Melt grafting of t-butylaminoethyl methacrylate onto polyethylene

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The preparation of a polymer containing secondary amino groups by grafting of t-butylaminoethyl methacrylate (t-BAEMA) onto linear low-density polyethylene (LLDPE) in the melt has been investigated. Using a peroxide initiator, the effects of feed composition and reaction time were studied. Materials containing up to 3 wt% grafted t-BAEMA, 5 wt% t-BAEMA homopolymer and displaying minor crosslinking were obtained by the choice of appropriate feed composition and reaction conditions. Attempts were made to increase the degree of grafting and to minimize the homopolymerization by adding a variety of compounds. The homopolymerization was considerably reduced and relatively high grafting efficiency achieved by using *p*-benzoquinone as a chain terminator. Carbon tetrabromide, a chain transfer agent, suppressed polyethylene crosslinking but decreased grafting and increased homopolymerization. n-Hexane, known to be able to accelerate radiation-induced solution grafting of t-BAEMA onto a PE film, only accelerated t-BAEMA homopolymerization rather than grafting for this peroxide-initiated melt grafting case. Other compounds containing nitrogen, phosphorous or sulphur, known to be chain terminators for maleic anhydride and methyl methacrylate homopolymerization, acted only as inert additives. Preliminary studies on the potential interpolymer melt reaction between this graft polymer and acid polymers are also reported.

(Keywords: melt grafting; amino functionality; reactive processing; reactive blending; chain terminators)

INTRODUCTION

Over the last decade commercial interest has grown in chemically modifying existing polymers by grafting. In so doing, new or improved properties can be obtained without resorting to synthesizing new polymers. This has been particularly evident in the drive to modify commodity polymers such as polyolefins with acid functional monomers such as maleic anhydride. If done in a relatively efficient melt processing operation, economical, grafted polymers can be made for use as adhesives, coextrusion tie layers and compatibilizing agents for polymer blends.

Relatively few examples of copolymers exist that have nucleophilic 'basic' groups melt grafted onto the polymer backbone. Some work has shown that a few allyl compounds can be grafted onto atactic polypropylene in sealed glass ampoules[1]. More recently the melt grafting of a tertiary amine, i.e. 2-(dimethylamino)ethyl methacrylate (DMAEMA), onto linear low-density polyethylene (LLDPE) has been reported[2,3]. Blending this DMAEMA grafted polyethylene with a styrene–maleic anhydride copolymer resulted in blends with much finer morphology owing to a polar interaction[4].

The basicities of DMAEMA and its homopolymer and copolymers have been investigated. Values of the intrinsic dissociation contant of the amine $pK_0 = 8.14$ and 7.94 for DMAEMA monomer[5–7] and 7.60 for DMAEMA polymers[5] were much lower than the value of $pK_0 = 9.40$ for poly(vinyl amine)[8,9]. Interaction between the carbonyl and the amino group to form a cyclic conformation was believed to be responsible for the low pK_0 values of DMAEMA and its polymers[5,10]. In order to prepare compatibilized blends through reactive blending with acidic polymers, polymers having functional groups of strong basicity and nucleophilicity are desirable. In this sense, a potentially more useful secondary amine, namely t-butylaminoethyl methacrylate (t-BAEMA), which has a stronger basicity ($pK_0 = 9.12$)[6,7], was chosen for grafting in this work.

The homopolymer of t-BAEMA and its copolymer with styrene have been used as polybases to increase the viscosity of formic acid in the printing of wool with reactive dyes[11]. Radiation-induced grafting of t-BAEMA onto polyethylene in solution has been reported by Odian *et al.*[12,13]. In this work, melt grafting of t-BAEMA onto LLDPE is described. Preliminary studies on the potential interpolymer melt reaction between this graft polymer and acidic polymers will also be reported.

EXPERIMENTAL

Materials

The linear low-density polyethylene supplied by Esso Chemical Canada is an ethylene–butene copolymer with a density of 922.5 kg m^{-3}, a melt flow index of 4.2 dg min^{-1}, a weight-average molecular weight of approximately 85 000 and an M_w/M_n of about 4. Proton n.m.r. analysis indicated a comonomer content of 3.6 mol% butene. The LLDPE contained about 70 ppm of hindered phenol antioxidant.

t-Butylaminoethyl methacrylate (t-BAEMA), supplied by Pfaltz & Bauer, was used as received. Lupersol 130

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(L130), kindly supplied by Organic Peroxide Div. of Atochem NA, is a $\geqslant 90$ wt% solution of 2,5-dimethyl-2,5-di(t-butylperoxy)hexyne-3. Carbon tetrabromide, n-hexane, *N,N*-dimethylformamide, *N,N*-dimethylaniline, triphenyl phosphite, hexamethyl phosphoramide, *p*-tolyl disulphide and succinic acid from Aldrich Chemical Co. and *p*-benzoquinine from Sigma Chemical Co. were used as received.

The reactive polyethylene used is a copolymer of ethylene/acrylic acid containing 9 wt% acrylic acid supplied by the Dow Chemical Company (Primacor 1430). The reactive polystyrene used is a styrene/maleic anhydride (SMA) copolymer containing 6 wt% maleic anhydride supplied by Arco Chemical Company (Dylark 132).

Procedure and equipment

The melt grafting reaction was carried out in a Haake-Buchler mixer using Lupersol 130 as an initiator. All components, including LLDPE, t-BAEMA, the initiator and other additives such as CBr_4 or n-hexane, were preweighed, mixed into a homogeneous moist powder and then charged into the mixer, which was operating at 100 rpm and 150°C. The grafting reaction was also carried out in a ZSK30 intermeshing co-rotating twin-screw extruder with an L/D of 39:1. There were two sets of kneading elements, each with a short left-hand reversing section at its end. In this case, the initiator was dissolved in the monomer and the monomer/initiator solution was pumped into the extruder at an intermediate point just before the first set of kneading elements, where it mixed with the molten LLDPE. (The initiator and monomer were fed together rather than in sequence because in an earlier work[17] prefeeding the monomer resulted in lower grafting levels and prefeeding the initiator resulted in extensive crosslinking.) The mixture was allowed to react in the extruder for a specific residence time. The unreacted monomer was vacuum vented from the extruder just after the second set of kneading elements and before the reaction product exited the extruder through a die to be cooled and pelletized.

The reactive blending of the t-BAEMA grafted PE with the acidic polymers was carried out in the Haake mixer at 100 rpm and 200°C for about 20 min.

Purification and analysis

Reaction products were purified by first dissolving in refluxing toluene and selectively precipitating in 10 times the solution volume of methanol. The t-BAEMA homopolymer, unreacted peroxide and t-BAEMA monomer remained dissolved in the methanol solution, while grafted and ungrafted PE were precipitated out. The precipitated polymer was filtered, washed with more methanol and dried in a vacuum oven at 80°C. Successive reprecipitation showed that one step was adequate to remove the homopolymer.

The t-BAEMA grafted PE so purified was analysed by Fourier-transform infra-red (*FT*i.r.) and nuclear magnetic resonance (n.m.r.) to determine the degree of grafting, *DG*. Films compression moulded at 170°C and 2000 psi were analysed with a Bruker IFS85 spectrometer to obtain *FT*i.r. spectra. ^{1}H n.m.r. spectra were measured at 383 K in toluene-d_8 using a Bruker AM400 spectrometer. ^{13}C n.m.r. spectra in *o*-dichlorobenzene-d_4 at 383 K were obtained on a Bruker CXP200 spectrometer using a 45° pulse angle. The quantification of the competing reactions has been described elsewhere[3] and is summarized below. The monomer conversion, x, was measured gravimetrically. The grafting efficiency, GE, and the homopolymer content, w_h, were calculated from data for DG and x through a mass balance using the following equations:

$$GE = \frac{\text{weight of t-BAEMA grafts on PE}}{\text{weight of total converted t-BAEMA}} = \frac{(DG)w_p}{xw_m} \times 100 \quad (1)$$

$$w_h = \frac{\text{weight of homopoly(t-BAEMA)}}{\text{weight of reaction product}} = \frac{xw_m - (DG)w_p}{w_p + xw_m} \times 100 \quad (2)$$

where w_m and w_p are weight percentages of monomer and LLDPE, respectively.

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

Thermal properties of the starting polymers and the reaction products were measured with a Mettler TA3000 thermal analysis system equipped with a d.s.c. cell.

RESULTS AND DISCUSSION

Typical *FT*i.r. and ^{1}H n.m.r. spectra of purified reaction products are shown in *Figures 1* and *2*, respectively. The shaded areas in *Figures 1* and *2* are not observed in the corresponding spectra of the original LLDPE and are attributed to the t-BAEMA grafts. The absorption band at 1730 cm^{-1} is due to the carbonyl stretching of the methacrylic ester. This new peak is clear evidence of grafting but also indicates that t-BAEMA did not undergo the acyl transfer from amino methacrylate to hydroxyl methacrylamide, a possible reaction between the secondary amino group and the ester group contained in t-BAEMA[14,15]. The tertiary hydroxyl methacrylamide that might be produced from the acyl transfer reaction would give a carbonyl stretching absorption[16] at about 1670 cm^{-1}, which is not observed in *FT*i.r. spectrum of the t-BAEMA grafted product (*Figure 1*). This was further confirmed from the ^{1}H n.m.r. The argument that

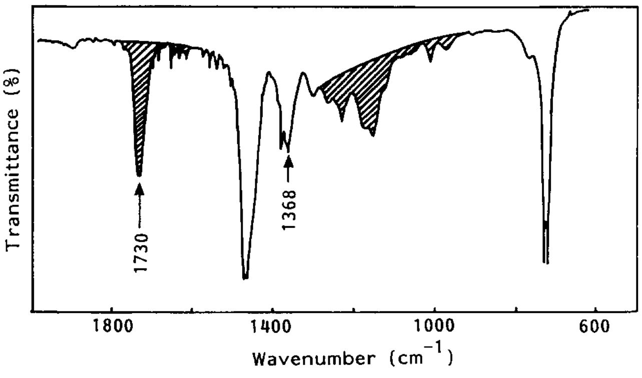


Figure 1 Infra-red spectrum of t-BAEMA grafted LLDPE; shaded areas are not observed in the i.r. spectrum of the original LLDPE

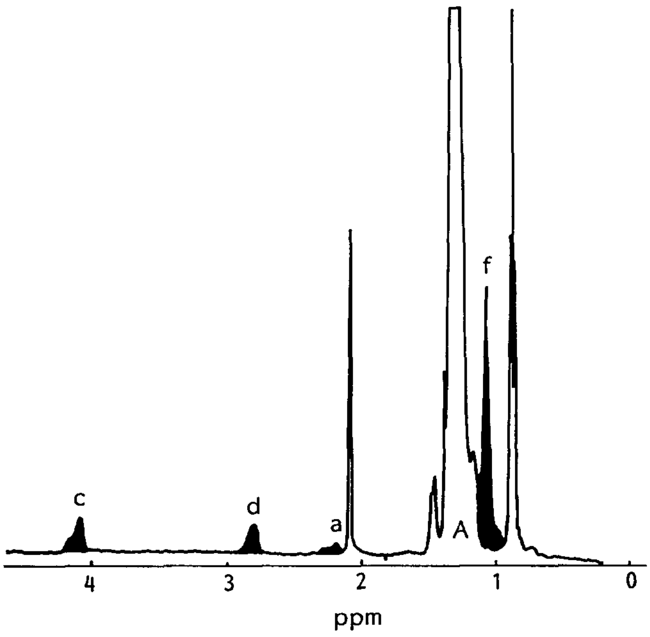


Figure 2 ^1H n.m.r. spectrum of t-BAEMA grafted LLDPE; shaded areas are not observed for the original LLDPE

the secondary amino group in t-BAEMA remains unchanged in the grafted product is further proved by the ability of this grafted material to react with carboxylic acid to form amide and amine salt, as will be discussed later when we consider reactive blending.

The peak height ratio of the C=O peak at 1730 cm^{-1} to that for the C–H peak at 1368 cm^{-1} in the *FT*i.r. spectrum (*Figure 1*) was used as a measure for the relative degree of grafting. Calibration for routine *FT*i.r. determination of the absolute degree of grafting was obtained from ^1H n.m.r. measurement.

The absolute degree of grafting, *DG*, was determined with the ^1H n.m.r. by comparing the integral of the resonance of the two protons on the methylene carbon attached to the nitrogen at 2.8 ppm (d) with that of protons on the PE backbones from about 1.1 to 1.4 ppm (A) (*Figure 2*). The resonance of the two protons on the carbon attached to the oxygen at 4.1 ppm (c) gave the same estimation of *DG*. A more accurate determination of *DG* might be expected using the strongest new resonance at about 1.1 ppm due to the nine amino-t-butyl protons (f), were it not that this resonance is partially overlapped by the resonance of the protons on the PE backbone spanning the range 1.1 to 1.4 ppm. The resonance due to the α-methyl protons (b), observed to be in the region of 1.2 to 1.5 ppm as a triple in the ^1H n.m.r. spectrum of the t-BAEMA homopolymer, is completely buried under the resonance of the protons on the PE backbone of the t-BAEMA graft copolymer. The small resonance at around 2.2 ppm in *Figure 2* can be assigned to the methylene protons (a) on the carbon attached to the PE backbone.

The ^{13}C n.m.r. spectra of the starting LLDPE, the t-BAEMA homopolymer and the t-BAEMA grafted PE was also obtained. The largest new resonance in the t-BAEMA grafted PE is a peak at about 29.1 ppm (*Figure 3*) due to the three methyl carbons in the t-butyl group. The other single carbon resonances due to t-BAEMA grafts on PE are also shown by the shaded areas in *Figure 3*.

In results similar to those of a previous study[3] involving grafting a tertiary amino methacrylate (DMAEMA), three competing reactions are observed during the melt grafting: homopolymerization of t-BAEMA, polyethylene crosslinking and the desired grafting of t-BAEMA onto polyethylene. In order to achieve high degrees of grafting with minimum homopolymerization, the effects of initiator concentration, monomer concentration and reaction time on these reactions were investigated. The results are summarized in *Table 1*. Increasing initiator concentration has little influence on the degree of grafting within the experimental range investigated but results in considerably more homopolymerization and crosslinking. The half-life of the L130 is 1.2 h at 150°C and 0.4 h at 160°C as measured in dodecane. Consequently, the amount of initiator breakdown is small under the experimental conditions used. However, in a blank test with only the initiator deleted from the experiment, no grafting was observed, confirming the active, but not optimized, role of the initiator.

The influence of monomer concentration can be seen more clearly with *Figure 4*. Both the degree of grafting and homopolymerization increased as monomer concentration was increased. Like DMAEMA, the t-BAEMA monomer also has the ability to suppress crosslinking of LLDPE chains by competing for initiator and polymer

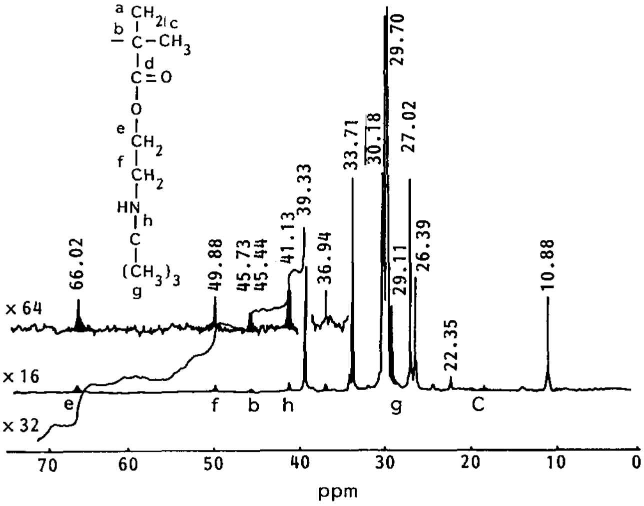


Figure 3 ^{13}C n.m.r. spectrum of t-BAEMA grafted LLDPE; shaded areas are not observed for the original LLDPE

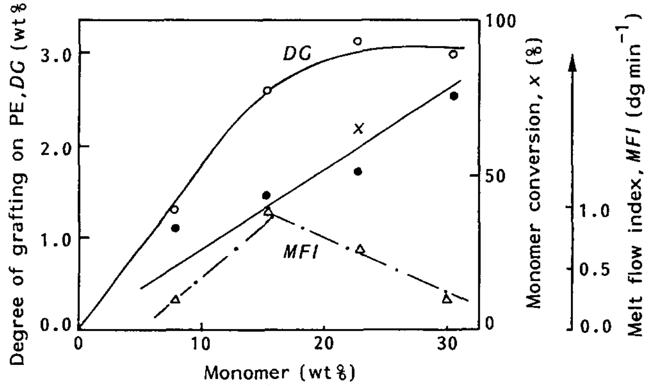


Figure 4 Influence of monomer concentration on the t-BAEMA grafting onto LLDPE; initiator concentration $w_i = 1.14$ wt%

Table 1 Grafting of t-butylaminoethyl methacrylate onto LLDPE. Runs that begin with an H designation were carried out in a Haake-Buchler mixer (batch reactor) at 100 rpm rotor speed and 150°C; and those beginning with T were carried out in a twin-screw extruder (continuous reactor) at 100 rpm screw speed and 160°C. The symbols t, w_m and w_i are reaction time and weight percentages of monomer and initiator, respectively

Run	t (min)	w_m (wt%)	w_i (wt%)	x (%)	DG (wt%)	GE (%)	w_h (wt%)	MFI (dg min^{-1})	$w_m(1-x)$ (wt%)
H101	10	22.8	1.14	52	3.1	20	10.9	0.64	10.9
H102	10	22.7	1.70	60	3.1	17	12.6	0.24	9.1
H103	10	22.8	0.57	47	3.0	21	9.7	1.6	12.1
H104	10	22.8	0.21	30	3.1	35	5.2	2.9	16.0
H105	10	7.6	1.14	33	1.3	48	1.4	0.22	5.1
H106	10	15.2	1.16	44	2.6	33	4.9	0.98	8.5
H107	10	30.4	1.14	77	3.0	9	23.1	0.24	7.0
H111	2	22.8	1.14	27	2.9	36	4.8	4.2	16.6
H110	5	22.8	1.14	57	3.1	18	11.9	1.3	9.8
H112	8	22.8	1.16	54	3.2	19	11.3	0.79	10.5
H113	12	22.8	1.16	55	3.3	20	11.3	0.69	10.3
H114	15	22.8	1.16	59	3.1	18	12.4	0.57	9.4
T101	2.4	22.8	0.57	32	1.6	15	7.3	2.3	9.8
T102	2.4	35.1	0.88	39	2.7	13	15.5	1.3	21.4
T103	2.4	22.5	0.92	38	1.3	12	8.8	0.91	14.0

radicals. This is well demonstrated by the increase in the melt flow index (MFI) in the small monomer concentration (w_m) range ($w_m < 15$ wt%, *Figure 4*). The decrease in MFI when $w_m > 15$ wt% can be attributed to the lower monomer concentration, a result of the significant increase in the total monomer conversion (x) with increasing w_m (*Figure 4*). High monomer conversion leads to a large decrease in the final monomer concentration, as is indicated by the term $w_m(1-x)$. Values of $w_m(1-x)$ are listed in the last column of *Table 1*. For example, the initial w_m of run H107 is high at 30 wt%. When the reaction is stopped 77% of this monomer was converted to polymer and the final monomer concentration $w_m(1-x)$ was just about 7 wt%, which is comparable to the initial w_m ($= 7.6$ wt%) of run H105. Thus, the extents of crosslinking from runs H107 and H105 are almost the same ($MFI = 0.2$ dg min^{-1}). However, it should be borne in mind that most of the crosslinking in run H107 probably occurred later in the reaction when high monomer conversion has been achieved, while the crosslinking in run H105 probably occurred from the beginning.

The influence of reaction time can be seen from the data for runs H101 and H110–H114 in *Table 1*. The degree of grafting remains unchanged for reaction times longer than 5 min but homopolymerization and crosslinking both continue to increase with increasing reaction time. In fact, most of the grafts obtained were formed before 2 min (run H111). Under the favourable conditions of run H111 one obtains up to 3 wt% grafting, about 35% grafting efficiency and little crosslinking ($MFI = 4.2$ dg min^{-1}).

The relatively high DG obtained in run H111 with a short reaction time (2 min) suggests the possibility of carrying out the melt grafting reaction in a twin-screw extruder, which is, in particular, suitable for short-residence-time reactions as a continuous reactor. Thus, runs T101–T103 were carried out in an intermeshing co-rotating twin-screw extruder operated at 100 rpm screw speed and 160°C. The results from these runs show that grafting in the extruder gave much lower degrees of grafting and more significant homopolymerization than those obtained in the batch reactor (the Haake mixer). The decreased grafting and increased homopolymerization in the extruder compared with in the batch reactor were also observed for the grafting with DMAEMA[17]. This may be attributable to initially separate phases of the polymer and monomer resulting from the different methods of adding reactants to the batch reactor and the extruder.

Evidence of two distinct glass transition temperatures and thermal transition peaks in d.s.c. thermograms from a sample of 3 wt% DMAEMA grafted LLDPE containing about 20 wt% of DMAEMA homopolymer suggests that poly(DMAEMA) is not miscible with LLDPE[18]. Considering the similarity in chemical structure between t-BAEMA and DMAEMA, it may be possible that poly(t-BAEMA) is also incompatible with LLDPE. In the case of the batch reactor, the monomer, the initiator and LLDPE were premixed and then charged into the reactor at the reaction temperature. The reacting system was initially well distributed and fairly homogeneous immediately after the LLDPE was melted. The homopolymerization competed with the grafting in this homogeneous system until a certain amount of homopolymer was produced, when the phase separation took place. Afterwards, the polymerization took place in two phases, one being rich in LLDPE and the other rich in the homopolymer. Only the monomer converted in the LLDPE phase had a chance for grafting, and all the monomer converted in the homopolymer phase would yield only homopolymer. As a result, the grafting efficiency would decrease after the phase separation. The decrease in the grafting efficiency could be great for unfavourable distributions of the monomer and the initiator between the two phases. This can serve to explain why the degree of grafting increased little after 2 min and the grafting efficiency decreased as the reaction time was further increased in the batch reactor. When the extruder was used as a continuous reactor, the solution of the monomer and the initiator was pumped

Table 2 Grafting of t-butylaminoethyl methacrylate onto LLDPE in the presence of different chemical additives carried out in a Haake-Buchler mixer (batch reactor) at 100 rpm rotor speed and 150°C for 10 min. The symbols w_m, w_i and w_a are weight percentages of monomer, initiator and additives, respectively

Additives[a]	Run	w_m (wt%)	w_i (wt%)	w_a (wt%)	w_a (mol%)	x (%)	DG (wt%)	GE (%)	w_h (wt%)	MFI (dg min^{-1})
	H101	22.8	1.14	0.0	0.0	52	3.1	20	10.9	0.64
n-Hexane	H120	20.7	1.17	1.5	0.63	48	3.0	23	8.9	0.70
	H121	16.3	1.16	5.1	2.8	67	2.6	19	10.0	0.29
	H122	11.8	1.19	8.5	3.4	79	2.2	18	8.7	0.97
	H123	22.8	1.14	1.8	0.77	57	3.0	18	12.1	0.61
	H124	22.8	1.14	6.7	3.0	75	3.1	14	15.8	0.86
	H125	22.8	1.14	14.1	6.8	92	2.9	11	19.4	1.2
CBr_4	H130	22.8	1.14	0.23	0.025	60	2.9	16	12.8	2.6
	H132	22.8	1.16	1.16	0.13	75	2.0	9	16.6	4.8
	H132′	22.8	1.14	1.17	0.13	73	2.1	10	16.1	4.7
	H133	22.8	1.14	2.28	0.25	87	1.2	5	19.8	5.4
DMF	H141	22.5	1.14	1.26	0.68	53	3.0	19	11.4	0.63
DMA	H143	22.7	1.14	0.44	0.13	56	3.1	19	11.5	0.68
TPP	H144	22.7	1.16	1.38	0.16	52	2.9	19	10.8	0.65
HMPA	H145	22.7	1.13	0.68	0.14	52	2.9	19	11.0	0.45
p-TDS	H146	22.6	1.15	0.86	0.13	64	3.0	16	13.5	0.61
p-BQ	H147	22.7	1.16	0.38	0.13	15	1.9	43	2.5	0.18

[a] DMF = dimethylformamide; DMA = *N*,*N*-dimethylaniline; TPP = triphenyl phosphite; HMPA = hexamethyl phosphoramide; *p*-TDS = *p*-tolyl disulphide; *p*-BQ = *p*-benzoquinone

into the extruder to mix with the LLDPE melt. Some homopolymer probably was produced before the monomer/initiator solution came into contact with the LLDPE melt. Despite the use of intensive mixing elements in the twin-screw extruder, some degree of phase separation between the monomer and polymer phases probably remained and the reacting system never reached a comparable homogeneous state as was the case for the batch reactor during the initial stage of the reaction. Consequently, decreased grafting efficiency and increased homopolymerization were observed in the extruder as compared with the batch reactor. In earlier work with DMAEMA[17] sequential additions of monomer and initiator to the twin-screw extruder were evaluated but no improvement in the grafting efficiency over simultaneous monomer/initiator addition was observed. Improved dispersive mixers at the feed point may help. More work is required to understand the phase relationships in these complex mixing regimes.

In order to increase the degree of grafting and reduce homopolymerization, a variety of chemicals, including a known graft promoting agent (n-hexane), a known chain transfer agent (CBr_4) and a known inhibitor (*p*-benzoquinone), were included with the reactants added to the Haake-Buchler system. The results are summarized in *Table 2*.

It was reported in the literature[12,13] that the use of n-hexane as a solvent in the radiation-induced grafting of t-BAEMA onto low-density polyethylene film increased the rate of grafting. The effect of n-hexane on the peroxide-initiated melt grafting of t-BAEMA onto LLDPE was therefore studied in this work in the expectation of achieving higher degrees of grafting. The results showed, however, that the degree of grafting was not affected by n-hexane. Rather, the homopolymerization of t-BAEMA was accelerated by the presence of n-hexane, leading to a lower grafting efficiency (*Figure 5*).

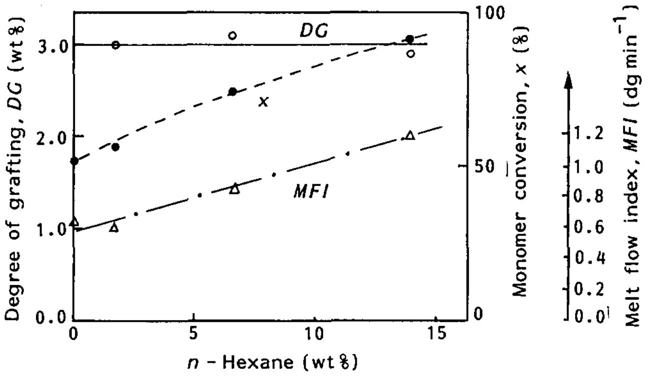


Figure 5 Influence of n-hexane on the t-BAEMA grafting onto LLDPE; $w_m = 22.8$ wt%, $w_i = 1.14$ wt%

In the presence of CBr_4, a known chain transfer agent, the degree of grafting decreased almost linearly while the monomer conversion increased with increasing CBr_4 concentration (*Figure 6*). This suggests that a chain transfer reaction occurred on the growing grafts, reducing the final graft chain length and increasing the number of growing homopolymer chains. On the other hand, the melt flow index of the grafted polyethylene increased significantly with increasing CBr_4 concentration, indicating that CBr_4 suppresses polyethylene crosslinking, possibly by reducing the concentration of radical sites on the polymer backbone. Some chain degradation may have occurred at high CBr_4 concentration (2.3 wt% in run H133) since the final value of *MFI* (5.4 dg min^{-1}) exceeded the *MFI* (4.2 dg min^{-1}) of the original LLDPE.

Compounds containing nitrogen, phosphorous or sulphur atoms, such as dimethylformamide (DMF), *N,N*-dimethylaniline (DMA), triphenyl phosphite (TPP), hexamethyl phosphoramide (HMPA) and *p*-tolyl disulphide (*p*-TDS), were reported to be capable of inhibiting the homopolymerization of maleic anhydride (MAH), retarding the homopolymerization of methyl methacrylate and preventing crosslinking/degradation, which normally accompanies MAH grafting on molten polymers[19]. Hence, the effects of these compounds on t-BAEMA grafting on molten LLDPE (runs H141–146) were also evaluated. The results in *Table 2* show, however, that these compounds have little influence on the t-BAEMA grafting. Essentially the same results as those without any of these compounds (run H101) were obtained for DMF, DMA and TPP, indicating that these three compounds acted only as inert additives in the grafting system. Although crosslinking increased somewhat in the presence of HMPA, as indicated by the slight decrease in *MFI* from 0.6 to 0.4 dg min^{-1}, both the degree of grafting and homopolymerization were not affected. In the presence of *p*-TDS, the homopolymerization increased, as indicated by the increase in monomer conversion from 52% to 64%, but both degree of grafting and crosslinking remained unchanged.

The results obtained by adding *p*-benzoquinone (*p*-BQ), a known polymerization inhibitor, are encouraging since the homopolymerization of t-BAEMA was greatly reduced. The decrease in the degree of grafting is relatively small (from 3 wt% to 2 wt%) compared with the decrease in homopolymerization (w_h from 10.9 wt% to 2.5 wt%), resulting in a relatively high grafting efficiency (43%). The relatively small decrease in *DG* is probably a result of reduced graft chain length accompanied by an increased number of grafts. The decrease in graft chain length is speculated because of the considerable reduction in t-BAEMA homopolymerization as *p*-BQ inhibited the propagation of t-BAEMA radicals. The increase in the number of grafts may be supported by the significant increase in crosslinking (decrease in *MFI* from 0.6 to 0.2 dg min^{-1}). It appears that *p*-BQ is likely to terminate the t-BAEMA radicals but not the radical sites on the PE backbones. Also, some of the t-BAEMA radicals may have been transferred by *p*-BQ to PE backbones, resulting in higher concentration of radical sites on the PE backbones for grafting and crosslinking.

The thermal stability of these graft-modified polymers was also evaluated. It is undesirable to produce a new functionalized polyethylene that is thermally less stable. Thermal analysis with d.s.c. was carried out as described in the 'Experimental' section. The second d.s.c heating scans of (1) the original LLDPE (Escorene), (2) Escorne processed alone and purified in the same way as a reaction run (EM20), (3) purified reaction product from run T102 (T102), and (4) crude reaction product from run T102 (T102C) are shown in *Figure 7*. The observed crystallinities, melting points and oxidation temperatures from these scans are summarized in *Table 3*. There

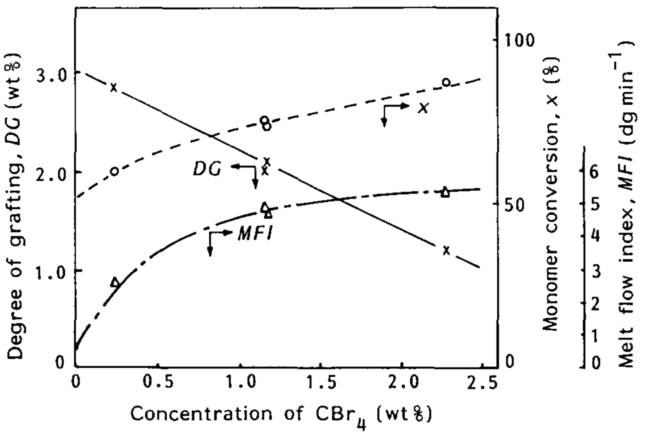


Figure 6 Influence of CBr$_4$ on the t-BAEMA grafting onto LLDPE; w_m = 22.8 wt%, w_i = 1.14 wt%

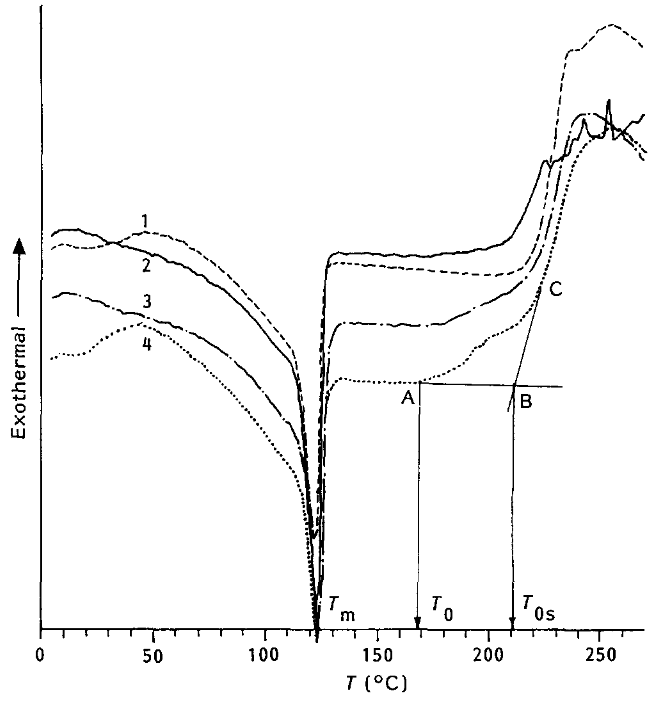


Figure 7 D.s.c. traces for (1) Escorene, (2) EM20, (3) T102 and (4) T102C

Table 3 D.s.c. results for the original LLDPE and t-BAEMA grafted LLDPE

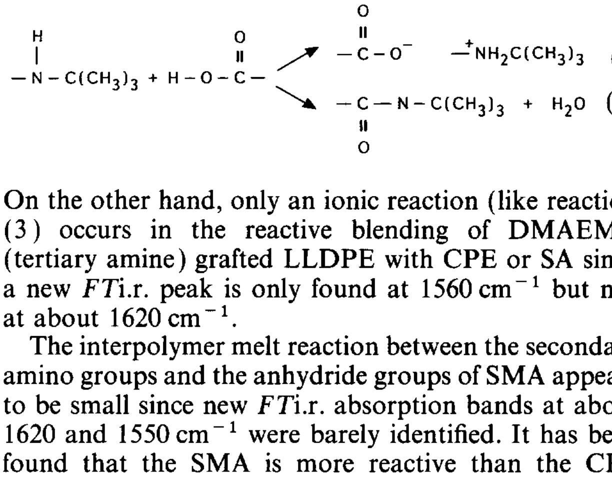
Sample[a]	Escorene	EM20	T102	T102C
Crystallinity (%)	35	40	34	39
Melting point, T_m (°C)	122	122	123	122
Onset oxidation temp., T_0 (°C)	203	175	180	168
Significant oxidation temp., T_{0s} (°C)	219	207	216	210
Pre-oxidation, ($T_{0s} - T_0$) (°C)	16	32	36	42

[a] *Escorene* = original LLDPE containing about 70 ppm of antioxidant; EM20 = pure LLDPE obtained by processing and purifying Escorene alone in the same way as a charge containing initiator and t-BAEMA; T102 = purified t-BAEMA grafted LLDPE from run T102; T102C = crude reaction product from run T102

appears, within the experimental errors, to be little difference in percentage crystallinity of the samples. The melting points of the samples are also essentially the same.

At point A after the melting of the samples was complete, an exothermic deviation from the baseline was observed (*Figure 7*) owing to oxidation of the samples. The temperature at which the onset of deviation from the baseline occurs, T_0, can be taken as a rough measure of the relative stability of the sample. However, significant oxidation did not begin until a higher temperature arrives. Therefore, the temperature at the intersection point (B) of the baseline (AB) and the tangential line (BC) of the sharp rising side of the oxidation exothermal peak, T_{0s}, illustrated in *Figure 7*, is probably a better indicator of the relative stability of the sample. Values of T_0 and T_{0s} are summarized in *Table 3*. The original Escorene contains about 70 ppm of antioxidants and therefore has highest values of T_0 and T_{0s}. When the antioxidants were removed as in sample EM20, T_0 and T_{0s} were reduced significantly. It is more reasonable to compare the stabilities of the grafted products with that of sample EM20. It appears that t-BAEMA grafted LLDPE is more stable than the original LLDPE since both T_0 and T_{0s} of sample T102 are higher than those of sample EM20. In fact, the value of T_{0s} (216°C) for sample T102 is comparable to that (219°C) for Escorene, indicating a mild antioxidant effect of grafted t-BAEMA to delay the significant oxidation. The decreases in both T_0 and T_{0s} for sample T102 may be attributed to the presence of initiator residue rather than t-BAEMA homopolymer in the crude reaction product. Some preoxidation has already taken place before the significant oxidation occurs. The extent of the preoxidation can be measured from the area of the region ABC shown in *Figure 7*, or estimated from ($T_{0s} - T_0$). It appears to increase with the increasing amount of t-BAEMA in the sample.

The reactivity of the secondary amino groups grafted on polyethylene with acid functional groups was studied by melt blending the t-BAEMA grafted polyethylene with (1) succinic acid (SA), (2) a polyethylene containing carboxyl groups (CPE) and (3) a styrene–maleic anhydride copolymer (SMA). A torque increase during blending was observed with SA but not with CPE or with SMA polymers. New *FT*i.r. peaks at 1617, 1559 and 1404 cm^{-1} were also observed for the model system of t-BAEMA grafted polyethylene blended with succinic acid (*Figure 8*), indicating that the SA was participating in an interpolymer coupling reaction. The interpolymer melt reaction between the t-BAEMA grafted polyethylene and the carboxyl groups on the CPE was clearly demonstrated by the corresponding new *FT*i.r. peaks at 1621, 1545 and 1404 cm^{-1} (*Figure 9*). The peak at 1621 cm^{-1}, a mixed mode of amide groups with an approximate potential energy distribution of 60% C=O stretching and 20% C–N stretching[20,21], is an indication of the formation of C–N covalent bonds. The relatively low frequency of the amide groups at 1621 cm^{-1} can be attributed to hydrogen bonding between the nitrogens of the amide groups and the hydroxyls of the carboxylic acid groups[20]. The peaks at 1545 and 1404 cm^{-1} are due to resonance stretching of the carboxylate anion[16,22], which is produced through the ionic interaction between the amino groups of t-BAEMA and the carboxyl groups of CPE or SA. Thus, the following two simultaneous reactions are proposed for the reactive blending of the t-BAEMA grafted LLDPE with CPE or SA:



$$-\overset{H}{\overset{|}{N}}-C(CH_3)_3 + H-O-\overset{O}{\overset{\|}{C}}- \begin{cases} \nearrow -\overset{O}{\overset{\|}{C}}-O^- \quad {}^{+}NH_2C(CH_3)_3 & (3) \\ \searrow -\underset{O}{\underset{\|}{C}}-N-C(CH_3)_3 + H_2O & (4) \end{cases}$$

On the other hand, only an ionic reaction (like reaction (3) occurs in the reactive blending of DMAEMA (tertiary amine) grafted LLDPE with CPE or SA since a new *FT*i.r. peak is only found at 1560 cm^{-1} but not at about 1620 cm^{-1}.

The interpolymer melt reaction between the secondary amino groups and the anhydride groups of SMA appears to be small since new *FT*i.r. absorption bands at about 1620 and 1550 cm^{-1} were barely identified. It has been found that the SMA is more reactive than the CPE towards small-molecule secondary diamines in the melt reaction[23]. Thus the limited extent of reaction between SMA and t-BAEMA grafted PE in this study can probably be attributed to the inaccessibility of the anhydride and the amino groups borne on the two incompatible polymer backbones (PS and PE respectively). Nevertheless, compatibility of t-BAEMA grafted polyethylene and polystyrene containing anhydride groups is expected to be improved, as suggested in the case of the blend of tertiary amine grafted polyethylene with SMA, which showed a much finer morphology[4].

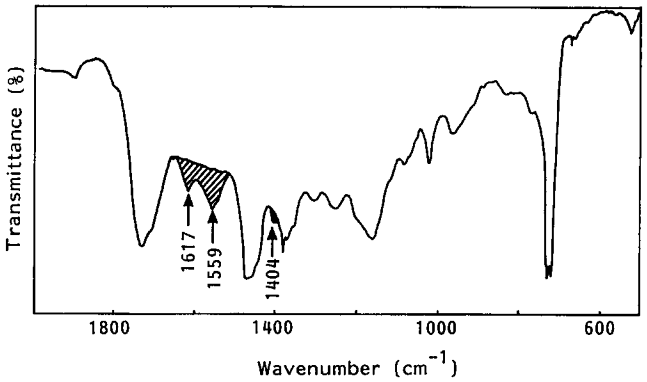


Figure 8 Infra-red spectrum of the blend of t-BAEMA grafted LLDPE and succinic acid; shaded areas are new peaks not evident in the blend components

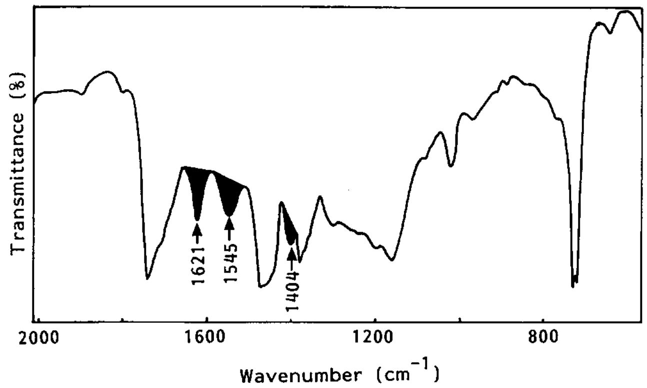


Figure 9 Infra-red spectrum of the blend of t-BAEMA grafted LLDPE and polyethylene containing carboxyl groups; shaded areas are new peaks not evident in the blend components

CONCLUSIONS

A secondary amine polymer capable of reacting with acidic polymers has been prepared by grafting t-BAEMA onto LLDPE in the melt. Under favourable conditions one obtains up to 3 wt% grafting, about 35% grafting efficiency and minor crosslinking. The addition of n-hexane did not affect the degree of grafting but did increase homopolymerization. CBr_4 has the effects of decreasing grafting, increasing the homopolymerization and suppressing PE crosslinking. Homopolymerization of t-BAEMA can be greately reduced and therefore relatively high grafting efficiency can be achieved with use of *p*-benzoquinone. The secondary amine in the t-BAEMA grafted LLDPE is capable of reacting with carboxylic acid to form both an amide group and amine salt.

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