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Monomer Reactivity in Functionalized Vinyl Copolymers: A Theoretical Approach

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ABSTRACT

This work studies how the variation of the inter-atomic distance affects the total energy in addition reactions of several vinyl radicals on vinyl monomers. Based on the energetic profiles obtained, the corresponding activation energies were evaluated and correlated with the relative reactivity of the monomers forming the vinyl copolymers poly(2-vinylpyridine-co-*N*-vinyl-2-pyrrolidone), poly(4-vinylpyridine-co-*N*-vinyl-2-pyrrolidone), poly(vinyltrimethylsilane-co-*N*-vinyl-2-pyrrolidone) and poly(vinylcyclohexane-co-*N*-vinyl-2-pyrrolidone), previously characterized with an estimation of their monomer reactivity ratios (MRR). The results are discussed as a theoretical support to a work developed in the general framework of the synthesis and characterization of functionalized vinyl copolymers.

Key Words: Monomer reactivity ratios; Addition reactions; Activation energy; Functionalized vinyl copolymers.

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INTRODUCTION

Comonomer propagation rates are influenced by different factors depending on the kind of polymerization involved. In radical vinyl copolymerizations, the monomer relative reactivity can be correlated with the stabilization by resonance, the polarity, and steric effects. At the same time, all these factors depend on the chemical nature of the groups close to the radical, that is, the substituent side chains.^[1]

If in a vinyl monomer like $\text{CH}_2=\text{CHR}$, R can induce the resonance delocalization of the radical electron, radical stability increases. When monomers with very different polarities react, copolymers with a high tendency towards alternation are formed. Likewise, besides these resonance and polar effects, the vinyl substituents in a radical copolymerization can provide a steric hindrance at the reaction site, which would disadvantage the molecular propagation.^[1]

The structural and electronic factors mentioned above contribute significantly to the propagation rate in a radical copolymerization process, but they do so in such a way that it is difficult to distinguish the magnitude of each effect. However, there are a large number of procedures that permit quantification of the result of all these effects by calculating the monomer reactivity ratios (MRR, r_1 and r_2). An important group of these is represented by the classical linear least squares fitting procedures that, although statistically invalid, can be used as a powerful tool to obtain good, approximate MRR-like initial values for r_1 and r_2 .^[2] Other recently developed methods are based on the "error in variables model" (EVM) or on its modifications.^[2] These methods use statistically valid computer procedures incorporating correctly all the experimental error sources. As a result, MRR values with high reliability are generated.

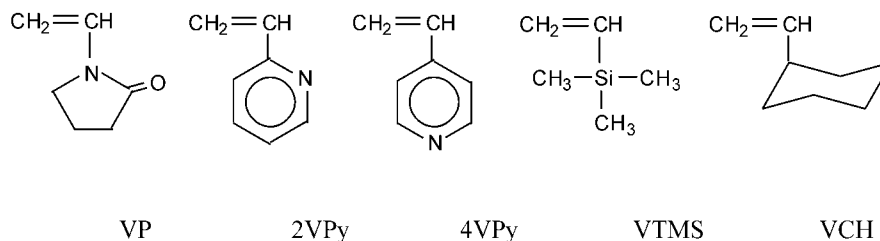
Both classical and computer procedures to estimate MRR use experimental measures to determine the copolymer composition: classical procedures in a direct way and computer ones, indirectly. For this reason, it is interesting to complement the experimental estimation of MRR with the application of different procedures using some of the computer tools suitable for use in molecular and macromolecular chemistry.

This work presents the theoretical calculations for the energetic barriers corresponding to the activation energies in the addition reaction between different vinyl radicals and monomers. These monomers have been used to synthesize a series of functionalized vinyl copolymers previously reported within a general research project in the radical comonomer reactivity field.^[3–8] A correlation between the activation energies obtained for each system and the MRR values estimated for the corresponding comonomers was performed. The copolymers studied are poly(2-vinylpyridine-co-*N*-vinyl-2-pyrrolidone) (2VPy-co-VP), poly(4-vinylpyridine-co-*N*-vinyl-2-pyrrolidone) (4VPy-co-VP), poly(vinyltrimethylsilane-co-*N*-vinyl-2-pyrrolidone) (VTMS-co-VP) and poly(vinylcyclohexane-co-*N*-vinyl-2-pyrrolidone) (VCH-co-VP). The structural formulas of the monomers, *N*-vinyl-2-pyrrolidone (VP), 2-vinylpyridine (2VPy), 4-vinylpyridine (4VPy), vinyltrimethylsilane (VTMS) and vinylcyclohexane (VCH), are presented in Sch. 1.

EXPERIMENTAL

The calculations and corresponding molecular geometry optimization for the estimation of the activation energies of the addition reactions, were performed using a PM3-type method^[9] with the Spartan computer package.^[10]





Scheme 1.

The objective is to study the attack of vinyl free radicals with different substituents on monomers of their own class (shown in Sch. 1). Scheme 2 presents this reaction, where the addition of the radical $\text{C}_2\text{H}_4\text{R}$ to the monomer $\text{C}_2\text{H}_3\text{R}'$ is represented.

Simulations were performed to analyze the total energy variation of the systems as both molecules (radical and monomer) moved closer to each other. In this way, the procedure varies the distance between the radical carbon and the non-substituted carbon of the monomer from 4.5 to 1.45 Å. The aim of this procedure is to ensure that the distance between both molecules corresponds to the single carbon-carbon bond distance.

Simulations were carried out in the absence of solvent. This condition is equivalent to experimental conditions since the studied copolymers synthesis was always a radical copolymerization in bulk.^[3,4,8] We sought to quantify the energetic barrier that is generated for some vinyl radicals (varying R) in their addition reactions with other different vinyl monomers (varying R'). As a result, it was possible to correlate these energy quantities with the reactivity of the corresponding monomers.

In all cases, the fourth valence of the tetrahedral carbon of the $\text{C}_2\text{H}_4\text{R}$ radical was covered with a bond of a third hydrogen atom (Sch. 2). Thus, this factor is kept constant for the different radical/monomer pairs. For that, the activation energies obtained give an account of electronic, polar and even steric factors due to the vinyl radical attack on the vinyl monomer, exclusively. In this way, the analysis becomes independent of the macroradical size reacting with a monomer molecule in the propagation stage of the copolymerization.

RESULTS AND DISCUSSION

Table 1 collects the total energy values obtained for the indicated addition reactions as a function of the inter-atomic distance, involving the radical/monomer pairs studied. From this table energy profiles were obtained. They represent the total energy variation of the system with respect to the inter-atomic distance between the radical carbon and the



Scheme 2.



Table I. Total energy (kJ/mol) for the specified addition reactions and inter-atomic distances.

Reaction	Distance (Å)										
	4.5000	3.7375	2.9750	2.7500	2.5000	2.2125	2.1000	1.9000	Min ^a	1.4500	
2VPy radical on VP ^b	13.77	13.33	27.82	40.18	46.54	69.49	71.77	36.16	-44.43	-31.46	
VP radical on 2VPy	31.48	25.04	40.84	50.02	59.46	75.72	70.59	28.48	-52.29	-38.86	
4VPy radical on VP	14.14	10.01	25.92	38.59	43.97	67.11	69.61	34.81	-44.95	-31.78	
VP radical on 4VPy	55.82	31.64	46.96	63.43	64.44	94.65	78.88	36.93	-45.37	-32.30	
VP radical on VTMS	-277.55	-282.07	-265.97	-265.09	—	-232.23	-227.73	-258.12	-334.95	-320.78	
VTMS radical on VP	-267.93	-272.84	-261.11	-251.55	-246.42	-230.50	-232.12	-275.31	-373.01	-364.83	
VCH radical on VP	-191.16	-202.44	-193.84	-183.56	-173.68	-149.46	-149.89	-194.12	-282.61	-271.35	
2VPy radical on VTMS	23.55	19.61	32.19	41.26	52.91	80.52	87.12	59.42	-25.39	8.33	

^aDistance corresponding to the lowest energy obtained. It varied from 1.5183 to 1.5432 Å.

^bFor this reaction, there are two more available values: 66.87 and -19.79 kJ/mol for 2.2500 and 1.7000 Å, respectively.



non-substituted carbon of the monomer represented in Sch. 2. Figure 1 presents the case of the monomer pair of 2VPy-co-VP as a representative example of this behavior. Based on this profile type, the activation energies for all the systems studied were obtained, which are compiled in Table 2. Table 3 summarizes the MRR values previously obtained for the copolymers included in this work. These parameters were calculated using the Fineman-Ross (FR)^[11] and Kelen-Tüdös (KT)^[12] classical linear procedures as well as by the non-linear computer method RREVM.^[12] Monomer reactivity ratio represents the relative reactivity of a comonomer couple in a determined copolymer.

The activation energies obtained for the attack of the 2VPy radical on VP and of the VP radical on 2VPy were 60.7 and 46.0 kJ/mol, respectively. In the first reaction, the molecules of the reactants have to overcome a higher energetic barrier to produce the effective attack of the 2VPy radical on the VP monomer. In other words, the opposite attack (of the VP radical over 2VPy) is a more favored process. The experimental results confirm this interpretation that the experimental monomer reactivity ratio for VP is significantly lower than the one for 2VPy (0.3 and 4.3, respectively). Every time that one monomer unit of VP incorporates to the macromolecule, there is a greater tendency to react with 2VPy, since its corresponding energetic barrier is lower than in the opposite reaction. A decrease in the incorporation probability of VP to the copolymer is then expected.

A similar situation is obtained for the comonomer pair of 4VPy-co-VP. Activation energies of the reactions between the 4VPy radical and VP and between the VP radical and

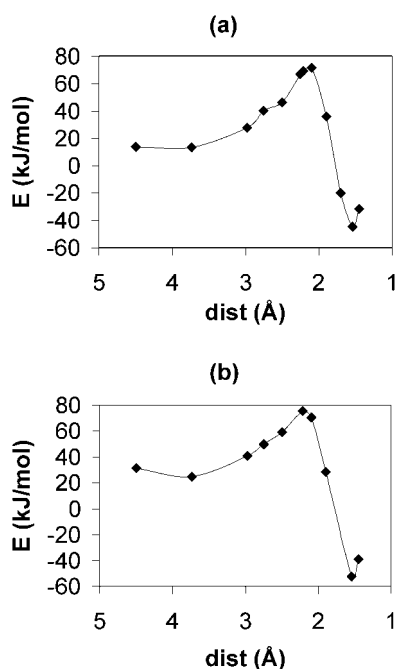


Figure 1. Total energy variation with the inter-atomic distance for the comonomer pair of 2VPy-co-VP: (a) attack of radical 2VPy over monomer VP; and (b) attack of radical VP over monomer 2VPy.



Table 2. Activation energy (E_{act}) for the addition reactions studied.

Reaction	E_{act} (kJ/mol)
Radical 2VPy \rightarrow monomer VP	60.7
Radical VP \rightarrow monomer 2VPy	46.0
Radical 4VPy \rightarrow monomer VP	54.4
Radical VP \rightarrow monomer 4VPy	39.8
Radical VP \rightarrow monomer VTMS	50.2
Radical VTMS \rightarrow monomer VP	41.8
Radical VCH \rightarrow monomer VP	43.9
Radical 2VPy \rightarrow monomer VTMS	64.9

4VPy are 54.4 and 39.8 kJ/mol, respectively. These values confirm the similar MRR obtained for both 2VPy-co-VP and 4VPy-co-VP (Table 3).

When the more reactive monomer is VP (which lacks an aromatic system conjugated with the vinyl group), the qualitative situation is similar to the cases of 2VPy-co-VP and 4VPy-co-VP. VP radical attacks on VTMS and of the VTMS radical on VP present

Table 3. Monomer reactivity ratios (MRR, r_1 and r_2) for the 2VPy-co-VP, 4VPy-co-VP, VTMS-co-VP and VCH-co-VP determined by the FR, KT and RREVM methods.

Copolymer	Method	MRR ^a	
		r_1	r_2
2VPy-co-VP	FR ^b		
	1 = 2VPy	6.9	0.9
	1 = VP	5.2	0.4
	KT	5.5	0.4
	RREVM	4.3	0.3
4VPy-co-VP	FR ^b		
	1 = 4VPy	3.2	0.3
	1 = VP	3.6	0.5
	KT	3.3	0.4
	RREVM	3.9	0.5
VTMS-co-VP	FR ^b		
	1 = VTMS	0.1	1.4
	1 = VP	0.0	0.7
	KT	0.0	1.0
	RREVM	0.0	1.3
VCH-co-VP	FR ^b		
	1 = VCH	0.0	2.3
	1 = VP	0.0	0.8
	KT	0.0	1.1
	RREVM	0.0	2.2

^aMonomer 1 is that written in first place.

^bIn the FR method the monomer indexing influences over the obtained MRR.



energetic barriers of 50.2 and 41.8 kJ/mol, respectively. However, the lower stabilization by electronic delocalization on the amide group of VP relative to 2VPy and 4VPy is reflected in a smaller energy difference with VTMS, without any structural possibility of delocalization.

It is interesting to compare comonomer pairs, using as reference one of the comonomers forming the copolymer. If VP is considered as a common comonomer, the least energy required to produce the attack of the radicals from the aromatic monomers like 2VPy and 4VPy is significantly higher than in the case of the attack of VTMS radicals. This fact gives rise to the 2VPy and 4VPy blocks formation in 2VPy-co-VP and 4VPy-co-VP, respectively. However, VTMS in VTMS-co-VP experiences only a cross propagation ($r_{VTMS} = 0.0$).

The total energy variation against the inter-atomic distance for the comonomer pair of VCH-co-VP was also analyzed. VCH corresponds to a monomer containing a saturated ring as side chain. For that reason, it can be useful for analyzing the loss of the aromatic character on the comonomer of VP. This loss provokes a behavior of VCH relative to VP that is similar to VTMS in that it is not capable of exercising electronic delocalization. In fact, the activation energy involved in the attack of the VCH radical on the VP monomer is 43.9 kJ/mol, very similar to that corresponding to the attack of the VTMS radical to the VP monomer (41.8 kJ/mol). Results obtained for these systems agree with the experimentally obtained reactivity ratios: zero for both VCH and VTMS, in VCH-co-VP and VTMS-co-VP, respectively, and larger than the unity for VP on both copolymers.

The variation of energy of the system was also analyzed when the 2VPy radical (whose corresponding monomer is one of the more reactive ones^[3-8]) moved closer to the VTMS monomer (one of the less reactive monomers^[3-8]). This case presents the highest energetic barrier for the copolymers studied: 64.9 kJ/mol. This addition reaction, therefore, is clearly disadvantaged with respect to the addition of other radicals on the corresponding monomers, indicating that the attack of the 2VPy radical on VTMS is a highly unfavorable process. Experimental evidence corroborates these results: when the copolymerization between 2VPy and VTMS was attempted, the product obtained was the homopolymer of 2VPy, Poly(2-vinylpyridine), irrespective of the different initial monomer compositions.^[5]

CONCLUSION

The theoretical calculation of the activation energy of addition reactions between the vinyl radicals and monomers complements the radical monomer reactivity studies performed for a series of functionalized vinyl copolymers. A direct relation between the activation energy quantity and the incorporation frequency into the macromolecular chain (monomer reactivity) is obtained.

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