Free Radical Melt Grafting of Methacrylic ester onto Polyolefin Backbone: Model Compound Approach

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Summary: Polymer reactive extrusion conducted in the presence of functional monomers results in the modification of the original polymer by graft copolymerization or substitution by single monomeric units. However, such modifications are generally difficult to control due to the appearance of side reactions. This is in particular the case in free radical processes like the grafting of poly(methylmethacrylate) from poly(ethylene-co-1-octene) by in situ radical polymerisation of methyl methacrylate. In order to understand both the nature and the extent of such reactions, products resulting from the same chemical system, where polymer is replaced by model compounds such as squalane and/or pentadecane, are analyzed. The most appropriate statistical method for fitting X_{MMA} and $\overline{DP_n}$ data for this grafting reaction is also described. Thanks to the experimental data, this method enabled to fit variables and to validate a chemical scenario.

Keywords: ethylene/octene/methyl methacrylate terpolymers; hydrogen abstraction; low molar mass hydrocarbon substrate; radical graft polymerization; reactive extrusion

Introduction

The more convenient route for a chemical modification of polyethylene in an extruder is to use free radical initiators such as peroxides.[1,2] The grafting reaction starts with hydrogen abstraction by alkoxyl radical generated from thermal decomposition of the peroxide. Then, the active species generated onto the hydrocarbon backbone react with unsaturated monomers. Nevertheless, the main drawback of the free radical grafting is the low selectivity of the radical center leading to side reactions such as coupling, chain scission and homopolymer formation.[3,4] This is in particular the case in free radical processes such as the grafting of poly(methylmethacrylate) from poly(ethylene-co-1-octene) by in situ radical polymerisation of methyl methacrylate. The homopolymerisation often competes successfully with the grafting reaction in these systems making kinetic analyses of the overall process more complicated. Moreover, performing this chemical modification by reactive processing brings many constraints inherent to the process (e.g., short reaction time, viscous dissipation and high temperature). For example, the difference of viscosity between the monomer and the molten polymer could enhance these side reactions. So, to separate these physical influences from the chemical modification, our work includes a model compounds approach based on a radical grafting reaction between peroxide-derived alkoxyl radicals, methyl methacrylate and a selection of low molar mass alkanes representing characteristics moieties from poly(ethylene-co-1-octene) (Engage 8200, 38% w 1-octene). A few authors[3–8] developed a model compound approach. We resorted to pentadecane ($C_{15}H_{32}$) and 2,6,10,15,19,23-hexamethyltetracosane (Squalane, $C_{30}H_{62}$) as models for both the copolymer ethylene and octene moieties. Indeed, high boiling

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points of long chain alkanes permit study under high temperature conditions, typically over 150 °C. It also gives clues to low viscosity at 170 °C, all the more as the formed products in the grafting experiment can be analysed more easily than in the melt.

A kinetic approach of the MMA polymerisation in the presence of model compounds, is also investigated with a numerical simulation. Based on a simplified chemical scenario, this simulation enabled to systematically predict the experimental results. Thus, the numerical simulation has shown that the depropagation reaction is of strong influence when increasing temperature and decreasing monomer concentration.

Results and Discussion

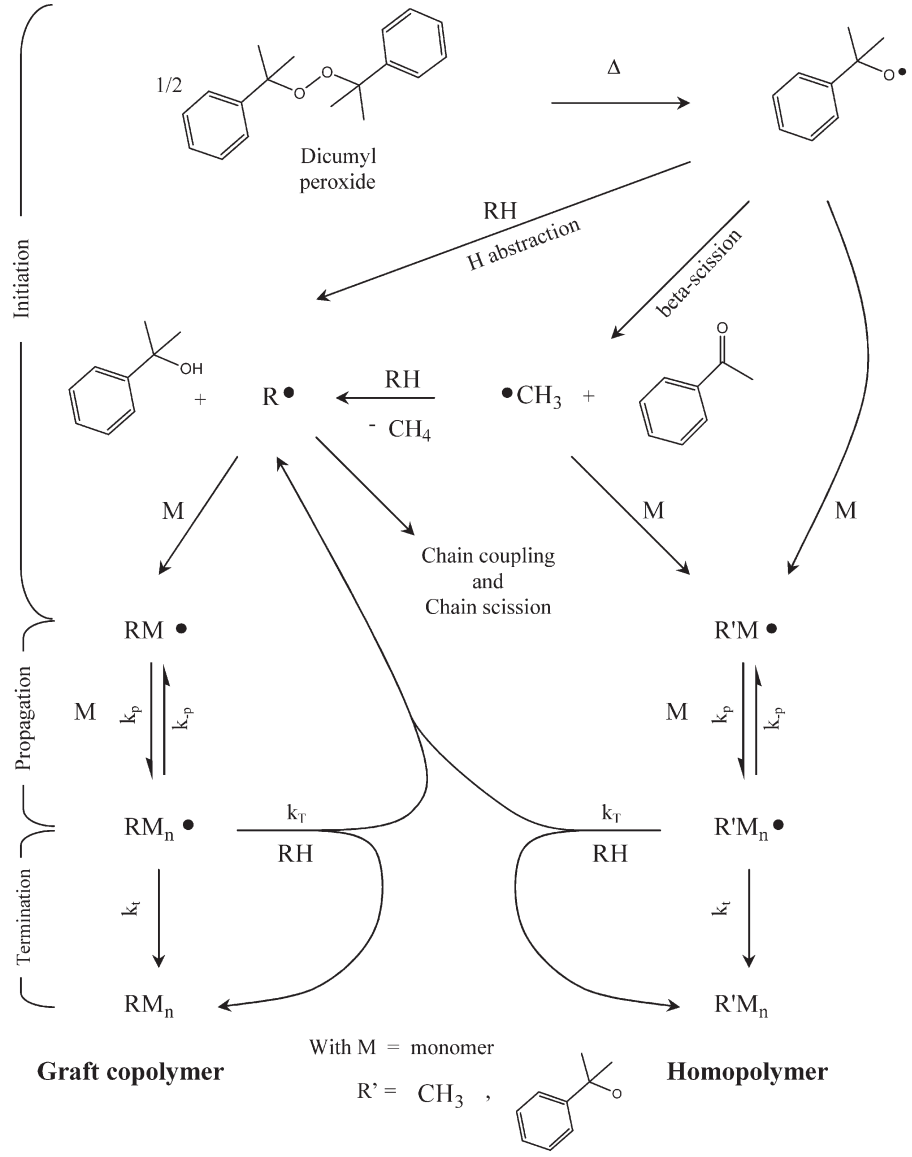
Scheme 1 sums up main reactive pathways of free radical grafting from a hydrocarbon backbone (RH) with dicumyl peroxide as hydrogen abstractor. However, the alkoxy radicals can undergo additional reactions including β-scission or addition to monomer. This would mainly lead to homopolymerization. The rate constant k_T corresponds to the sum of the common termination reaction occurring with polymerization of MMA (i.e. disproportionation and combination reaction) whereas the rate constants k_p and k_{-p} (Scheme 1) respectively refer to the propagation reaction of the polymerization of MMA and to the opposite reaction, that is depropagation. The latter reaction is usually seen in the literature[4] as a ceiling temperature (T_c), i.e. the temperature at which propagation rate equals depropagation rate.

Therefore, T_c depends on polymerization characteristics, that is monomer concentration, enthalpy and entropy of polymerisation (equation 1).

$$T_c = \frac{\Delta H^o}{\Delta S^o + R^* Ln([M])} \quad (1)$$

Our experiments involved a blend of the hydrocarbon substrate with a solution of initiator in MMA (peroxide concentration from 0,5% to 1,5% w/w) using a batch mixer at 150 and 170 °C. Hydrocarbon substrate/MMA ratio were varied from 70/30 to 60/40 w/w to reach nanostructuration when transposed to polymer modification according to the work published by Leibler[9] for PMMA/PA blends. In addition, for polyolefin backbones, the higher the monomer concentration is, the lower degradation and crosslinking are.[4,10]

PMMA derivatives, arising from the decomposition of the peroxy derivatives in a blend MMA/hydrocarbon substrate, were collected by filtration and purified by successive dissolution in chloroform and then precipitation in cold heptane. The solid we got was dried under vacuum and analysed by SEC using a Waters gel permeation chromatograph equipped with two low molecular weight Styragel columns (HR1 and HR4). It was performed using a 410 Waters differential refractometer, a 996 Waters photodiode array detector and a 515 Waters HPLC pump. As for THF, it was used as eluent at a flow rate of 1 mL/min. We needed linear PMMA standards for calibration. Contrary to the work published by Baker[11] dedicated to the peroxide initiated grafting of dimethylaminoethylmethacrylate onto squalane, the treatment of the media does not enable graft PMMA to separate from homopolymer. SEC traces of samples M1 to M5 (Table 1) were published earlier[12] and all of them present either a shouldering or a double peak which could be ascribed to coupling reactions. Chain end-group analysis by MALDI-TOF mass spectrometry of PMMA samples were also investigated and MALDI-TOF spectra displayed molar masses corresponding to cationic species such as methyl radical initiating chains with a termination by disproportionation and pentadecyl radical initiating chains with a termination by disproportionation.[12] These results suggest that the β-scission reaction of cumyloxyl radical gets better as the temperature increases, leading to the formation of methyl radicals. These latter preferentially initiate homopolymerization



Scheme 1.
General reactive pathways of free radical grafting of a vinyl compound from hydrocarbon substrate.

whereas cumyloxyl radicals are more prone to hydrogen abstraction from pentadecane.[4]

Experiments from M1 to M4 (Table 1) show that the more the temperature increases the lower the average polymerization degree of PMMA is.

We logically got the same results when the DCP concentration increases (M1/M3 and M2/M4). Besides, the monomer conversion is significantly affected by increasing temperature (M1/M2 and M3/M4). As a consequence, to get high molar mass PMMA with a higher monomer conversion, one should rather use low initiator concentration with a moderate temperature. These results highlight the deleterious influence of temperature on monomer conversion, suggesting that depropagation

Table 1.
Evolution of the PMMA polymerization degree according to the initial experimental condition.

Experiment	M1	M2	M3	M4	M5	M6	M7	M8
Pentadecane	70%w	70%w	70%w	70%w	60%w	55%w	49%w	–
Squalane	–	–	–	–	–	15%w	21%w	70%w
MMA	30%w	30%w	30%w	30%w	40%w	30%w	30%w	30%w
DCP	1,5%w	1,5%w	0,5%w	0,5%w	0,5%w	0,5%w	0,5%w	0,5%w
Temperature	150°C	170°C	150°C	170°C	170°C	170°C	170 °C	170°C
X_{MMA}	71%	42%	73%	43%	59%	46%	43%	49%
$\overline{DP_n}$	37	29	82	44	71	49	50	56
$\overline{DP_w}$	96	71	159	98	137	99	99	121

reaction could occur in these experimental conditions. As the temperature increases, this reaction limits the growth of the polymer chain, decreasing both the degree of polymerization and the monomer conversion. According to equation (1), the monomer concentration increases together with the ceiling temperature so that the depropagation reaction was not favoured. This was mainly noted when comparing experiments M4 and M5 (Table 1). Indeed, with a higher monomer concentration, monomer conversion and PMMA molar mass both increase.

The experiments M6 to M8, performed with an growing proportion of squalane, made it possible for us to study the influence of a transfer reaction and more specifically the role of the tertiary carbon atoms of the hydrocarbon substrate. The results (Table 1) reveal that the proportion of squalane has no significant effect (both on the monomer conversion and on the chain molar mass). Actually, the transfer reaction to the hydrocarbon substrate does not alter the kinetic chain length, nor the monomer consumption and the monomer conversion. Assuming a transfer reaction to the hydrocarbon substrate, we however expected a decrease of the molar mass of the PMMA synthesized.

The results of this model compound approach indicate that the preparation of grafts with a polymerisation degree higher than 50 would be possible, proviso controlling and decreasing temperature. Numerical simulation of the polymerization in the model aforementioned enables to fit these experimental results. The kinetic behaviour of this system is complicated and do not allow to take into account all the parameters in a simple numerical simulation, thus imposing some approximations. The aforementioned experimental model compound approach gives rise to two main experimental indicators (i.e. the monomer conversion, X_{MMA} and the polymerisation degree of the PMMA chains, $\overline{DP_n}$) and the formed PMMA species (grafted and non-grafted) have no influence on these indicators. It means that however the alkoxy radicals reacts (Scheme 1), this would mainly lead to homopolymerization. As a result, the simulation assumes that the initiator simply generates radicals R• (Scheme 1) that add to the monomer. This approximation enables to follow the well-known kinetic scheme of conventional radical polymerisation leading to equation 2.

$$X_{MMA} = 1 - \left(\frac{k_{-p}}{k_p[M]_0} + \left(1 - \frac{k_{-p}}{k_p[M]_0}\right) e^{\left[-2k_p \left(\frac{2f[I]_0}{k_t k_d}\right)^{1/2} \left(1 - e^{-\frac{k_d t}{2}}\right)\right]} \right) \quad (2)$$

Considering a depropagation rate coefficient k_{-p} equals to 0, equation (2) gives the usual expression of the monomer conversion for a conventional radical polymerisation system. The transfer reaction has no influence on the monomer conversion. However, the average polymerisation degree depends both on the kinetic chain length and on the transfer reaction

Table 2.
Kinetic parameters used in the simulation.

Rate coefficient	Value	Ea (J/mol)	Reference
$k_{d\ DCP}$	7.47 10^{15} s^{-1}	153644	[13]
k_p	2.65 10^6 L/mol · s	22309	[7,14]
$k_{recombinaison}$	1.06 10^7 L/mol · s	2930	[7]
$k_{dismutation}$	8.74 10^7 L/mol · s	2930	[7]
	Enthalpy of polymerisation:	$\Delta H^\circ = -54$ kJ/mol	[7]

to hydrocarbon substrates (equation 3).

$$\frac{1}{DP_n} = \frac{1}{DP_{n0}} + C_{TP} \cdot \frac{[P]}{[M] - \frac{k_{-p}}{k_p}} + C_{TS} \cdot \frac{[S]}{[M] - \frac{k_{-p}}{k_p}} \qquad (3)$$

$$DP_{n0} = \frac{k_p[M] - k_{-p}}{\frac{1+2\delta}{2(1+\delta)}\left(2 \cdot f \cdot k_t \cdot k_d[I]^{1/2}\right)}$$

Here, δ is the ratio of disproportionation and combination rate constants. C_{TP} and C_{TS} are the transfer constants to respectively pentadecane and squalane, defined by the ratio of the transfer and propagation rate constants.

Table 2 summarizes some rate coefficients and activation energy data obtained from literature[7,13–14]

Both calculation of X_{MMA} and $\overline{DP_n}$ depend on parameters such as f_{DCP}, Ea_{TP}, A_{TP} so that the fitting procedure of all these parameters is performed simultaneously using the least squares method. First, the sum of the squares of differencies between the theoretical value and the experimental value is calculated for X_{MMA} and $\overline{DP_n}$ from equations (4).

$$\sum \left[100^*(X_{MMA\_th} - X_{MMA\_exp})\right]^2; \quad \sum \left[\overline{DP_n}_{th} - \overline{DP_n}_{exp}\right]^2 \qquad (4)$$

Monomer conversions are calculated in base 100 to be of the same order of the $\overline{DP_n}$ values.

Then, the sum of squares of these sums is minimised using a Newton algorithm in order to determine the convergence of the simulation through a minimum. Consequently, the unity of monomer conversion is pondered as much as the unity of $\overline{DP_n}$ and considering the experimental errors on these parameters (~10% for both X_{MMA} and $\overline{DP_n}$), the fitting procedure remains consistent. Table 3 gives range values of some parameters involved in the fitting procedure in order to avoid the calculation of irealistic values. This fitting procedure succeeds in converging through a minimum (Table 4).

Another important conclusion is that it is correct to neglect the transfer reaction to the monomer. Indeed, at 150 °C, transfer rate coefficients in our experiments are somehow 10 times higher than the one[15] corresponding to the transfer reaction to the monomer (at 150 °C: $C_{TP} = 1.2\ 10^{-3}$, $C_{TS} = 0.8\ 10^{-3}$ and $C_{TMMA} = 1.0\ 10^{-4}$).

Figure 1 and 2 emphasizes the accuracy of the benchmark data. A good agreement between calculated monomer conversion X_{MMA}, mean polymerisation degree in number $\overline{DP_n}$, and the experimental ones (Figure 1a and 1b respectively). Moreover,

Table 3.
Fitted range values of some parameters for pentadecane.

Variable	Lower limit	Upper limit
100 f_{DCP}	1	100
$-\Delta S^\circ$	unconstrained	unconstrained
$A_{TP} \cdot 10^{-7}$	20	50
$Ea_{TP} \cdot 10^{-3}$	unconstrained	unconstrained

Table 4.
Fitted parameters for pentadecane.

Parameter	Value
A_{-p}	5.86 10^{12} s^{-1}
Ea_{-p}	76309 J/mol
A_{TP}	4.59 10^8 L/mol · s
Ea_{TP}	64227 J/mol
f_{DCP}	0.49
ΔS°	−121 J/mol · K

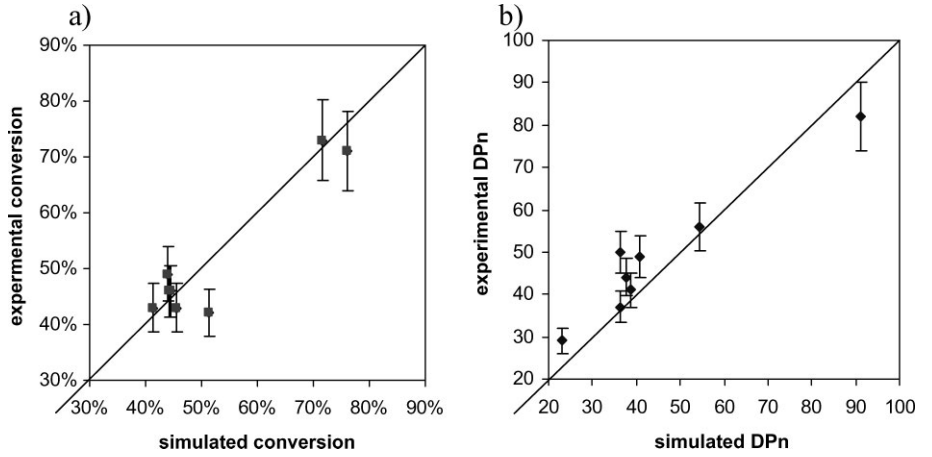


Figure 1.
Comparison between experimental and calculated data for *(a* monomer conversion and b) polymerization degree in the presence of transfer reaction.

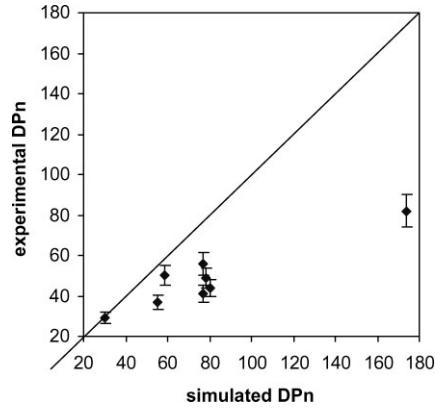


Figure 2.
Comparison between experimental and calculated data for polymerization degree without transfer reaction.

the sum of the square of differences between experimental and calculated values is of the same order of the experimental error (~10%). Therefore, the fitting procedure is satisfying enough regarding the experimental accuracy. Figure 2 points up the deviation between experimental and calculated values, if one assumes no transfer reaction to the hydrocarbon substrates.

Conclusion

Free radical melt grafting of methacrylic ester onto low molecular weight alkanes, both linear and branched, set up to chemically modify poly(ethylene-co-1-octene) appeared to induce alkane grafting from polymerization and homopolymerization. At high temperature, the graft propagation reaction seems to face up to a depropagation phenomenon, which would lower chain molar mass and monomer conversion. The low enthalpy of polymerization of MMA would promote this reaction in the 150–170 °C domain. Since chains with molar mass of about 5000 g/mol are produced, the propagation reaction is efficient in our conditions.

Based on a simplified chemical scenario using alkanes, the numerical simulation enabled to systematically tune the unknown or inaccurate kinetical parameters. Fitted parameters have been found to show excellent consistency, and so these results are recommended as constituting benchmarks for the grafting polymerisation of MMA from hydrocarbon backbone in the presence of a peroxide compound at elevated temperatures varying from 100 °C to 200 °C. The calculated monomer conversion and mean polymerisation degree confirm experimental data showing the strong influence of the depropagation reaction at temperatures up to 150 °C. Moreover, the numerical simulation suggests transfer reactions to hydrocarbon substrates: these reactions advantageously

initiate graft chains although decreasing the PMMA molar mass.

Symbols

$[I]$: concentration in initiator.
$[M]$: concentration in MMA.
$[P]$: concentration in pentadecane.
ΔH°: enthalpy of polymerization.
ΔS°: entropy of polymerization.
A_p: pre-exponential factor for propagation.
A_{-p}: pre-exponential factor for depropagation.
A_{TP}: pre-exponential factor for transfer reaction to pentadecane.
A_{TS}: pre-exponential factor for transfer reaction to squalane.
$\overline{DP_n}$: mean degree of polymerization in number.
DP_{no}: instant degree of polymerization number, with no transfer reaction.
$\overline{DP_{n\,exp}}$: experimental mean degree of polymerization in number.
$\overline{DP_{nth}}$: theoretical mean degree of polymerization in number.
Ea_p: activation energy for propagation.
Ea_{-p}: activation energy for depropagation.
Ea_{TP}: activation energy for transfer reaction to pentadecane.
Ea_{TS}: activation energy for transfer reaction to squalane.
f: initiator efficiency factor.
$k_{diproportionation}$: kinetical constant of disproportionation
k_p: kinetical constant of propagation.
$k_{combination}$: kinetical constant of combination.
k_T: kinetical constant of transfer
$[S]$: concentration in squalane.
X_{MMA}: monomer conversion
X_{MMA_th}: theoretical monomer conversion.
X_{MMA_exp}: experimental monomer conversion

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