

Effects of solvent polarity on mutual styrene grafting onto polypropylene by electron beam irradiation

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ABSTRACT

Radiation induced mutual grafting of styrene onto polypropylene has been carried using several grafting solutions with different organic solvents and polarity levels. In the mixture of styrene and protic polar solvents high grafting yields were obtained. This behavior suggests that grafting process does not have dependence on swelling of the substrate, something that is expected when a non-polar substrate and a non-polar media are in contact. In this case, the grafting yield may be related to the free radical generation at protic polar solvent; these reactive specimens start the reaction on substrate surface to allow the accessibility of monomer species to active sites. Some reaction mechanisms are proposed.

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1. Introduction

The use of solvents in radiation grafting is fundamental to allow the access of monomers to polymeric substrates due to their ability for swelling the polymer and their influence on grafting kinetics, the length of grafted chains and the polymer micro-structure. A correct choice of solvents is one of the essential elements towards the success of radiation-induced grafting process. There are many works relating the influence of solvents on radiation-induced grafting of different monomer/base film combinations (Geraldos et al., 2008; Nasef, 2001; Bucio and Burillo, 2009). However, the understanding of the mechanism of the solvent-grafting interaction and its influence on new co-polymer properties is not complete and must be investigated, since a set of parameters must also be considered.

In the literature, there are indications that polar solvents allow high percentages of styrene grafting (Bhattacharyya and Misra, 2004; Tabata et al., 1991). In the mutual irradiation grafting process, swelling polymeric substrate solvents do not contribute to accelerate the grafting reaction due to the higher viscosity of the grafting zone, which hinders its diffusion to the polymer bulk. In the pre-irradiation process, the reaction happens through a frontal mechanism: first, the grafting layer is formed on the substrate surface, and then, the monomer diffuses through the grafted portion and reacts with more radicals (Dworjanyan and Garnett, 1992). It is customary to carry out the reaction in a solvent that swells the polystyrene grafts (e.g., toluene or benzene) to ease the monomer penetration.

Walsby et al. (2000) claimed that styrene grafting onto PVDF has a high yield when *n*-propanol is used as a solvent; they supported these results based on the occurrence of the high concentration of monomer in the reaction zone. Whereas, the higher degree of grafting is the result of the higher viscosity of the grafted zone which did not allow the reaction to complete. The greater efficiency of the grafting reaction in *n*-propanol allowed the reduction of the absorbed dose which was necessary to achieve reasonable degrees of grafting. However, the mechanical characteristics of the samples were poor and the material had low elongation at break when compared to the styrene films grafted using toluene as a solvent.

In this work, mutual styrene grafting by electron beam irradiation has been used due to some advantages such as its extensive penetration in the polymer matrix and its rapid and uniform formation of radicals to initiate the grafting (Nho et al., 1999). Besides, the process is fast and does not need reagents hazardous to the health and the environment. The co-polymerization of polypropylene (widely used polymer in the manufacturing industry) with styrene (a monomer used both as organic solvent and in polymer synthesis) has been chosen due to the low cost of these raw materials and to the possibilities for obtaining new substances. The aromatic ring from styrene molecule has high reactivity according to specific mechanisms—electrophilic and nucleophilic substitution, addition and elimination. Inexpensive solvents such as aromatic hydrocarbons, ketone and alcohols were used. The grafting was evaluated with gravimetric and spectrometric analysis.

2. Experimental

Polypropylene (PP) was purchased from Goodfellow. Before the irradiation, polymer samples of $30 \times 30 \times 0.05\text{--}0.10 \text{ mm}^3$

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were washed in analytical grade ethanol and dried at room temperature; the monomer used for grafting was commercial grade styrene pre-treated by inhibitor removal with molecular sieves. The grafting media was 1:1 styrene/solvent mixture. The solvents applied at this study were analytical grade xylene, toluene, dichloromethane, acetone, methanol, *n*-propanol, isopropanol, *n*-butanol and *n*-octanol and were used without any pre-treatment.

The mutual irradiation grafting was performed using a Job 188 Dynamitron[®] Electron Beam Accelerator with 1.5 MeV energy, the beam current was 25 mA, the beam power was 37.5 kW and the scan was 50–120 cm. The adsorbed doses changed from 30 kGy to 100 kGy and dose rates were 22.4 kGy/s and 2.2 kGy/s.

The post-irradiation treatment of the samples was homopolymer extraction by toluene immersion (2 days), followed by ethanol washing (several times) and finally vacuum drying at 50 °C. The styrene grafted samples were analyzed by gravimetry to determine the grafting yield; the final values have been averaged from a series of three measurements. Transmission Mid-FTIR was the spectrometric technique used for qualitative and quantitative styrene analyses.

3. Results

The grafting yield performed at high dose rates is shown in Fig. 1. As expected, the degree of grafting increases proportionally to the absorbed dose. Maximum grafting degree occurs for the doses in the range of 50–70 kGy. The reactions performed either with 50% of styrene in xylene, in toluene mixtures or in pure styrene resulted in low degrees of grafting (maximum of 3%). When polar and protic solvents are used, particularly with *n*-butanol, the degree of grafting is close to 10%.

At low dose rates (Fig. 2), the behavior using apolar solvents is similar to the previous results. However, when polar solvents are used – in our case, an alcohol homologous series – the greater the size of the carbon chain, the higher the degree of grafting is. The grafting in *n*-octanol is particularly interesting, since the degree of grafting in this case is close to 40% at 70 kGy and close to 70% at 100 kGy. Fig. 3 shows the influence of monomer concentration in grafting yields. These yields are high when the grafting solution contains equal parts of monomer and solvent. However, even

when the grafting solution is composed by only 25% of monomer, one gets similar results.

The qualitative analysis by FTIR in Fig. 4 shows the characteristic bands of styrene proving the occurrence of styrene grafting. Styrene has absorption bands at 690 cm⁻¹, which is related to out-of-plane C–H bond vibrations of the aromatic ring; at 750 cm⁻¹, related to the out-of-plane bending of H atoms bonds in the aromatic ring, and finally a broadening of the band at 1060 cm⁻¹, related to planar vibrations of C–H bond in the aromatic ring.

The grafted styrene was also quantified by transmission FTIR spectrometry (Fig. 5). For this analysis, the integration method of absorption band at 1060–1069 cm⁻¹ has been used. The results are shown in Table 1. The values of grafting degree obtained by both methods are very close even for samples with high degree of grafting, such as those obtained with *n*-octanol.

4. Discussion

When using several mixtures of apolar solvents, the yield of grafting with styrene increases in the following order:

xylene < pure styrene ≈ toluene

To explain this behavior, we refer to the mechanism proposed by Lehrle and Pattenden (1999) for the mutual irradiation method, for which, the solvent radiolysis occurs first. In this case, the solvent molecule dissociation is achieved simply by considering the dissociation bond energies for these solvent molecules to generate the respective radicals, as shown in Table 2.

The bond dissociation energy for xylene is close to that of styrene, which means that styrene and xylene radicals are formed almost simultaneously. In this case, the radicals formed in the xylene/styrene mixture are in competition, and thus the effective and non-effective collisions occur with the same frequency. This hinders the success of reaction of styrene radicals onto polymer substrate and leads to the lowest observed grafting degree.

In the case of pure styrene, the monomer and the solvent are same substances. Effective collisions will happen much more often than non-effective ones; these collisions are related to the

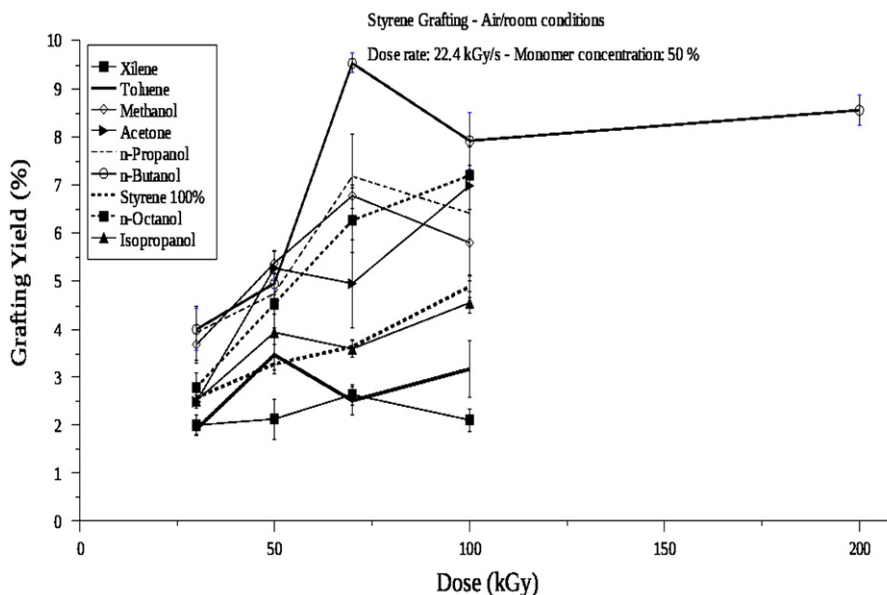


Fig. 1. Styrene grafting yield for polypropylene for mutual electron beam irradiation at 22.4 kGy/s and 25 °C. Grafting medium: 1:1 styrene/organic solvent mixture.

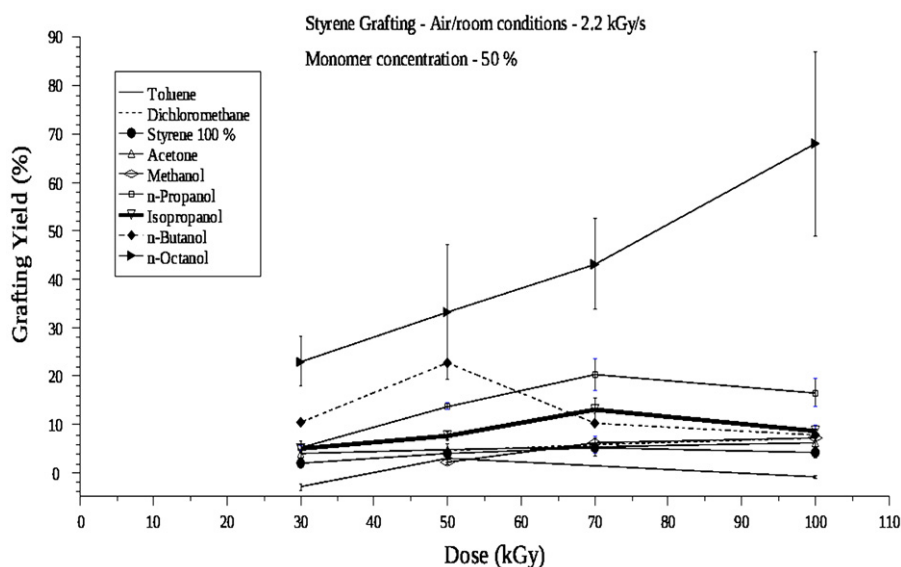


Fig. 2. Styrene grafting yield for polypropylene for mutual electron beam irradiation at 2.2 kGy/s and 25 °C. Grafting medium: 1:1 styrene/organic solvent mixture.

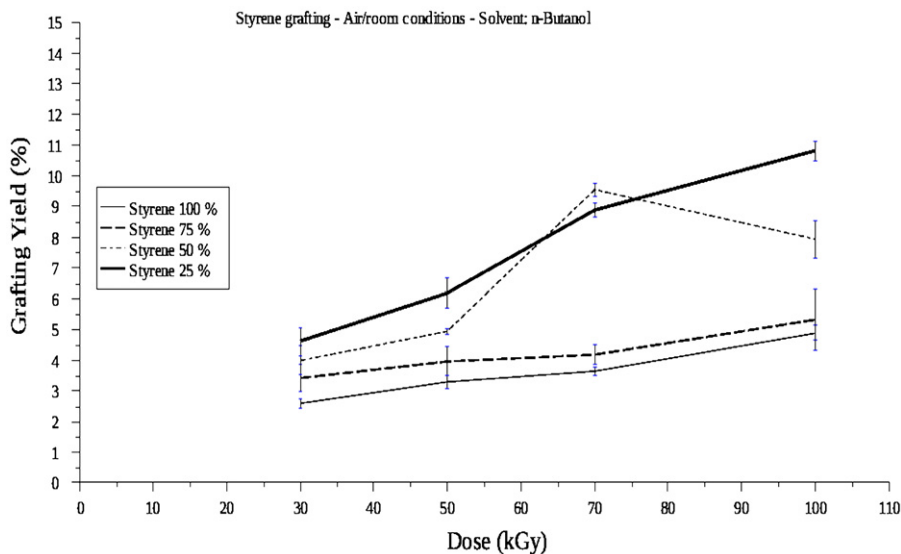


Fig. 3. Grafting concentration effect on styrene grafting yield for polypropylene for mutual electron beam irradiation at 22.4 kGy/s and 25 °C. Solvent used: *n*-butanol.

active sites of the polymeric substrate due to their natural reactive heterogeneity (Cropper, 1962).

Finally, the dissociation bond energy for toluene is a little higher than that of styrene molecules. In this case, the radicals from styrene dissociation are formed first, which leads to effective collisions happening much more often than non-effective ones since the radicals do not compete among themselves; one can say that toluene does not hinder the grafting, and thus the yield of the styrene–toluene mixture is very close to that of the pure styrene.

On the other hand, polar and protic solvents show a different behavior, since the orders of grafting degrees for each dose rate are

isopropanol < *n*-octanol < methanol < *n*-propanol < *n*-butanol
(22.4 kGy/s)

methanol < isopropanol < propanol < *n*-butanol < *n*-octanol
(2.2 kGy/s)

The reasoning based on the energies of bond dissociation which were valid for apolar solvents cannot be applied here

because the dissociation bond energies for homolytic scission of O–H bond are about of 430–440 kJ/mol for alcohols (Gribov et al., 2007). Thus the atomic structure of the alcohols is preserved, styrene radicals are quickly formed and the grafting is achieved. This consideration is in agreement with the references (Bhattacharyya and Misra, 2004; Tabata et al., 1991).

On the other hand, the difference among distinct kinds of alcohols in a homologous series may be the dielectric constant for these protic polar solvents and the generation of solvated electrons. In this case, methanol has the highest dielectric constant value and *n*-octanol, the lowest (Table 3).

According to the literature (Vannikov, 1975; Watson Jr. and Roy, 1972), when compounds with high dielectric constant are submitted to the radiolysis they generate high level of solvated electrons of high reactivity. Fig. 6 outlines a proposed reaction mechanism for our system which leads to the formation of stable compounds, such as diols and aldehydes. When this mechanism is applied to methanol, a high level of solvated electrons are generated in the system; by this parallel mechanism styrene radicals will form which initiate grafting. On the other hand, the

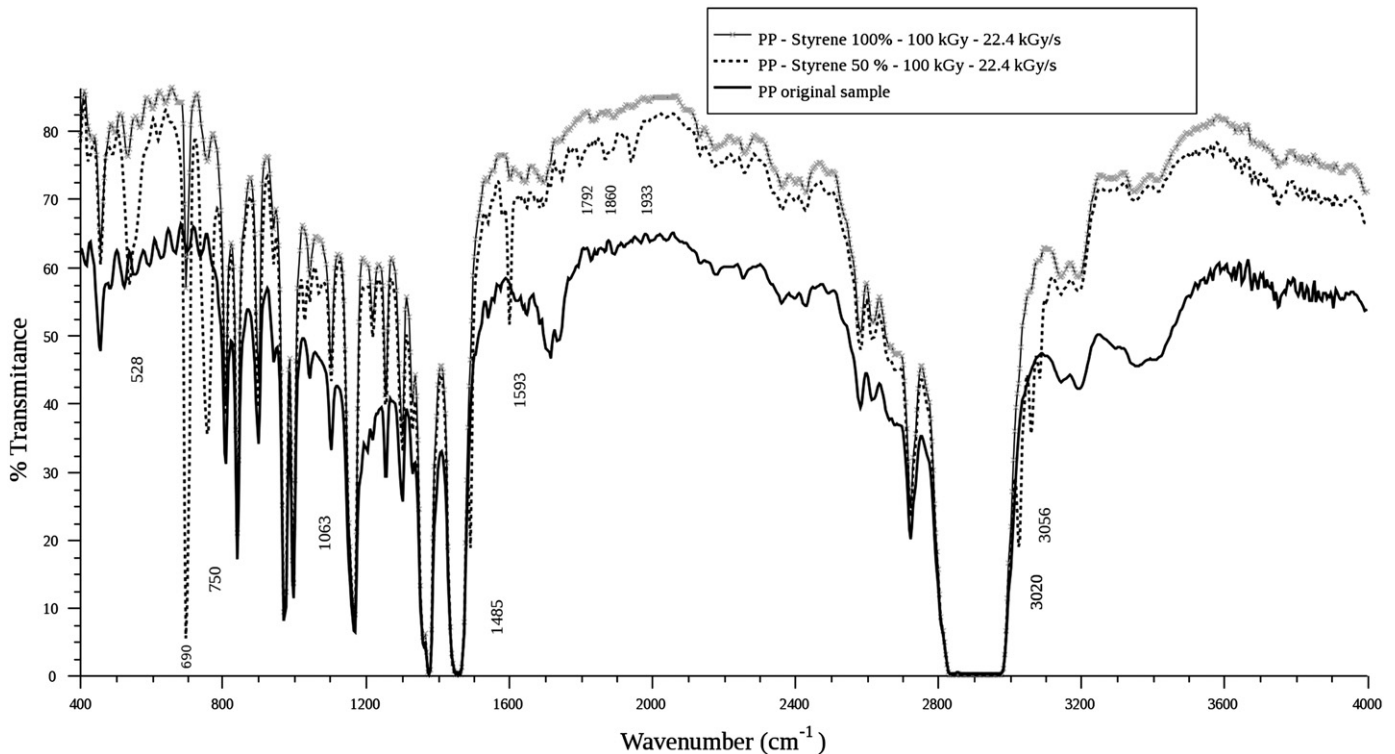


Fig. 4. Mid-FTIR spectra of original and grafted PP samples for mutual electron beam irradiation (100 kGy, 22.4 kGy/s, 25 °C, and grafting medium: styrene 50% in *n*-butanol mixture and styrene 100%).

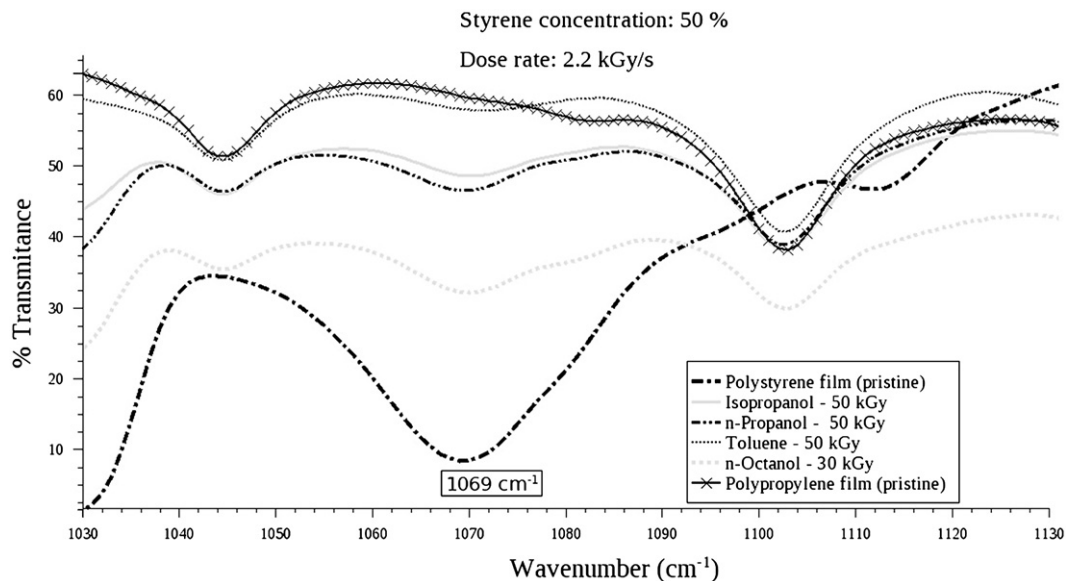


Fig. 5. Quantitative analysis by Mid-FTIR spectrometry of grafted PP samples for mutual electron beam irradiation (50 kGy, 2.2 kGy/s, 25 °C, and grafting medium: 50% styrene/organic solvent mixture). Comparison with PP and PS original samples.

radiolysis of *n*-octanol probably does not produce high levels of solvated electrons compared to methanol; the characteristics of *n*-octanol are thus preserved and the grafting process can be carried out by styryl radicals.

For lower dose rates, the grafting process also shows high yields and for a given absorbed dose such yields increase in the order of the alcohol homologous series. Thus, the non-polarity of the carbon chain (up to eight carbon atoms) may play a role to stabilize the styrene radicals and promote the grafting process through dipole interaction.

In the case of aqueous (non-dehydrated) acetone, which is a polar and non-protic solvent and also has been evaluated in this work, the electron solvation was generated by water radiolysis, and acetone was responsible for electron scavenging; this mechanism does not contribute to increase of the grafting yield:

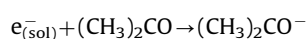
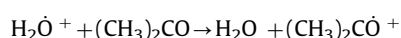
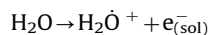


Table 1

Comparison between gravimetry and spectrometry methods for styrene grafting onto PP in several grafting organic solvent mixtures. Monomer concentration in solvent mixtures: 50%.

Grafting method	Styrene (gravimetry) (%)	Styrene (spectrometry) (%)	Grafting method	Styrene (gravimetry) (%)	Styrene (spectrometry) (%)
<i>n</i> -Octanol 30–0.2.2 kGy/s	22.8 (5.2)	20.7	<i>n</i> -Butanol 30–2.2 kGy/s	10.2 (2.9)	11.7
<i>n</i> -Octanol 50–0.2.2 kGy/s	33.0 (13.9)	16.6	<i>n</i> -Butanol 50–2.2 kGy/s	22.5 (8.7)	14.3
<i>n</i> -Octanol 70–0.2.2 kGy/s	42.9 (9.3)	26.7	<i>n</i> -Butanol:styrene 1:1 70–2.2 kGy/s	10.1 (0.4)	9.2
<i>n</i> -Octanol 100–0.2.2 kGy/s	67.7 (19.1)	45.8	<i>n</i> -Butanol 100–2.2 kGy/s	11.0 (1.5)	22.7
<i>n</i> -Propanol 50–2.2 kGy/s	13.5 (0.7)	13.6	Styrene 100% 50–2.2 kGy/s	3.7 (0.9)	4.4
Isopropanol 50 kGy–2.2 kGy/s	7.4 (0.9)	10.3	Toluene 50–2.2 kGy/s	2.8 (0.9)	6.6
Methanol 50–2.2 kGy/s	2.0 (0.6)	0.9	Acetone 50–2.2 kGy/s	4.6 (1.2)	2.2

Table 2

Dissociation bond energies of organic radicals from respective organic molecules.

Organic molecule	Radical	Dissociation bond energies (kJ/mol)	References
Styrene	Styryl (C ₆ H ₅ -Ċ=CH ₂)	324.5	Lehrle and Pattenden (1999)
Xylene	Xylil (C ₆ H ₅ (-CH ₃) ₂ -ĊH ₂)	331	Schefgen (1954)
Toluene	Benzil (C ₆ H ₅ -ĊH ₂)	354	Walling (1960)

Table 3

Dielectric constants of alcohols in a homologous series.

Solvent	Dielectric constant
Methanol	32.7
Isopropanol	20.2
<i>n</i> -Propanol	20.1
<i>n</i> -Butanol	17.8
<i>n</i> -Octanol	10.3

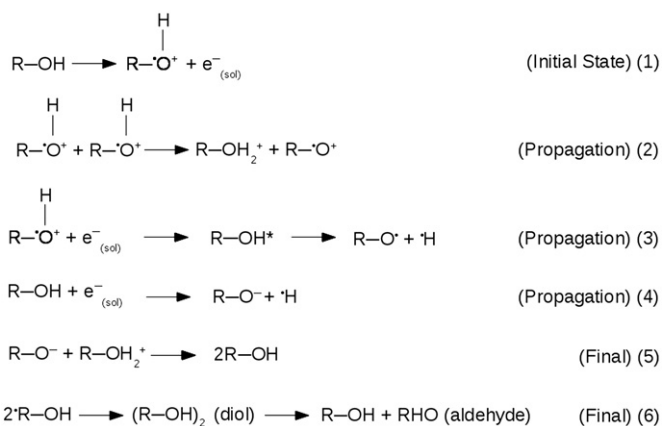


Fig. 6. Proposed chemical mechanism of protic-polar solvents in mixture composed by styrene monomer to grafting onto polypropylene.

5. Conclusions

Styrene grafting onto PP films is performed with higher grafting yields when protic-polar solvents are used instead of apolar solvents. This happens either for low dose rates with

solvents such as *n*-octanol and for high dose rates with solvents such as *n*-butanol.

Among the polar solvents, the intensity of dipole interaction is not the only effect to be considered. Electron solvation also seems to play an important role in the grafting process. Thus, higher styrene grafting yields depend on the physical properties of the solvent when it is exposed to radiation.

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