744	1.24	4.38
VP-DEAEMA 40/60	0.1410	0.3578	0.5011	1.62	2.30
VP- DEAEMA 50/50	0.2324	0.2403	0.5273	1.95	1.85
VP-DEAEMA 60/40	0.3542	0.1432	0.5026	2.42	1.57
VP-DEAEMA 80/20	0.6560	0.0302	0.3139	4.88	1.21
VP-DEGMA 20/80	0.1350	0.4572	0.4079	1.40	4.62
VP- DEGMA 40/60	0.4019	0.1695	0.4286	2.04	2.39
VP-DEGMA 50/50	0.5388	0.0932	0.3679	2.56	1.92
VP-DEGMA 60/40	0.6226	0.0600	0.3174	3.36	1.61
VP-DEGMA 80/20	0.8311	0.0111	0.1578	7.11	1.24
VP-BuOEMA 20/80	0.2312	0.3192	0.4497	1.98	2.49
VP-BuOEMA 40/60	0.3954	0.1724	0.4322	3.02	1.72
VP-BuOEMA 50/50	0.5443	0.0897	0.3659	4.05	1.48
VP-BuOEMA 60/40	0.6806	0.0414	0.2780	5.48	1.32
VP-BuOEMA 80/20	0.8503	0.0085	0.1411	13.14	1.12

Thermal properties of the statistical copolymers

The thermal properties of the copolymers are influenced by their chemical structure and composition and the monomer sequence distributions. Several relationships have been employed to describe the effect of these parameters on the glass transition temperature of the copolymers[20]. The simplest equation describing the effect of composition on Tg is the Gibbs-Di Marzio equation[21]:

$$Tg=\varphi_{VP}Tg_{VP}+\varphi_{A}Tg_{A} \qquad (13)$$

where φ_{VP}, φ_A are the mole fractions of VP and the comonomer DEAEMA, DEGMA or BuOEMA, respectively, in the copolymer and Tg_{VP}, Tg_A the glass transition temperatures of the two homopolymers, respectively.

A similar relationship was introduced by Fox[22]:

$$\frac{1}{Tg} = \frac{w_{VP}}{Tg_{VP}} + \frac{w_{A}}{Tg_{A}} \qquad (14)$$

where w_{VP} and w_A are the weight fractions of VP and the comonomer in the copolymer.

The experimental results concerning the Tg of the P (VP-*co*-A) copolymers along with the predictions of the Gibbs-Di Marzio and Fox equations are given in TABLE 5. It is obvious that in most cases positive deviations are obtained by both methods due to the fact that they are based only on thermodynamic and free volume theories of the glass transition and they do not take into consideration the monomer sequence distribution and the effect of their compatibility on steric and energetic interactions. The deviations are much more pronounced with the Gibbs-Di Marzio equation, since it takes into account the volume fractions of the components. For statistical copolymers bearing monomers without a large difference in molecular weight, such as in our case, it is more reasonable to use the weight fractions of the components. Several models have been proposed that take the effect of the monomer sequence distribution along the copolymer into account.

TABLE 5 : Glass transition temperatures for the statistical copolymers

Sample	$(Tg)_{exp}$, K	$(Tg)_{GM}$	$(Tg)_{FOX}$
VP-DEAEMA 0/100	299.15		
VP-DEAEMA 20/80	300.29	316.6	308.3
VP-DEAEMA 40/60	303.52	328.1	315.9
VP- DEAEMA 50/50	313.80	355.8	322.1
VP-DEAEMA 60/40	319.57	344.0	329.6
VP-DEAEMA 80/20	334.21	359.3	348.3
VP-DEAEMA 100/0	373.15		
VP-DEGMA 0/100	241.85		
VP-DEGMA 20/80	258.45	286.3	262.4
VP- DEGMA 40/60	279.85	321.9	289.3
VP-DEGMA 50/50	292.50	336.6	305.5
VP-DEGMA 60/40	304.25	344.3	315.8
VP-DEGMA 80/20	323.70	361.2	344.9
VP-DEGMA 100/0	373.15		
VP-BuOEMA 0/100	241.28		
VP-BuOEMA 20/80	266.75	301.5	272.8
VP-BuOEMA 40/60	290.39	322.0	290.0
VP-BuOEMA 50/50	310.72	337.2	306.8
VP-BuOEMA 60/40	332.76	349.4	323.9
VP-BuOEMA 80/20	353.18	362.7	348.3
VP-BuOEMA 100/0	373.15		

Based on the free volume concept, Johnston proposed the following equation[23]:

$$\frac{1}{Tg} = \frac{w_{VP}P_{VP-VP}}{Tg_{VP-VP}} + \frac{w_{A}P_{A-A}}{Tg_{A-A}} + \frac{w_{VP}P_{VP-A} + w_{A}P_{A-VP}}{Tg_{VP-A}} \qquad (15)$$

It is assumed that the VP-VP, A-A and A-VP or VP-A dyads have their own glass transition, Tg_{VP-VP}, Tg_{A-A} and Tg_{VP-A}, respectively. Tg_{VP-VP} and Tg_{A-A} can be considered as the glass transition temperatures for the respective homopolymers, whereas Tg_{VP-A} is the glass transition temperature of the alternating copolymer P (VP-*alt*-A). W_i is the weight fraction of the i component and P_{VP-VP}, P_{A-A}, P_{VP-A} and P_{A-VP} are the probabilities of having various linkages. These probabilities can be calculated using the monomer reactivity ratios[19]:

$$P_{VP-VP} = \frac{r_{VP}}{r_{VP} + \frac{[M_A]}{[M_{VP}]}} \qquad (16)$$

$$P_{VP-A} = \frac{[M_A]}{r_{VP}[M_{VP}] + [M_A]} \qquad (17)$$

$$P_{A-VP} = \frac{[M_{VP}]}{r_A[M_A] + [M_{VP}]} \qquad (18)$$

$$P_{A-A} = \frac{r_A[M_A]}{r_A[M_A] + [M_{VP}]} \qquad (19)$$

Barton suggested the following equation[24]:

$$Tg = XTg_{VP-VP} + YTg_{A-A} + ZTg_{VP-A} \qquad (20)$$

where X, Y, Z are the monomer dyad fractions (equations 8-10).

To apply these theories it is necessary to know the glass transition temperature of the respective alternating copolymers. However these data are not provided in the literature. Therefore, the linearized forms of the Johnston and Barton equations are used to obtain the Tg_{VP-A} values. The plots, given in Figures 8 and 9, are straight lines passing through the origin. This is an indication that these theoretical methods can better predict the Tg values of statistical copolymers, or in other words, that the monomer sequence distribution is an important parameter defining the Tg of a statistical copolymer. The Tg_{VP-A} values, calculated by the Johnston and Barton equations, are given in TABLE 6 for all copolymers. It is evident that the results obtained by the two methods are not similar. However, the predictions of the Johnston equation seem to be more reasonable since the weight fraction of the copolymer component is more representative of the overall copolymer composition, as also indicated by the better fit of the Fox equation with the experimental results, compared to the Gibbs-Di Marzio equation.

TABLE 6 : Tg_{12} values obtained by the Johnston and Barton equations

Sample	$(Tg_{12})_{Johnston}$	$(Tg_{12})_{Barton}$
VP-DEAEMA	319.49	329.03
VP-DEGMA	327.87	309.70
VP-BuOEMA	258.40	233.20

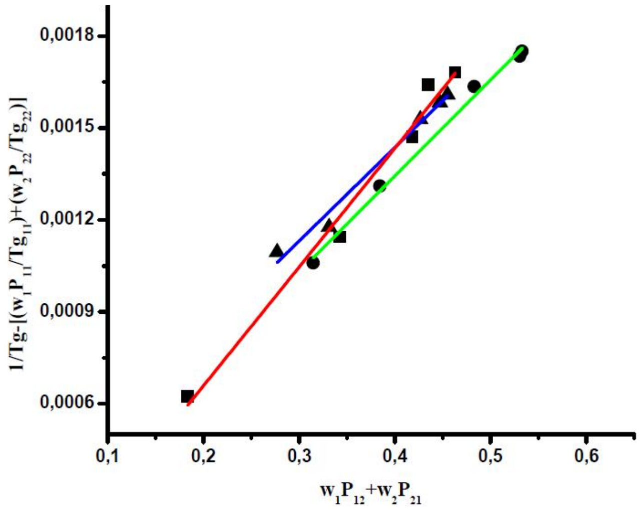


Figure 8 : Linearized form of the Johnston equation for the VP-DEAEMA (•), VP-DEGMA (▲) and VP-BuOEMA (■) statistical copolymers.

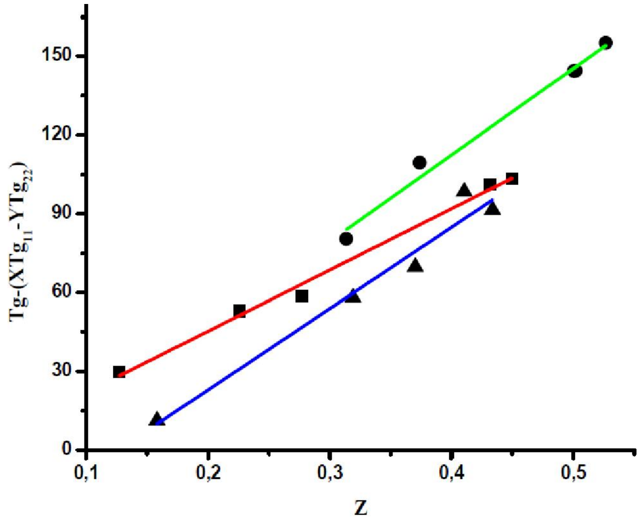


Figure 9 : Linearized form of the Barton equation for the VP-DEAEMA (•), VP-DEGMA (▲) and VP-BuOEMA (■) statistical copolymers.

CONCLUSIONS

Copolymers of 2-vinylpyridine (VP) with 2-diethyl amino ethyl methacrylate (DEAEMA), di (ethylene glycol) methyl ether methacrylate (DEGMA), and 2-butoxyethyl methacrylate (BuOEMA), have been prepared by free radical polymerization. In all cases the copolymerization was conducted in bulk at 50°C. The reactivity ratios of the copolymers were estimated using linear graphical methods. The r_{VP} values were higher than the corresponding r_A values in all cases, meaning that a kinetic preference exists for the incorporation of VP in the copolymer structure. These results were confirmed by the calculation of the monomer dyad sequence fractions. The glass transition temperatures of the statistical copolymers were obtained and compared with the predictions provided by several theoretical models. Among these models, the Johnston equation offers the best fit to the experimental data, because it takes into consideration the effect of the monomer sequence distribution on the glass transition temperature and uses the weight fractions of the copolymer components.

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