Relevance of Backbiting and Beta-Scission Reactions in the Free Radical Polymerization of Acrylonitrile

*M. Dossi, G. Storti, D. Moscatelli**

Summary: In this work, backbiting and beta-scission reactions are investigated through Quantum Chemistry methods by adopting the Becke 3 parameters and Lee Yang Parr functional (B3LYP) and 6-31G(d,p) basis set. Namely, the 1:3, 1:5 and 1:7 backbiting reactions are studied for acrylonitrile polymerization. It was found that the backbiting 1:5 is the most favorited because this kinetic event leads to the formation of a 6 membered transition state, while the backbiting 1:3 requires high activation energy due to the formation of a highly strained 4 membered ring. 7:3 backbiting reaction was also examined, since it is an alternative pathway that can explain the formation of defects generated by radicals in the third position. Simulations showed that this kinetic step is characterized by high rate constant because of its low activation energy.

The right and left beta-scission reactions from the mid chain radicals formed by the considered backbiting reactions are also studied. Computational analysis demonstrated that all beta-scission reactions are endothermic and both the right and left beta-scission reactions have the same activation energy, which seems to be more influenced by the position of the mid chain radical.

Keywords: backbiting; beta-scission; DFT; polymerization; quantum chemistry

Introduction

Free Radical Polymerization is a widespread process for the synthesis of polymeric materials, and it finds application in many industrial fields, primarily in producing plastics.

The most conventional kinetic scheme of free radical polymerization includes initiation, propagation and bimolecular termination reaction steps. When needed, additional reactions such as chain transfer to solvent and to monomer are introduced to improve the process description.[1] However, recent studies convincingly proved the existence of mid-chain radicals (MCRs) and of the so called secondary reactions, that are responsible for the MCRs formation during the polymerization process.[2–4] These species are usually well-stabilized by the existence of a tertiary carbon radical and the reactions in which they are involved can affect the final properties of the polymer at a significant extent. The reactivity differences between secondary and tertiary carbon radicals make difficult the estimation of the polymerization rates even with the most advanced techniques (e.g. PLP-SEC).[5]

In this work the secondary reactions involving mid-chain radicals were investigated through a computational approach based on Density Functional Theory (DFT).[6] In particular the attention was focused on the study of Poly-AcryloNitrile (PAN). Even if PAN is a material of high industrial relevance, the corresponding monomer is very toxic and classified as Class 2B carcinogen.[7] Moreover, the degradation products of acrylonitrile and PAN can be toxic as well.[7] This is the main reason for the lack of experimental studies on this system, especially compared to

---

Dipartimento di Chimica, Materiali e Ingegneria Chimica "Giulio Natta", Politecnico di Milano, 20131 Milano, Italy
E-mail: davide.moscatelli@polimi.it

other relevant polymeric materials such as acrylates, styrene, etc. No data are present in the literature on the relevance of these secondary reactions for the free radical polymerization of acrylonitrile although evidences of these reactions are found for the anionic polymerization of the same monomer.[8] Accordingly, the aim of this work is to perform a computational analysis focused on PAN in order to quantify the relevance of secondary reactions in the free radical polymerization process. For this system the kinetics of 1:3, 1:5, 1:7 and 7:3 backbiting reactions, and the corresponding reverse reactions, were examined. Moreover, the right and left beta-scissions from the mid chain radicals (MCRs) formed by such backbiting reactions were studied.

Computational Details

Thermodynamic and kinetic parameters have been evaluated adopting Density Functional Theory (DFT). In particular, the Becke 3 parameters and Lee Yang Parr functional (B3LYP) were adopted in all the DFT calculations to evaluate exchange and correlation energies.[6,9]All quantum chemical calculations of radicals were performed with a spin multiplicity of 2 and using an unrestricted wave function in order to avoid spin contamination (UB3-LYP). The all electron 6-31 basis set with added polarization functions (6-31G(d,p)) was used as basis set.[10,11] In order to combine the requirement of simulating a realistic polymeric radical chain without exceeding the maximum number of atoms which can be accounted for with this kind of computational approach, the molecular model chosen as representative of the whole polymer was approximated as composed by six monomer units.

As a general rule, all geometries were optimized with the Berny algorithm and were followed by frequency calculations.[10] The geometry of each molecular structure was considered stable only after calculating vibrational frequencies and force constants and if no imaginary vibrational frequency were found. Activation energies and enthalpy changes are expressed as:

$$E_a = (EE + ZPE)_{TST} - \sum_{i=reactants} (EE + ZPE)_i \tag{1}$$

$$\Delta H = \sum_{j=products} (EE + ZPE + TC) - \sum_{i=reactants} (EE + ZPE + TC)_i \tag{2}$$

where EE represents the electron energy, ZPE the zero point energy and TC the thermal energy correction. Transition state structures were located adopting the synchronous transit-guided quasi-Newton method and were characterized by a single imaginary vibrational frequency.[11] The kinetic constants were determined adopting the conventional Transition State Theory (TST) as:

$$k(T) = A \cdot e^{-Ea/k_b T} = \frac{k_b T}{h} \cdot \frac{q^{rot}_{TS} q^{vib}_{TS} q^{el}_{TS}}{\prod_{reactants} q^{rot} q^{vib} q^{el}} \cdot e^{-Ea/k_b T} \tag{3}$$

where k_b and h are Boltzmann and Plank constant, respectively, T is the temperature, E_a is the activation energy of the process, $Q^{vib}_{\neq}, Q^{rot}_{\neq}, Q^{vib}, Q^{rot}$ are the vibrational and rotational partition functions for transition state and reactants. As reported for the acrylonitrile and methacrylonitrile systems,[12] vibrational frequencies smaller than $150\,\mathrm{cm}^{-1}$ were explicitly considered as rotors or hindered rotors.[13] All quantum chemistry calculations were performed with the Gaussian 03 suite of programs[14] and all pictures drawn with Molden 4.2.[15]

Results and Discussion

Previous computational and experimental studies emphasized that the secondary reactions play an important role in high-temperature radical polymerization of styrene and, more in general, in the free radical polymerization of acrylates, vinyl chloride, etc.... In these cases, secondary reactions are responsible for the production of low molecular weight species.[13,16–17] In the case of polyvinyl chloride (PVC), the presence of the MCRs leads to the formation of chain defects which can affect the physical properties and the main applicative features of the final polymeric material.[18]

Backbiting

The backbiting reactions consist in the hydrogen transposition in a terminal radical chain that takes place because of the higher reactivity of the radical in the terminal position with respect to the MCRs. A scheme of the 1:3, 1:5, 1:7 and 7:3 backbiting reactions for PAN is reported in Figure 1.

The 1:3, 1:5, 1:7 and 7:3 hydrogen transpositions were investigated with the computational procedure previously described. The calculated kinetic parameters for both forward and reverse reactions are collected in Table 1. Moreover, it is found that all forward reactions are slightly exothermic. In particular the calculated enthalpy changes for the 1:3, 1:5, 1:7 and 7:3 transposition of PAN are −1.81, −0.97, −0.98 and −0.83 kcal/mol, respectively. It is found that the 1:5 and 7:3 hydrogen transpositions are the most favorite, while the activation energy values increase moving to backbiting 1:7 and 1:3. These results may be explained in terms of transition state stability. In fact, the 1:5 and 7:3 backbiting reactions lead to the formation of a 6 membered ring transition state characterized by low internal strain, while the 1:7 and 1:3 backbiting reactions are less favorable. Molecular structures of different transition states for the backbiting reactions of PAN are shown in Figure 2.

Table 1.
Calculated rate coefficients both direct and reverse 1:3, 1:5, 1:7 and 7:3 hydrogen transpositions. Pre-exponential factors and activation energies reported in units consistent with kcal, K, s, mol, and cm as $k = A \cdot T \cdot \exp(-E_a/R/T)$.

	k_{bb} (direct hydrogen transposition)		k_{bb}^{-1} (reverse hydrogen transposition)	
	$\mathrm{Log_{10}}A$	E_a	$\mathrm{Log_{10}}A$	E_a
$R_{n,1} \rightarrow R_{n,3}$	9.681	37.847	10.203	41.54
$R_{n,1} \rightarrow R_{n,5}$	8.811	17.75	9.196	20.89
$R_{n,1} \rightarrow R_{n,7}$	8.157	23.65	8.558	26.83
$R_{n,7} \rightarrow R_{n,3}$	8.630	16.38	8.752	16.89

Beta-Scissions

These reactions are responsible for the formation of defects, which can be produced either directly or following further reactions.

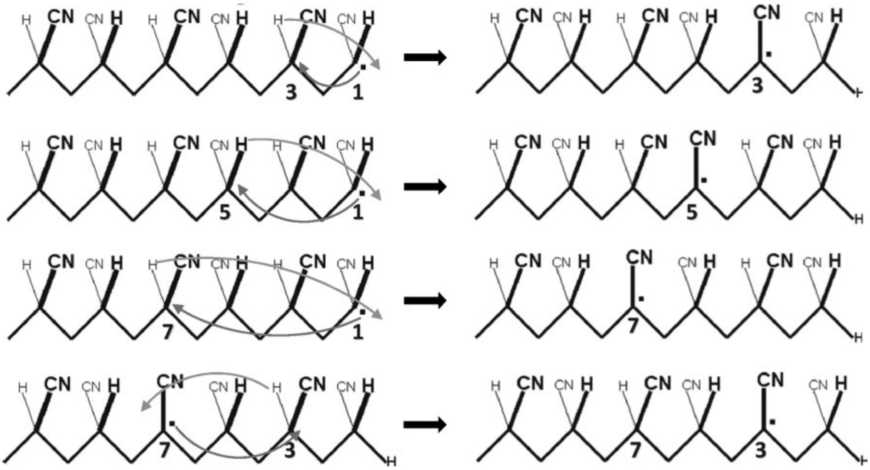

Figure 1.
Poly-AcryloNitrile backbiting reactions scheme for 1:3, 1:5, 1:7 and 7:3 hydrogen transpositions.

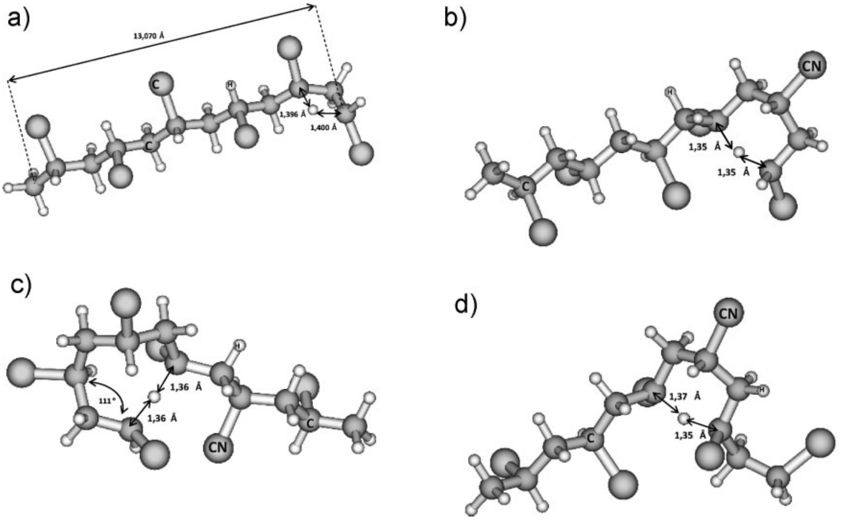

Figure 2.
Transition state geometry for the PAN 1:3 (a), 1:5 (b), 1:7 (c) and 7:3 (d) backbiting reactions calculated with computational approach. Distances are reported in angstroms (syndiotactic molecular model).

The beta-scission reaction is symmetric in the sense that each mid chain radical can react to form the π bond with the secondary carbon atoms positioned at its closest left or right position. For this reason these reactions lead to the formation of different products (radical or dead chains) characterized by lower molecular weights. Kinetic parameter values estimated by the computational approach are collected in Table 2, while molecular geometries for all the species produced by beta-scission reaction

Table 2.
Calculated rate coefficients for both right and left beta-scission reactions. Pre-exponential factors and activation energies reported in units consistent with kcal, K, s, mol, and cm as $k = A \cdot T \cdot \exp(-E_a/R/T)$.

	$k_{\beta\text{-s}}$ (right beta-scission)		$k_{\beta\text{-s}}$ (left beta-scission)	
	$\mathrm{Log}_{10}A$	E_a	$\mathrm{Log}_{10}A$	E_a
$R_{n,3}$	10.560	26.27	11.563	22.64
$R_{n,5}$	10.866	23.49	10.664	23.40
$R_{n,7}$	10.604	23.43	10.306	22.67

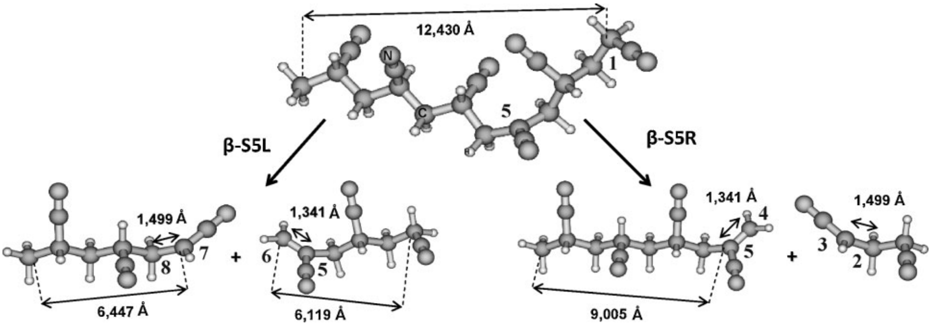

Figure 3.
Molecular geometries of all species produced by the Poly-AcryloNitrile beta-scission reactions for the MCR with radical in position 5. Distances are reported in angstroms.

from the mid chain radical in position 5 are shown in Figure 3.

All beta-scission reactions studied are endothermic and this is consistent with the breaking of a σ bond only partially compensated by the formation of a π bond. In particular the enthalpy change for all reactions assumes values between 16 and 20 kcal/mol.

Conclusions

Two important classes of secondary reactions, backbiting and beta-scission, were investigated. With reference to the free radical homo-polymerization of acrylonitrile, all the rate coefficients involved in backbiting and beta-scission reactions were calculated using density functional theory and adopting the conventional transition state theory.

The backbiting 1:3, 1:5, 1:7 and 7:3 reactions have been investigated and it has been found that the 1:5 and 7:3 backbiting reactions are the most favorite. For all the mid radicals produced the right and left beta-scission reactions have been also studied. It has been found that both the right and left beta-scission reactions require the same activation energy, while the activation energy seems to be more affected by the position of the mid chain radical. The values of the rate coefficients estimated through the proposed computational approach are in the same order of magnitude of the ones estimated for other systems, primarily styrene, but also acrylates. These results suggest that secondary reactions may play a significant role also in the free radical polymerization of acrylonitrile: accordingly, experiments aimed to validate such computational evidences are very welcome.

[1] G. Odian, "*Principle of polymerization*", J. Wiley & Sons, New York 2004.

[2] R. S. Lehrle, C. S. Pattenden, *Polymer Degradation and Stability* **1999**, *6,3*, 153.

[3] M. Buback, P. Hesse, T. Junkers, T. Sergeeva, T. Theis, *Macromolecules* **2008**, *41*, 288.

[4] A. N. Nikitin, R. A. Hutchinson, M. Buback, P. Hesse, *Macromolecules* **2007**, *40*, 8631.

[5] J. M. Asua, S. Beuermann, M. Buback, P. Castignolles, B. Charleux, R. G. Gilbert, R. A. Hutchinson, J. R. Leiza, A. N. Nikitin, J. P. Vairon, A. M. van Herk, *Macromol. Chem. Phys.* **2004**, *205*, 2151.

[6] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648.

[7] A. Leonard, G. B. Gerber, C. Stecca, J. Rueff, H. Borba, P. B. Farmer, R. J. Sram, A. E. Czeizel, I. Kalina, *Mutat. Res.* **1999**, *436*, 263.

[8] H. Ono, K. Hisatani, K. Kamide, *Polymer Journal* **1993**, *25*, 245.

[9] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785.

[10] C. Peng, H. B. Schlegel, *Israel J. Chem.* **1994**, *33*, 449.

[11] C. Peng, P. Y. Ayala, H. B. Schlegel, M. J. Frisch, *J. Comp. Chem.* **1996**, *17*, 49.

[12] D. M. Huang, M. J. Monteiro, R. G. Gilbert, *Macromolecules* **1998**, *31*, 5175.

[13] D. Moscatelli, C. Cavallotti, M. Morbidelli, *Macromolecules* **2006**, *39*(26), 9641.

[14] Gaussian 03, Revision C.02, M. J. Frisch et al., Gaussian, Inc., Wallingford, CT **2004**.

[15] G. Schaftenaar, J. H. Noordik, *J. Comput.-Aided Mol. Design* **2000**, *14*, 123.

[16] R. S. Lehrle, C. S. Pattenden, *Polym. Degr. Stab.* **1999**, *63*, 153.

[17] S. E. Levine, L. J. Broadbelt, *Polym. Degr. Stab.* **2008**, *93*, 941–951.

[18] K. Van Cauter, B. J. Van Den Bossche, V. Van Speybroeck, M. Waroquier, *Macromolecules* **2007**, *40*, 1321.