BUTTERWORTH HEINEMANN

Polymer Vol. 36 No. 8, pp. 1597–1603, 1995

0032-3861/95/$10.00 + 0.00

Melt grafting of a basic monomer on to polyethylene in a twin-screw extruder: reaction kinetics

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(Received 13 June 1994; revised 20 August 1994)

The grafting of 2-(dimethylamino) ethyl methacrylate (DMAEMA) on to linear low-density polyethylene (LLDPE) using peroxide initiators was studied in an intermeshing co-rotating twin-screw extruder. The grafting reactions were carried out above the apparent ceiling temperature of the DMAEMA monomer. It was observed that above this ceiling temperature homopolymer propagation reactions are no longer occurring. The homopolymer initiation step was seen, however, to consume significant quantities of monomer, thus resulting in low grafting efficiencies (*GE*). Reducing the monomer concentration was shown to suppress the homopolymer initiation reaction and provide high grafting efficiencies with little loss in graft levels. It was also observed that initiator concentration controls the overall conversion and degree of grafting (*DG*) as well as crosslinking. Graft levels are therefore limited by the amount of crosslinking that can be tolerated in the final graft product.

(Keywords: reactive extrusion; melt grafting; amino methacrylate)

INTRODUCTION

The functionalization of polyolefins in the melt through grafting reactions is becoming an increasingly important industrial process. One of the classic examples of these reactions is the functionalization of polyolefins through the peroxide-induced grafting of malcic anhydride (MA)[1]. Because of the 1,2-disubstitution, MA is not readily polymerized under the conditions employed in grafting reactions and is therefore grafted at high efficiency without the accompanying formation of any homopolymer.

Most monomers do, however, readily homopolymerize under the conditions generally employed in grafting studies. The resulting competition between the homopolymerization and grafting reactions often leads to poor grafting efficiencies. The grafting efficiency relates the amount of monomer converted to graft to the total monomer converted to both graft and homopolymer and is defined as follows:

$$GE = \frac{\text{monomer converted to graft}}{\text{total monomer converted to graft and homopolymer}} \times 100\% \quad (1)$$

Examples of monomers which homopolymerize in addition to grafting include: acrylic acid, glycidyl methacrylate, hydroxypropyl methacrylate, and 2-(dimethylamino) ethyl methacrylate (DMAEMA). For most applications it would be desirable to reduce or eliminate the homopolymerization reaction in order to produce products which consist largely of graft material.

In our laboratories, we have been exploring the conditions for maximizing grafting and minimizing homopolymer formation in the peroxide-induced grafting of DMAEMA on to polyethylene. In initial studies[2–4] it was observed that although grafting is occurring it is for the most part overshadowed by the homopolymerization reaction, thus leading to poor grafting efficiencies.

Because of the difficulties in studying the details of the kinetics directly in a melt grafting process, low-molecular-weight analogue systems were examined in an effort to further our understanding of the grafting process[5,6]. In these studies, the kinetics of the peroxide-induced grafting of DMAEMA on to low-molecular-weight hydrocarbons were determined under much more controlled conditions than are attainable in the polymer melt.

These studies suggest that the main reactions in the grafting process are as follows:

$R'OOR' \rightarrow 2R'O^{\bullet}$	Initiator decomposition	(2)
$R'O^{\bullet} + P \rightarrow R'OH + P^{\bullet}$	Hydrogen abstraction	(3)
$P^{\bullet} + M \rightarrow PM^{\bullet}$	Graft initiation	(4)
$PM^{\bullet} \rightarrow P^{\bullet} + PMH$	Intramolecular H-abstraction	(5)
$PM_n^{\bullet} + M \rightarrow PM_{n+1}^{\bullet}$	Graft propagation	(6)
$R'O^{\bullet} + M \rightarrow R'OM^{\bullet}$	Homopolymer initiation	(7)
$M_n^{\bullet} + M \rightarrow M_{n+1}^{\bullet}$	Propagation	(8)
$M_{n+1}^{\bullet} \rightarrow M_n^{\bullet} + M$	Depropagation	(9)

plus, in addition, termination and crosslinking reactions.

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At lower temperatures (below 130°C) the homopolymerization reactions dominated the kinetics, leading to high-molecular-weight homopolymer and little grafting. As the temperature was increased, however, the increasing importance of the depropagation reaction (equation (9)) led to a decrease in both homopolymer formation and homopolymer molecular weights. From these studies the ceiling temperature for the polymerization of DMAEMA was estimated to be 170°C for a 0.5 M monomer concentration. Unlike the homopolymerization reaction, the rate of the grafting reaction continued to increase with increasing temperature, leading to an increase in the degree of grafting (*DG*). This *DG* parameter is a measure of the weight percentage of monomer bound in the final product and is defined as follows:

$$DG = \frac{\text{mass of DMAEMA grafts on substrate}}{\text{initial mass of substrate}} \times 100\% \quad (10)$$

The combination of decreasing homopolymer formation and increasing grafting led, in addition, to an increase in the *GE* with increasing temperature, i.e. in the fraction of the monomer converted to grafts compared with the total amount of monomer reacting to form both grafts and homopolymer.

The continued increase of the rate of grafting with temperature while the rate of homopolymerization is decreasing suggests different mechanisms for the two reactions[6]. Analysis of the grafted hydrocarbon revealed DMAEMA grafts of 1 to 2 monomer units, even under conditions where high-molecular-weight homopolymer was being formed. It was further seen that these grafts were concentrated on a fraction of the hydrocarbon molecules and not statistically distributed throughout the sample. This suggests that intramolecular H-abstraction (equation (5)) in which the PM$^{\cdot}$ radical abstracts a hydrogen atom from a $-CH_2$ group which is probably β to the branch carbon, plays an important role in grafting, overshadowing the graft propagation reaction. The importance of intramolecular hydrogen abstraction is widely reported for MA graft systems[7].

These model studies suggest that for grafting reactions carried out above the ceiling temperature the absence of homopolymerization should lead to high grafting efficiencies, analogous to MA grafting. Due to the nature of the experimental set-up and the close proximity of the boiling point of the DMAEMA monomer ($\sim$190°C) to the ceiling temperature, it was not possible, however, to examine the grafting behaviour above the ceiling temperature in these model studies[6].

Previously it was shown that these model system studies successfully predict the trends observed in melt grafting studies[8]. Grafting reactions carried out in the melt at high temperatures would therefore be expected to yield high grafting efficiencies. Through proper design it should be possible to work at these high temperatures in a twin-screw extruder. In this work, therefore, we seek to examine the grafting behaviour above the apparent ceiling temperature of the monomer in an intermeshing co-rotating twin-screw extruder. The influence of both monomer and initiator concentration on the grafting reaction at high temperatures is also presented. The development of the twin-screw extruder grafting process used in this study is presented elsewhere[9].

EXPERIMENTAL

Materials

2-(Dimethylamino) ethyl methacrylate (98%, Aldrich), inhibited with 2000 ppm *p*-methoxyphenol (MEHQ), and 1,1-di-(t-butylperoxy)-3,3,5-trimethylcyclohexane (92% minimum, Atochem (L231)) were used as received. The linear low-density polyethylene (Escorene 5103, Esso Chemical, Canada) was an ethylene/butene copolymer with a M_w of 58 000 and a polydispersity of 3.5. Proton nuclear magnetic resonance (^{1}H n.m.r.) spectroscopy indicated 7 wt% butene comonomer content. The density and melt flow index (*MFI*) are 0.925 g cm^{-3} and 12 g (10 min)$^{-1}$, respectively.

Twin-screw extruder system

The grafting reactions were carried out on a 30 mm Werner and Pfleiderer ZSK intermeshing co-rotating twin-screw extruder with an operating *l/d* of 39:1. Details of the screw design and the experimental set-up of the extrusion system are presented elsewhere[9]. The polymer was fed to the extruder by a loss-in-weight feeder with a nitrogen purge at the extruder hopper. Premixed monomer (0.5–5 wt%) and initiator (0.25–1 wt%) were added downstream to the polymer melt through a liquid-cooled injection line. Mixing of the liquid additives into the polymer melt was accomplished by using mixing gears backed up with a reversing element. The reaction occurred in a highly filled reaction zone as described elsewhere[9]. The extruder was operated with the heating and cooling units cycling at the barrel set point for a minimum of 20 min before sample collection. Unless otherwise stated, polymer throughput and screw speed were held constant at 40 g min^{-1} and 90 rev min^{-1}, respectively. Volatile residual reactants and reaction by-products were removed at a vacuum vent port downstream from the reaction zone. Two vacuum traps (in series) positioned in liquid nitrogen were used to collect the volatile material for analysis. Graft product was collected for analysis after extrusion through a water bath and pelletizing. For analysis of the *DG* and *GE* the extruder was operated without any vacuum.

Purification and analysis

Graft product. The graft product was purified three times by dissolving in refluxing toluene (0.25 wt% polymer solution), followed by precipitation into ten times the solution volume of methanol. The DMAEMA monomer, homopolymer and other reaction by-products remained dissolved in the methanol while the grafted and ungrafted polyethylene were precipitated out. The precipitate was filtered and dried in a vacuum oven. Homopolymer, monomer and other reaction by-products were recovered from the filtrate by rotoevaporation.

The purified DMAEMA-grafted polyethylene and unpurified graft product were dissolved in toluene-d_8 and analysed by ^{1}H n.m.r. on a Bruker AM 400 spectrometer. Spectra were determined at 393 K using a minimum of 120 scans. At least three samples were analysed for each extruder run.

The recovered homopolymer and reaction by-products were analysed by ^{1}H n.m.r. spectroscopy and size exclusion chromatography (s.e.c.). ^{1}H n.m.r. spectra were measured at room temperature in toluene-d_8 on a Bruker AM 400 spectrometer. Approximate molecular weights

were estimated from s.e.c. by comparing the retention times of 2 wt% solutions in THF against polystyrene (PS) standards on a Waters liquid chromatograph with three μ-styragel columns (10^4, 10^3, and 100 Å). Retention times of the very-low-molecular-weight materials were compared to that of pure DMAEMA. The polystyrene calibration gave a satisfactory estimate for the molecular weight of a poly(methyl methacrylate) standard[10].

An indication of the extent of crosslinking was obtained by measuring the melt flow index (*MFI*) of the purified DMAEMA-grafted PE with a Tinius Olsen Extrusion Plastometer under a load of 2160 g at 190°C (ASTM D1238).

Vacuum vent port material. The vacuum vent port material was separated into fractions by vacuum distillation in a Kugelrohr apparatus. Each fraction was analysed by ^{1}H n.m.r. spectroscopy, s.e.c. and gas chromatography–mass spectrometry (g.c.–m.s.). The g.c.–m.s. data were obtained on a Fisons GC8000 gas chromatograph connected to a Fisons VG Quatro mass spectrometer.

Haake batch melt grafting

Some grafting runs were performed on a Haake–Buchler batch melt mixer. The polymer, monomer and initiator were premixed and charged into the mixer, which was operating at 100 rev min^{-1} and the set temperature (150, 175, or 200°C). The run times used were 5 or 10 min at 150°C.

The stability of the grafted product was tested by adding unpurified graft product from the extruder runs to the Haake mixer, operating at 100 rev min^{-1} and 200°C, for run times of 2, 5 and 10 min.

RESULTS AND DISCUSSION

Analysis of degree of grafting and grafting efficiency

Figure 1 shows the ^{1}H n.m.r. spectra of (a) pure monomer, (b) graft polymer product and (c) purified graft material. The resonance at 4.2 ppm assigned to the $-O-CH_2-$ protons is not altered significantly for monomer, homopolymer and graft material[5]. Integration of this peak, relative to the polyethylene $-CH_2-$ (1.3 ppm) and $-CH_3$ (0.9 ppm) peaks, was used to determine the total DMAEMA (free monomer, DMAEMA-*g*-PE, and polyDMAEMA) content in the unpurified graft material (b) and the graft content (*DG*) of the purified graft material (c). The unreacted monomer content in the unpurified graft material was determined by integration of the resonances at 5.5 and 6.2 ppm for the two DMAEMA protons in the vicinity of the double bond. Subtraction of the residual unreacted monomer content from the total monomer content enabled the calculation of the total DMAEMA-*g*-PE and polyDMAEMA content (or total monomer conversion). The *GE* was calculated as the amount of DMAEMA converted to graft (c) over the total DMAEMA conversion.

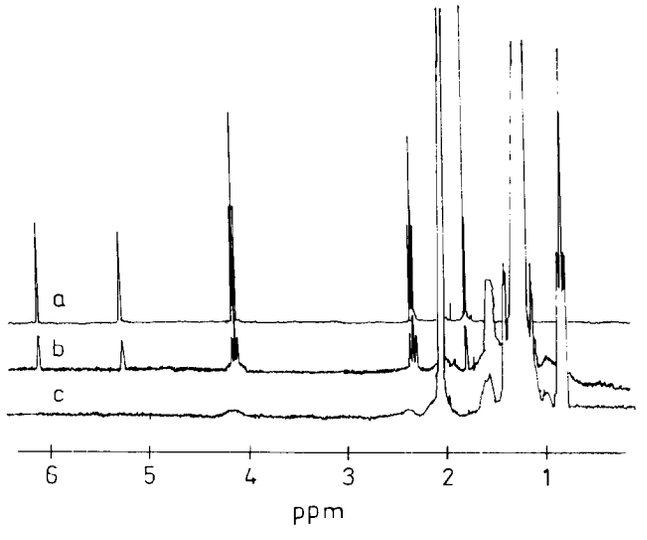

Figure 1 N.m.r. spectra of: (a) pure DMAEMA monomer; (b) unpurified graft product; (c) purified graft product

An overall mass balance revealed monomer losses of ~10–20%, with higher losses being observed at higher temperatures. Slightly higher losses are observed for runs with monomer and no initiator. There is considerable vaporization of monomer visible as the extrudate exits the die, which is certainly contributing to these losses. It is also observed that monomer is lost from the graft product the longer it is kept before analysis. For these reasons the conversion has been calculated based on the amount of reacted monomer found in the products and not on the residual unreacted monomer.

Reproducibility

Four extruder grafting trials (under identical conditions) were run over four months in order to determine the reproducibility of the extrusion process. The DMAEMA and L231 concentrations were 5 and 1 wt%, respectively, and the reaction zone temperature was approximately 200°C. The data are presented in *Table 1*. The standard deviations for the n.m.r. spectroscopic analysis of the *DG* are between ± 0.01 and ± 0.05 wt%. The observed variation in the *DG*s between different extrusion trials (0.49–0.60 wt%) is, therefore, within the accuracy of the spectroscopic analysis. The average *DG* for the four trials is 0.55 ± 0.05 wt%. There is also very good agreement between the calculated *GE*s for the four runs.

Table 1 Reproducibility of the extrusion grafting process[a]

Run	*DG* (wt%)	*GE* (%)	Conversion (%)
TS1A	0.56	–	–
TS1B	0.51	–	–
TS1C	0.54	–	–
TS1[b]	0.54 ± 0.03	27	40
TS2A	0.52	–	–
TS2B	0.55	–	–
TS2C	0.62	–	–
TS2[b]	0.56 ± 0.05	28	40
TS3A	0.48	–	–
TS3B	0.45	–	–
TS3C	0.54	–	–
TS3[b]	0.49 ± 0.05	26	37
TS4A	0.58	–	–
TS4B	0.59	–	–
TS4C	0.60	–	–
TS4[b]	0.59 ± 0.01	27	44

[a] All runs were carried out under the following conditions: 5 wt% DMAEMA; 1 wt% L231; 90 rev min^{-1}; 2.4 kg h^{-1}; 200°C
[b] Average values

Two different screw designs have been employed in this work. This leads to some differences in the *GE* and *DG* values for reactions which are otherwise run under the same conditions (run TS6, *Table 2* vs. TS8, *Table 3*) (see below). The details of the screw designs and an explanation of their grafting behaviour are presented elsewhere[9]. Data from one screw design are used to explain the temperature behaviour of the grafting reaction and from the other screw design to explain the influence of monomer and initiator concentration at a fixed temperature, so direct comparisons between results from the two screw designs are not made in this work.

Stability of the graft product

Unpurified graft material from the extruder runs was reprocessed on a Haake–Buchler batch melt mixer at 200°C for run times of 2, 5, and 10 min. No discernible change in the degree of grafting was observed, indicating that the graft product is stable under these conditions.

Influence of temperature on the grafting behaviour

Table 2 shows the grafting behaviour for a 5 wt% DMAEMA/1 wt% L231 system, in both the batch melt mixer and twin-screw extruder, as a function of reaction temperature. A comparison of grafting behaviour in the Haake and the twin-screw extruder has been presented previously[8]. The data for the batch melt mixer are included to show the grafting behaviour at 150°C. The batch melt mixer reaction time was set at 10 min to allow sufficient time for reaction. With the relatively high initiator half-life and short residence time of the extruder (~40 s in the reaction zone) no grafting was detected in the extrusion trials at this temperature (150°C).

In both systems, the *DG* and *GE* are seen to increase with increasing temperature. These increases with temperature were also observed in the model system studies[5,6] at temperatures below 160°C. As described previously, this was attributed to the onset of the depropagation reaction as the ceiling temperature was approached (estimated to be 170°C for 0.5 M DMAEMA). For the melt grafting runs above this temperature there would be expected to be little if any homopolymer formation and thus the *GE* values would be correspondingly high. The observed *GE*s, however, indicate significant consumption of monomer by processes other than grafting. This prompted a more detailed analysis of the reaction products to determine the nature of the monomer-consuming reactions above the apparent ceiling temperature.

At higher temperatures on the extruder (Run TS7, 220°C) the grafting efficiency is seen to drop off noticeably. The *DG*, however, is not affected. The reduced *GE* is, therefore, due to an increased consumption of monomer by processes other than grafting. There are a number of possible explanations for this behaviour. The higher temperatures may result in reaction of the monomer and initiator before proper mixing into the polymer melt. Temperatures in the injection and mixing zones are held constant in all screws, however, with the temperature varying only in the reaction zone. Differences in mixing before the point of reaction are therefore expected to be small for the different screws. Vaporization of monomer and initiator or initiator radicals is known to detract from the grafting reaction[9]. The screw used in this work was designed to minimize vaporization[9], but at these higher temperatures, however, vaporization may again be adversely affecting the grafting reaction. It is also possible that thermal initiation is beginning to play a role. This would consume monomer with little expected effect on the *DG*. Thermal polymerization of DMAEMA has been reported in the literature[11]. At high temperatures this reaction may, therefore, begin to play an important role in the grafting behaviour.

Table 2 Influence of temperature on the graft reaction[a]

Run[b]	Temperature (°C)	*DG* (wt%)	*GE* (%)
H1	150	0.4	15
H2	175	0.7	25
H3	200	0.8	31
TS5	175	0.6	25
TS6	200	0.9	42
TS7	220	0.8	26

[a] All runs are for 5 wt% DMAEMA, and 1 wt% L231
[b] H, Haake batch melt mixer; TS, twin-screw extruder

Analysis of homopolymer and reaction by-products. Size exclusion chromatography of the recovered homopolymer/reaction by-products for sample H1 (150°C, Haake) (see *Table 2*) revealed polyDMAEMA molecular weights in the region 2000–4000. These are slightly higher than the molecular weights observed in the model studies[5,6] under these conditions (2000) and have a much broader molecular-weight distribution. Higher molecular weights would be expected for homopolymerization occurring in the more viscous polymer melt because of the diffusion controlled termination reaction[12]. ^{1}H n.m.r. spectra of the recovered homopolymer, compared with the spectrum of polyDMAEMA prepared by free radical

Table 3 Influence of monomer and initiator concentration on the grafting reaction, with all runs carried out at 200°C

Run	Monomer concentration (wt%)	Initiator concentration (wt%)	*DG* (wt%)	*GE* (%)	Conversion (%)	*MFI* (g(10 min)$^{-1}$)
TS8	5	1	0.60	30	40	6
TS9	5	0.5	0.48	30	32	8
TS10	5	0.25	0.23	28	19	10
TS11	2.5	0.25	0.20	54	15	9.6
TS12	1	0.25	0.18	90	19	10
TS13	0.5	0.5	0.42	100	84	1.5

polymerization in bulk[10], confirmed that the recovered product was polyDMAEMA.

Analysis of sample TS6 (200°C, twin-screw) (*Table 2*) revealed no high-molecular-weight homopolymer, as expected for reactions above the ceiling temperature. Materials with retention times just below those of the pure monomer were, however, evident. As s.e.c. calibration at these low molecular weights is not expected to be very accurate, the molecular weights could only be estimated as corresponding roughly to DMAEMA dimers or trimers. The ^{1}H n.m.r. spectra of the reaction by-products are similar to that obtained for polyDMAEMA, although a number of additional peaks are evident. These are attributed to initiator decomposition products and initiator radicals which have added to the double bond of the monomer, as discussed below. The recovered reaction by-products for the batch melt grafting run at 200°C were similar to those found for the twin-screw grafting run.

It is observed, therefore, that for grafting reactions below the ceiling temperature polyDMAEMA is formed as a by-product of the reaction. Above the apparent ceiling temperature, however, there is no high-molecular-weight polyDMAEMA formed, although there is still a considerable consumption of monomer through the formation of low-molecular-weight materials. Analysis of the vacuum vent port material allowed more positive identification of these low-molecular-weight materials, which will be presented below.

Vacuum vent port material

As mentioned previously, the vacuum vent port was not operating in the extruder trials used to determine the *DG* and *GE* so that the complete reaction products were analysed. Under the conditions of TS6 (200°C) the vacuum vent port material was collected and analysed in an effort to further discern the products of the reaction above the ceiling temperature. Through separation into fractions and analysis by ^{1}H n.m.r. and g.c.–m.s. the main components (greater than 90%) were identified to be t-butanol and unreacted monomer. The formation of t-butanol is consistent with the t-butoxy radicals abstracting a hydrogen from the polymer backbone to produce PE macroradicals (see equation (3)). A referee has pointed out that hydrogen abstraction from the allylic position of the monomer may also be taking place, which can also result in t-butanol formation. A crude mass balance indicates $\sim 4 \times 10^{-3}$ mol of t-butanol per 100 g of PE. If the grafts are formed as single monomer units, as would be suggested by the model studies[6], then the amount of t-butanol produced corresponds well with the observed graft level of 3.5×10^{-3} mol of DMAEMA per 100 g of PE. No quantification of the amount of PE macroradicals that terminate by crosslinking can be made, however, to discern if there is any significant intramolecular hydrogen abstraction (equation (5)) occurring at these relatively high radical concentrations. As described previously, some evidence of intramolecular H-abstraction was observed in the model system studies[5,6].

In addition to the main products of t-butanol and monomer, some 10–20 additional products are evident in the g.c. trace. Although not all were positively identified a number are consistent with the expected by-products of the grafting reaction.

The mass peak at 231 is consistent with the addition of a t-butoxy radical to a monomer unit (equation (7)) followed by H-abstraction to quench the resulting radical. Above the ceiling temperature where propagation reactions are not likely, the reaction sequence just described is expected to be one of the main pathways (other than grafting) for the consumption of monomer.

At high temperatures, the β-scission of t-butoxy radicals to acetone and methyl radicals[13], as in the following:

$$(CH_3)_3CO^{\cdot} \rightarrow CH_3^{\cdot} + CH_3COCH_3 \qquad (11)$$

can be expected to occur to some extent. Although no methane or acetone is recovered there is a mass peak at 173, consistent with the addition of a methyl radical to a monomer unit followed by H-abstraction to quench the resulting radical. There is also a mass peak at 330 which is consistent with the addition of a second monomer unit before quenching takes place.

A second g.c. peak with mass 173 is also observed. This is believed to be due to the formation of the *N*-oxide of the monomer. This material is thought to be responsible for the discolouration of the graft product observed under many grafting conditions[14]. A mass peak at 190 is consistent with the oxidation of monomer that has been attacked by a methyl radical, followed by quenching of the resulting radical by hydrogen abstraction (expected molar mass, 189). This suggests that both oxidation of monomer (173) and attack on monomer by a methyl radical (173) are occurring.

N-oxides reportedly retard the polymerization of methyl methacrylate[1]. Substances which retard radical polymerizations have also been shown to inhibit grafting reactions[1]. Although no direct evidence for *N*-oxide retarding of the grafting reaction was found, it could explain the high initiator efficiency observed for a phenyl-azo initiator relative to peroxide initiators in a previous grafting study[14]. In this latter study the discolouration associated with the *N*-oxide of the monomer was present for graft systems using peroxide initiators but was not present for the phenyl-azo system where higher initiator efficiencies were observed. This would also suggest that the *N*-oxides are formed due to reaction with the peroxides or peroxide radicals, which would further reduce initiator efficiency. Extruder runs with just monomer and no initiator, in fact, show little discolouration relative to those with peroxide and the g.c. peak of mass 173 is very small. The *GE* for peroxide-induced grafting, however, remains higher than that observed in the phenyl-azo system, which could suggest that although monomer/peroxide interactions may be reducing initiator efficiency they do not seem to have a pronounced effect on the grafting efficiency. As discussed later, the proper choice of monomer and initiator concentrations appears to greatly reduce the formation of *N*-oxides.

Mass peaks consistent with the reaction products from the hydrolysis of monomer and amine oxide pyrolysis are also observed. These materials are, however, present in relatively small amounts and the reactions are, therefore, not thought to be playing a significant role in the grafting process.

Above the ceiling temperature, then, it is observed that the formation of DMAEMA homopolymer is not responsible for the low *GE*s. Instead, the major reaction consuming monomer other than grafting appears to be

the homopolymer initiation step (equation (7)) in which monomer is attacked by either t-butoxy or methyl radicals followed by quenching of the resulting radical, as follows:

$$(CH_3)_3CO^{\cdot} + M \rightarrow (CH_3)_3COM^{\cdot} \rightarrow (CH_3)_3COMH \quad (12)$$

$$CH_3^{\cdot} + M \rightarrow CH_3M^{\cdot} \rightarrow CH_3MH \quad (13)$$

Therefore, working just above the ceiling temperature of the DMAEMA is not sufficient to achieve high *GE* values.

It is interesting to note that the reaction by-products are essentially low-molecular-weight materials, and furthermore, that they may be removed from the graft product via the vacuum vent port. The *GE*s reported were for runs without any vacuum, and thus with proper optimization of the venting section (and perhaps gas stripping) much higher ratios of grafted to non-grafted material could be achieved.

Influence of monomer and initiator concentrations

Table 3 shows the influence of monomer and initiator concentration on the grafting reaction at a reaction temperature of 200°C. The screw design is different from that used for the results discussed in the previous section so that the *GE*s and *DG*s are not directly compared to those previously obtained for a 5 wt% monomer/1 wt% initiator system, at 200°C. Details of the screw design (screw 5) are presented elsewhere[9].

Runs TS8–TS10 show the influence of initiator concentration for a fixed monomer concentration of 5 wt%. As the initiator concentration is decreased from 1 to 0.25 wt% the *DG* falls off sharply, as does the total monomer conversion. The *MFI*, which is an indication of the extent of crosslinking, increases with decreasing initiator concentration, indicating a decrease in crosslinking. The *GE*, however, does not change over the range of initiator concentrations studied. These results show the same trends as observed in the model system studies[5,6] at lower temperatures.

Runs TS10–TS12 in *Table 3* show the influence of monomer concentration on the grafting reaction for a fixed initiator concentration of 0.25 wt%. As the monomer concentration is decreased from 5 wt% to 1 wt% the degree of grafting decreases only marginally, i.e. from 0.23 to 0.18 wt%. Given the accuracy of the n.m.r. spectroscopic analysis this difference may not be outside experimental error. The monomer conversion and *MFI* values are both unaffected by changing the monomer concentration. The *GE*, however, increases dramatically, from 28% at 5 wt% monomer concentration to 90% at 1 wt% monomer concentration. This indicates that consumption of monomer through the homopolymer initiation step can be essentially eliminated if low enough monomer concentrations are used. This is easily understood in terms of the kinetic scheme presented by Wong Shing *et al.*[5,6] (see Introduction). In the absence of propagation reactions, the ratio of the reaction rates for H-abstraction from the polymer to form a polymer radical (equation (2)) to that for attack of monomer by an initiator radical in the homopolymer initiation step (equation (6)) can be expected to be the major factor controlling the grafting efficiency. Even in the presence of homopolymerization, computer simulation has shown that the ratio of rate constants for these two reactions dominates the grafting behaviour[13]. As monomer concentration is decreased, then, the rate of the homopolymer initiation reaction is decreased, so leading to reduced monomer consumption via this route. As seen in *Table 3*, the *DG*s indicate that the grafting reaction is not greatly affected by reducing the monomer concentration. The combination of these two factors leads to an increase in the grafting efficiency.

Overall, it is seen that monomer concentration controls the *GE* (at a fixed temperature), while having only a small effect on the *DG*. The initiator concentration, on the other hand, largely controls the *DG*, overall conversion, and melt flow index (or crosslinking) without having any noticeable effect on the *GE*. This suggests that low monomer concentrations with as high an initiator concentration as is tolerable, based on the extent of crosslinking, should provide for both high *GE* and *DG* values.

Run TS13 in *Table 3* shows the grafting behaviour for a 0.5 wt% DMAEMA/0.5 wt% L231 system. Approximately 0.4 wt% (80%) of the DMAEMA ends up as DMAEMA-*g*-PE, with a *GE* of essentially 100%. With the proper choice of monomer and initiator concentrations, therefore, it is possible to achieve both high *GE* and *DG* values. The combination of low monomer concentrations and relatively high initiator concentrations does, however, lead to significant crosslinking, as evidenced by the low *MFI* value. Nevertheless, optimization of the monomer and initiator concentrations holds the potential for providing high *GE*s and reasonable *DG*s, with only moderate crosslinking. This would be attractive from an industrial standpoint.

Another attractive feature of operating at low monomer concentrations is that the discolouration associated with formation of the amine oxide of the monomer (seen at higher monomer concentrations) is greatly suppressed.

The essentially complete conversion of monomer to graft in run TS12, with no accompanying consumption of monomer through other paths, suggests that thermal initiation of homopolymerization is not occurring to any appreciable extent under these conditions.

CONCLUSIONS

At lower temperatures, homopolymerization detracts from the grafting reaction, thus resulting in low grafting efficiencies. As temperatures are increased above the apparent ceiling temperature of the monomer, high-molecular-weight homopolymer is no longer observed. The formation of low-molecular-weight material in the homopolymer initiation step, however, still leads to relatively poor grafting efficiencies. This reaction can be greatly suppressed by using low monomer concentrations, thus giving high grafting efficiencies (up to 100%). Relatively high initiator concentrations appear necessary, however, to obtain high degrees of grafting. Significant crosslinking is also occurring at these high initiator concentrations and so the level of peroxide that may be used is determined by the amount of crosslinking tolerable in the final graft product. With further optimization this process could, however, provide a commercially attractive route for the synthesis of a basic functionalized polyethylene.

ACKNOWLEDGEMENTS

The authors are grateful to the Ontario Centre for Materials Research (OCMR), Dupont Canada Inc., and

the R. S. McLaughlin Fellowship fund for financial support of this project. The authors also wish to thank Tom Hunter for performing the g.c.–m.s. analysis and R. A. Whitney for assistance in interpreting the g.c.–m.s. results obtained.

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