

Basic Functionalization of Molten Linear Low-Density Polyethylene with 2-(Dimethylamino)ethyl Methacrylate in an Intermeshing Corotating Twin-Screw Extruder

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Synopsis

Functionalization of molten linear low-density polyethylene (LLDPE) with 2-(dimethylamino)ethyl methacrylate (DMAEMA) was studied in an intermeshing co-rotating twin-screw extruder using a peroxide initiator. The influence of monomer concentration, initiator concentration, reaction temperature, the screw speed, and the mean reaction residence time on the grafting reaction was investigated in order to determine the reaction conditions necessary to obtain a controlled degree of grafting, DG, while minimizing homopolymerization and crosslinking. Relatively high grafting levels can be obtained without excessive polyethylene crosslinking by using high monomer concentrations, w_m , with low initiator concentrations, w_i . DG increased with increasing monomer concentration when w_m exceeded a certain value. Processing temperatures between 130 and 160°C are optimal to achieve high grafting efficiency, GE. Too high a processing temperature resulted in both low DG and GE. An optimal reaction residence time of about 5 min was found for $w_m = 23$ wt % and $w_i = 0.56$ wt % to obtain relatively high DG and GE. The melt flow index of the reaction product, *MFI*, increased with increasing w_m at constant w_i . This suggests that the DMAEMA monomer has the ability to suppress crosslinking of the LLDPE chains. The ability of the DMAEMA monomer to compete for initiator and polymer radicals and reduce LLDPE crosslinking was further demonstrated by the study of sequential addition of monomer and initiator along the extruder. The competition among the three reactions (i.e., the desired grafting, homopolymerization, and crosslinking) is discussed.

INTRODUCTION

Preparation of a tertiary amine functionalized polymer by grafting 2-(dimethylamino)ethyl methacrylate (DMAEMA) onto molten linear low density polyethylene (LLDPE) in a batch-type reactor has been reported in previous papers.^{1,2} Reactive blending of this DMAEMA grafted LLDPE with acidic polymers such as a styrene-maleic anhydride copolymer resulted in blends with much finer morphology.³ Because of potential industrial use of this amine functionalized polymer in compatibilized polymer blends and adhesives, it is of interest to scale up the grafting process in a continuous reactor. The grafting experiments in the batch reactor have shown that a relatively high degree of grafting can be obtained in a short reaction time. This suggests that the grafting reaction may be carried out in a twin-screw extruder which can serve as a continuous reactor for short residence time melt reactions.

The use of conventional single- or twin-screw extruders as mini-reactors to obtain new polymer materials with decisive property enhancement has recently

received much attention.^{4,5} Although many studies involving reactive extrusion are included in recent patents, relative few such studies are reported in the open literature.⁶⁻¹⁴ *In situ* polymerization of caprolactam in an intermeshing corotating twin-screw extruder was reported by Bartilla et al.⁶ Sulfonation of EPDM was carried out in a single-screw extruder⁷ while crosslinking of poly(arylene ether ketones) was achieved in corotating and counterrotating twin-screw extruders.⁸ Aharoni et al. reported the molecular weight increase of poly(ethylene terephthalate)⁹ and polyamides^{10,11} in the presence of triphenyl phosphite during extrusion in a single-screw extruder. Reactive extrusion, involving the addition of peroxides, has been used in the degradation of polypropylene to control molecular weight and molecular weight distribution.^{12,13} Direct functionalization of molten polymers in a twin-screw extruder has potential economic advantages over solution copolymerization in a conventional reactor since it does not require an entirely new facility and the costs of solvent recovery are eliminated.

The scaling up of the graft functionalization reaction from a small batch melt reactor, such as a Haake Buchler mixer to a continuous melt reactor, such as a twin-screw extruder is complicated because it offers the potential for variable temperature and mixing intensity, and sequential reactant addition while losing the potential for long reaction time. Indeed, the results obtained from the batch reactor may not be applicable to the continuous reactor especially when a heterogeneous system is involved. A typical example of kinetic behavior in a continuous stirred tank reactor being quite different from those in a batch reactor is emulsion polymerization.¹⁵ Therefore, it is desirable and necessary to study the functionalization processing directly in a twin-screw extruder to provide more useful data for continuous reactor scale up. In this study, the functionalization of LLDPE with DMAEMA was carried out in a 30 mm twin-screw extruder, operating as a continuous melt reactor. The objective of this study is to determine the process conditions which give controlled degrees of grafting while minimizing homopolymerization and crosslinking.

EXPERIMENTAL

Materials

The linear low density polyethylene supplied by ESSO Chemical Canada (LLDPE) is an ethylene-butene copolymer with a density of 922.5 kg/m³, a melt flow index of 4.2 dg/min, a weight average molecular weight of approximately 85,000, and an M_w/M_n of about 4. Proton NMR analysis indicated a comonomer content of 3.6 mol % butene.¹ The LLDPE contained about 150 ppm of hindered phenol antioxidant.

2-(Dimethylamino)ethyl methacrylate (DMAEMA), Aldrich reagent grade product, was used as received. Lupersol 130 (L130), kindly supplied by Pennwalt Corp. is a ≥ 90 wt % solution of 2,5-dimethyl-2,5-di(*t*-butylperoxy)hexyne-3.

Grafting Procedure

Grafting reactions were carried out in a ZSK 30 intermeshing corotating twin-screw extruder made by Werner & Pfleiderer Corp. The extruder is

equipped with three liquid injection ports and a vacuum venting port. Temperature control along the extruder is enhanced by cooling water in the barrel wall. The inner diameter of the barrel, D , is 30 mm. The total processing length of the extruder is $39D$.

The whole processing apparatus with one reactant addition point is shown schematically in Figure 1. The LLDPE powder was fed into the extruder by a K-Tron volumetric feeder through a hopper located in the one end of the extruder (feeder 1). A solution of monomer and initiator in a fixed proportion was fed, at ambient temperature, into the molten LLDPE through a liquid injection port, located $11D$ downstream from feeder 1, by a Model 5596 Zenith metering gear pump (feeder 2). The monomer/initiator solution was prepared by mixing the preweighed monomer and initiator and was stored in a dispensing tank for the Zenith gear pump. The combined reactants passed through a reaction zone of $20D$ in which 4 different sets of kneading blocks were located for intensive mixing. At the end of the reaction zone any unreacted monomer was removed by vacuum through the vent port. The final reaction product exiting from a die at the end of the extruder passed through a water bath and was pelletized with a Killion pelletizer.

Because of the starve fed nature of this device, the residence time of the processed material in the extruder depends mainly on its feed rate and the screw configuration and is nearly independent of the screw speed. The residence times were measured using a color tracer technique. The mean reaction residence time used in this paper is the elapsed time in the reaction zone between the liquid injection port where the initiator was fed, either in the monomer solution (Fig. 1) or in a mineral spirit solution (to be discussed later), and the vacuum venting port.

Individual experiments were run for more than 3 mean residence times to reach steady state for sampling. Analysis of these experiments showed that the degree of grafting, the monomer conversion and the melt flow index reach their steady-state values after 3 mean residence times (Fig. 2).

Analysis

The monomer conversion was measured gravimetrically. The vacuum pump was turned off for about 1 mean reaction residence time for the monomer conversion sampling. The reaction mixture exiting the die was then sampled and pressed into a thin sheet between a piece of folded aluminum foil when the sample was still in the molten state. This sample, wrapped between the folded

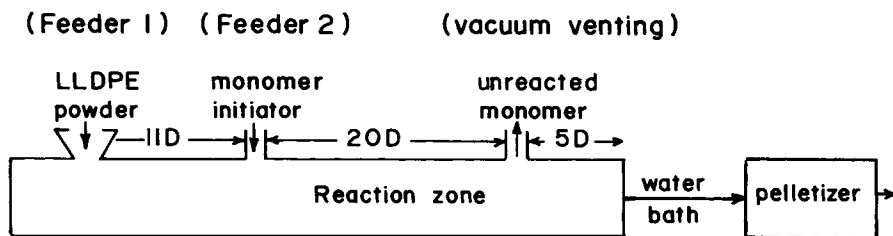


Fig. 1. Scheme of processing apparatus with mode 1 of monomer and initiator addition.

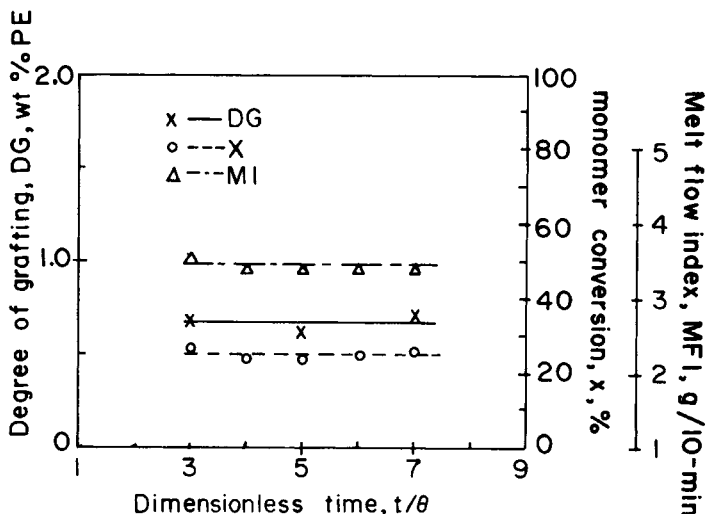


Fig. 2. Values of the degree of grafting, DG, monomer conversion x , and the melt flow index, MFI, for samples taken at different reduced time, t/θ , with mean residence time θ equal to 1.6 min. Monomer weight fraction = 0.23, initiator weight fraction = 0.0056, screw speed = 300 rpm, and processing temperature = 160°C.

aluminum foil, was weighed and then put in a vacuum oven at 80°C for drying to constant weight. The monomer conversion was then calculated from the weight loss through a mass balance.

In order to measure the degree of grafting (DG), samples of the pellet product were predried in a vacuum oven at 80°C to remove residual monomer. The dried samples were dissolved in refluxing toluene at a maximum concentration of 4 wt %. The polymer solutions were precipitated dropwise with stirring in 10 volumes of methanol, filtered and dried in a vacuum oven at 80°C. The Fourier transform infrared (FTIR) spectra of the purified grafted materials were measured with a Bruker IFS85 spectrometer at a resolution of about 1 cm^{-1} . The ratio of the peak height at 1730 cm^{-1} for the DMAEMA functional groups to the peak height at 1368 cm^{-1} for PE backbone was used to determine the degree of grafting after being calibrated using NMR.¹ The degree of grafting (DG) is expressed as the weight percentage of DMAEMA grafts based on the weight of the original LLDPE backbone.

The grafting efficiency, GE, and the weight percent of homopolyDMAEMA in the final reaction product, w_h , were calculated from the monomer conversion, x , and the degree of grafting, DG, using the following equations:

$$\text{GE} = \frac{\text{weight of DMAEMA grafts on PE}}{\text{weight of total converted monomer}} = \frac{DG \cdot w_p}{x \cdot w_m} \times 100 \quad (1)$$

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

where w_m and w_p are weight fractions of monomer and LLDPE, respectively, in the initial feed reactant mixture. Values of w_m and w_p were calculated from the feed rates of LLDPE and the monomer/initiator solution.

The melt flow indices (MFIs) of the pelletized raw products and the purified grafted materials were measured at 190°C using a Tinius Olsen extrusion plasmometer with a load of 2160 g (ASTM D1238, cond. E).

RESULTS AND DISCUSSION

Comparison With Results from the Batch Reactor

The grafting results obtained with reactant addition mode 1 (Fig. 1) in the twin-screw extruder are summarized in Table I. For comparison, a few data (run numbers beginning with H) obtained from the Haake batch mixer are also listed in Table I. In general, the extruder gave a lower degree of grafting (e.g., DG = 1.5 wt % from run 03) than the batch mixer (e.g., DG = 3.2 wt % from run H21) in similar reaction conditions. Also, the extruder (run 03) gave higher monomer conversion ($x = 44\%$) and therefore lower grafting efficiency (GE = 12%) than that obtained in the batch mixer ($x = 34\%$ and GE = 44% from run H21). The above stated differences are further confirmed by comparison of the data from runs 21–25 with the data from runs H20–H25 carried out at various reaction residence times. In spite of the lower initiator concentration used, runs 21–25 in the extruder achieved higher monomer conversions and therefore lower grafting efficiencies than did runs H20–H25 in the batch mixer when the data at the same reaction time are compared. Experiments from both the batch mixer and the twin-screw extruder have shown that the initiator concentration has little influence on the degree of grafting at monomer concentration above 20 wt %. Thus the fact that the degrees of grafting obtained from runs 21–25 are lower than those from runs H20–H25 results mainly from using different reactors and not from the different initiator concentration.

The functionalization of LLDPE with DMAEMA involves three competing reactions: (1) the desired grafting of DMAEMA onto LLDPE backbones; (2) homopolymerization of DMAEMA; and (3) crosslinking of ungrafted and/or grafted LLDPE. There is only a minor difference in the extent of crosslinking between runs carried out in the extruder and in the batch mixer as can be seen from the melt flow index (MFI) data from run 03 (2.5 dg/min) and run H21 (3.5 dg/min). The lower DG and GE obtained in the extruder suggests significant domination of the homopolymerization over the desired grafting in the twin-screw extruder compared to the batch mixer. One possible reason for this could be that the monomer/initiator solution is insoluble in the melt and does not as intimately contact the polymer in the extruder compared to the batch mixer. Other factors which may be responsible for the decreased grafting and increased homopolymerization in the twin-screw extruder include residence time distribution, backmixing, and temperature profiles across and along the extruder. Exactly how these factors influence the competition between the grafting and homopolymerization still remains unknown. Nevertheless, the fact that the continuous reactor and the batch reactor gave different results justifies the importance of detailed investigation of the functionalization processing in a twin-screw extruder reported in this paper.

Influence of Monomer Concentration and Initiator Concentration

In order to show the effects of monomer concentration, the data of runs 01–04 are plotted in Figures 3–5. The data of runs 01–04 listed in Table I are each

TABLE I
Functionalization of LLDPE with DMAEMA in the Twin-Screw Extruder
with Reactant Addition Mode 1^a

Run #	θ (min)	T (°C)	RPM (rpm)	w_m (wt fraction)	w_I^b	x (%)	DG (wt %)	GE (%)	w_h (wt %)	MFI ^c (dg/min)
H14	7	160	100	0.23	0.011	—	2.5	—	—	—
H20	2	160	100	0.23	0.011	20	2.6	47	3.4	(3.9)
H21	3	160	100	0.23	0.011	34	3.2	44	5.6	(3.5)
H22	4	160	100	0.23	0.011	43	3.2	35	7.8	(3.5)
H23	6	160	100	0.23	0.011	46	2.3	18	10.6	(1.5)
H24	10	160	100	0.23	0.011	54	2.2	10	15.5	(1.6)
H25	15	160	100	0.23	0.011	61	2.2	12	14.1	(1.1)
01	2.4	160	200	0.081	0.011	65	1.6	27	4.0	0.6 (0.08)
02	2.4	160	200	0.16	0.011	55	1.6	16	7.8	1.7 (0.44)
03	2.4	160	200	0.22	0.011	44	1.5	12	9.8	3.8 (2.5)
04	2.4	160	200	0.28	0.011	41	1.8	11	12	4.8 (3.2)
05	2.4	160	200	0.15	0.0075	48	1.3	14	7.0	2.8
06	2.4	160	200	0.23	0.0075	39	1.0	9.0	9.6	4.2
07	2.4	160	200	0.30	0.0075	29	1.9	17	11	4.0
08	2.4	160	200	0.13	0.0063	50	1.2	17	5.7	2.6
09	2.4	160	200	0.19	0.0063	40	1.0	12	7.8	3.8
10	2.4	160	200	0.25	0.063	31	1.5	15	8.6	3.9
11	2.4	160	200	0.10	0.0050	51	1.1	20	5.2	2.2
12	2.4	160	200	0.15	0.0050	40	0.9	13	6.2	3.5
13	2.4	160	200	0.20	0.0050	32	1.2	14	6.8	3.8
14	2.4	160	200	0.16	0.0055	38	0.9	12	6.2	3.3
15	2.4	160	200	0.23	0.012	50	1.5	10	11.8	3.8
16	4.9	160	300	0.46	0.012	52	3.9	8.5	22.3	—
21	1.6	160	300	0.23	0.0056	27	0.7	8.8	6.6	3.5
22	2.5	160	300	0.23	0.0056	33	0.8	8.2	8.1	3.7
23	4.0	160	300	0.23	0.0056	45	1.2	9.3	10.5	3.2
24	5.9	160	300	0.23	0.0056	53	1.3	8.5	12.3	3.3
25	11	160	300	0.23	0.0056	74	1.1	5.0	16.9	3.5
30	2.4	160	200	0.098	(30)	44	0.8	17	3.8	3.1
31	2.4	160	200	0.17	(30)	38	0.9	12	6.2	3.3
32	2.4	160	200	0.24	(30)	39	1.0	8.0	10	4.3
33	2.4	160	200	0.30	(30)	38	1.3	8.0	13	4.5
34	2.4	130	200	0.092	(30)	34	0.7	19	2.7	2.8
35	2.4	130	200	0.17	(30)	31	0.7	12	5.2	3.0
36	2.4	130	200	0.23	(30)	32	0.9	9.4	8.1	2.8
37	2.4	130	200	0.29	(30)	32	1.6	13	10	1.8
38	2.4	190	200	0.092	(30)	48	0.7	14	4.0	3.1
39	2.4	190	200	0.17	(30)	43	0.6	6.9	7.5	3.5
40	2.4	190	200	0.23	(30)	46	0.8	6.0	12	4.3
41	2.4	190	200	0.29	(30)	45	1.2	6.4	15	4.9
42	2.4	160	100	0.16	(30)	36	0.9	12	6.6	3.3
43	2.4	160	200	0.16	(30)	38	0.9	12	6.2	3.3
44	2.4	160	300	0.16	(30)	42	1.2	15	6.6	2.9
45	2.4	160	400	0.16	(30)	42	1.1	13	6.7	3.9
46	2.4	160	100	0.16	(40)	25	1.0	19	3.9	3.4
47	2.4	160	200	0.16	(40)	33	0.9	14	5.4	3.5
48	2.4	160	300	0.16	(40)	25	1.3	27	3.5	3.4
49	2.4	160	400	0.16	(40)	33	1.2	18	5.1	3.5

^a Runs beginning with H were carried out in a Haake Buchler mixer (batch reactor).

^b Numbers in parentheses are the monomer to initiator ratio w_m/w_I .

^c Numbers in parentheses are for purified products while others are for unpurified products.

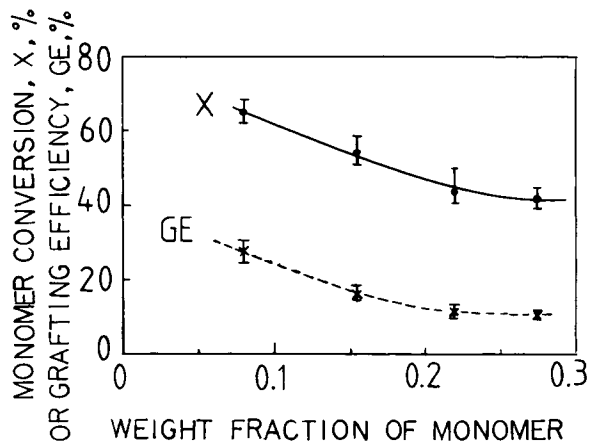


Fig. 3. Variation of the monomer conversion x and the grafting efficiency GE with monomer concentration w_m at an initiator weight fraction of 0.011, a temperature of 160°C, screw speed of 200 rpm, and mean reaction residence time of 2.4 min.

the average value of five data points obtained from five independent reaction runs. The ranges of values used to determine each data point in Figures 3–5 indicate the reproducibility of the experimental runs. Runs 05–09 provide more data (Table I) to show the effect of monomer concentration at different initiator concentrations. The overall monomer conversion decreased significantly with increasing monomer concentration (Fig. 3). Part of the overall monomer converted formed grafts on the LLDPE backbones while the remainder formed homopolymer. At this relatively high initiator fraction of 0.011, the degree of grafting, DG, was little influenced by increasing w_m except beyond $w_m = 0.22$

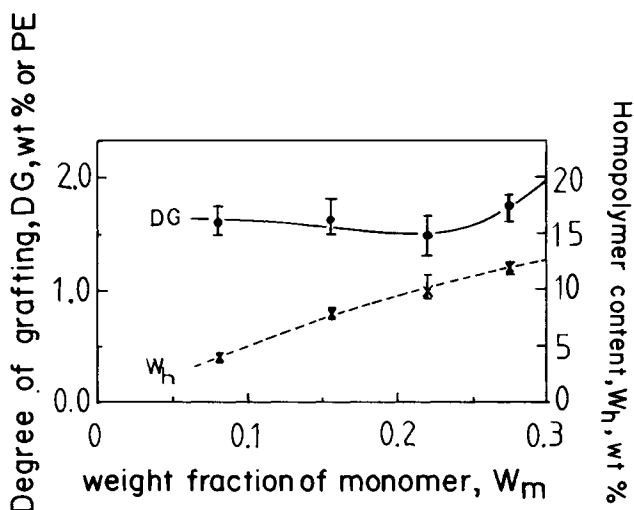


Fig. 4. Variation of the degree of grafting, DG, and the homopolymer content w_h with monomer concentration w_m at an initiator weight fraction of 0.011, a temperature of 160°C, screw speed of 200 rpm, and mean reaction residence time of 2.4 min.

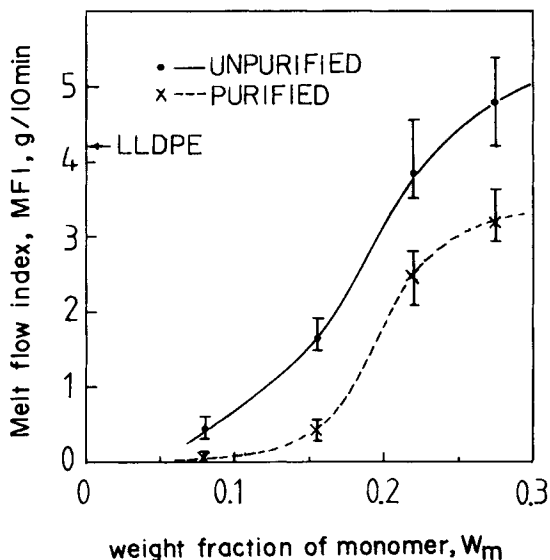


Fig. 5. Variation of the melt flow indices MFIs of the purified (---) and unpurified (—) with monomer concentration at an initiator weight fraction of 0.011, a temperature of 160°C, screw speed of 200 rpm and mean reaction residence time 2.4 min.

(Fig. 4). On the other hand, the homopolymer content w_h increased monotonically with increasing w_m . As a result, the grafting efficiency, defined as the percentage of the converted monomer to form grafts on the LLDPE backbones, decreased with increasing w_m and then level off (Fig. 3) consistent with the DG increase when w_m is greater than 0.22.

The overall monomer conversion, x , decreases both with increasing w_m and with decreasing initiator concentration (Fig. 3 and Table I). This observed decrease in the fractional conversion with increasing w_m may be attributed to the gel effect which causes a decrease in the chain termination rate. In the melt polymerization investigated here, low w_m means high LLDPE polymer concentration and high viscosity for the reacting system. The observed higher fractional conversion at low w_m may be a result of a more significant gel effect due to higher viscosity.

Parallel to the DMAEMA monomer converting to grafts and homopolymer, the LLDPE also undergoes crosslinking. The extent of crosslinking is indicated qualitatively by a decrease in the melt flow index (MFI) of the purified reaction products. The MFI of purified reaction products is always less than 4.2 dg/min of the original LLDPE and increases with increasing monomer concentration as shown in Figure 5. The MFI of the unpurified products, which contain not only grafted LLDPE but also DMAEMA homopolymer, follows the same trend but has higher values. The presence of DMAEMA homopolymer in the unpurified products is responsible for the higher MFI values. The DMAEMA homopolymer, whose relatively low molecular weight nature is evident from its soft appearance and from preliminary GPC measurements, may serve as a plasticizer to cause the increase in the MFI. It is interesting to note in Figure 5 that the effect of the homopolymer becomes so great at high monomer concentration that the value of MFI could exceed that of the original LLDPE.

The S-shaped curves in Figure 5 reflect the competition of several reactions involved in the reactive extrusion process. The free radicals generated from the initiator can attack the backbone by abstracting hydrogen atoms resulting in radical sites on LLDPE backbone. In the absence of DMAEMA monomer, the radical sites on the LLDPE backbone will cause significant crosslinking of the LLDPE chains resulting in almost zero MFI values. When DMAEMA monomer is present in the melt system, the DMAEMA monomer can prevent the significant crosslinking of LLDPE by competing for (1) the initiator free radicals for homopolymerization and (2) the radical site on the LLDPE backbone for the graft polymerization. This is indicated by the increase in MFI, as shown in Figure 5, and the decreases in both the measured screw torque, TQ , and the final barrel pressure P , as shown in Figure 6, with increasing monomer concentration. As can be seen from Figure 5, the competition for radicals by the monomer to prevent the LLDPE crosslinking begins to occur at $w_m = 0.1$ and becomes significant when $w_m > 0.2$.

The data in Figure 4 and Table I (runs 01–13) give more insight as to whether the free radicals are preferentially consumed in initiating homopolymerization or forming macroradicals on the LLDPE for grafting. When w_m is increased, the probability of the primary free radicals from the initiator attacking the monomer molecules and initiating homopolymerization increases and the probability of the initiator radicals attacking the LLDPE backbone for initiation of grafting decreases. As a result, the number of grafts decreases and therefore the DG should decrease. However, the value of DG depends not only on the number of grafts but also on the graft chain length. Grafts with longer chain length are likely to be formed at higher monomer concentration because of higher chain propagation rates compared to the chain termination rate. The degree of grafting is independent of w_m when the effect of the number of grafts is counterbalanced by the effect of graft chain length. When w_m is high enough (> 0.22 as shown in Fig. 4), the increase in the graft chain length eclipses the

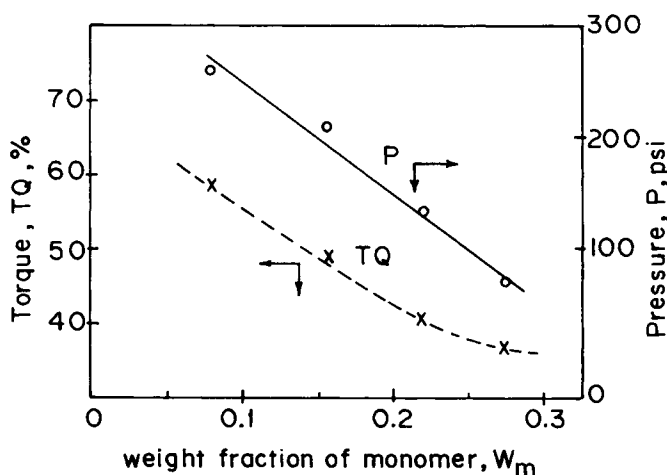


Fig. 6. Variation of the torque on the screw, TQ , and the pressure inside the end of the extruder, P , with monomer concentration w_m . Initiator concentration $w_i = 0.011$, temperature = 160°C , screw speed = 300 rpm, and mean reaction residence time = 2.4 min.

effect of the decrease in the number of grafts. The net effect is that the DG increases with increasing w_m as shown in Figure 4 for the high w_m range.

The influence of initiator concentration can also be seen from the data of runs 01–13 in Table I. The DG increased with increasing initiator concentration, w_I , in the lower monomer concentration range ($w_m < 0.22$). When w_m was greater than about 0.22, the DG became almost independent of w_I . These results support the argument that the effect of the number of grafts dominates at low w_m while the effect of the graft chain length dominates at high w_m . Increasing the initiator concentration has two side effects. It can cause an increase in the grafting initiation rate and therefore an increase in the number of grafts on the LLDPE backbone. It can also increase the chain termination rate and therefore give rise to shorter chain lengths. At low w_m , more grafts were produced at higher w_I so that the observed DG increased with increasing w_I . At high w_m , the graft chain length is more dependent on the monomer concentration than on the initiator concentration. Therefore, the observed DG became much less dependent on w_I .

Table I shows that relatively high GE (17%) can be obtained both for the combinations of a low w_m with a high w_I and a high w_m with a low w_I . However, the condition of a high w_m with a low w_I is preferred since it gave reasonable values of DG (1.8 wt %) and also higher values of the melt flow index for the reaction product (4.0 dg/min). The use of a low w_m with a high w_I produced a material with a high degree of crosslinking (MFI < 0.1 dg/min) and will likely cause difficulty in a subsequent processing step. Since the unreacted monomer can be recycled, the use of a high w_m with a low w_I to achieve high grafting efficiency is feasible.

Influence of Other Reaction Conditions

Runs 30–41 were carried out at different set processing temperatures while holding the monomer to initiator ratio, M/I, constant at 30, the screw speed at 200 rpm, and the mean reaction residence time for 2.4 min. Although the runs carried out at 160°C seemed to produce products with DG higher than those produced at either a lower temperature of 130°C or a higher temperature of 190°C, the effect of the reaction temperature is minor when w_m is less than 0.25 (Table I). At higher w_m of 0.29, however, low temperature of 130°C gave higher DG (run 37). This may be attributed to the stronger gel effect at low temperature which tends to cause longer grafts because of the limited chain termination.

The monomer conversion tended to increase with increasing temperature over the whole w_m range investigated. The homopolymer content in the reaction products, w_h , also increased somewhat with increasing temperature. The grafting efficiency GE was generally low and decreased with increasing reaction temperature. In general, the MFI increased as the reaction temperature was increased. As discussed above, the MFI of the reaction products is influenced by (1) the DMAEMA homopolymer content (w_h) which tends to increase MFI and (2) the crosslink density which tends to decrease MFI. Both w_h and the crosslinking density are favoured at high reaction temperature. The results shown in Table I indicate that the influence of w_h is more important in this experimental range.

Runs 42–49 in Table I were carried out to investigate the influence of the extruder speed at fixed reaction time. An increase in the twin-screw speed could enhance the mixing of the LLDPE melt and the monomer/initiator solution. The monomer/initiator solution was injected cold into the hot molten LLDPE. Good mixing with enhanced heat transfer could reduce the time for the cold monomer/initiator solution to come up to the reaction temperature and thus an increase in the monomer conversion might be expected.

In spite of the seeming increase in monomer conversion and the degree of grafting and decrease in MFI with the increasing screw speed shown by the data of runs 42–49 in Table I, the influence of RPM is minor considering the experimental error involved.

The data of runs 21–25 show the influence of the reaction residence time θ . The monomer conversion increased with increasing θ . The degree of grafting increased with increasing θ for small θ and then levelled off at an almost constant value (1.2 wt %) for θ greater than 4 min. The independence of the DG on the reaction time for larger reaction times suggests that when a certain DG has been achieved homopolymerization dominated over the graft polymerization. Therefore, the grafting efficiency is highest at around $\theta = 4$ min. The MFI, however, remains essentially unchanged with increasing θ .

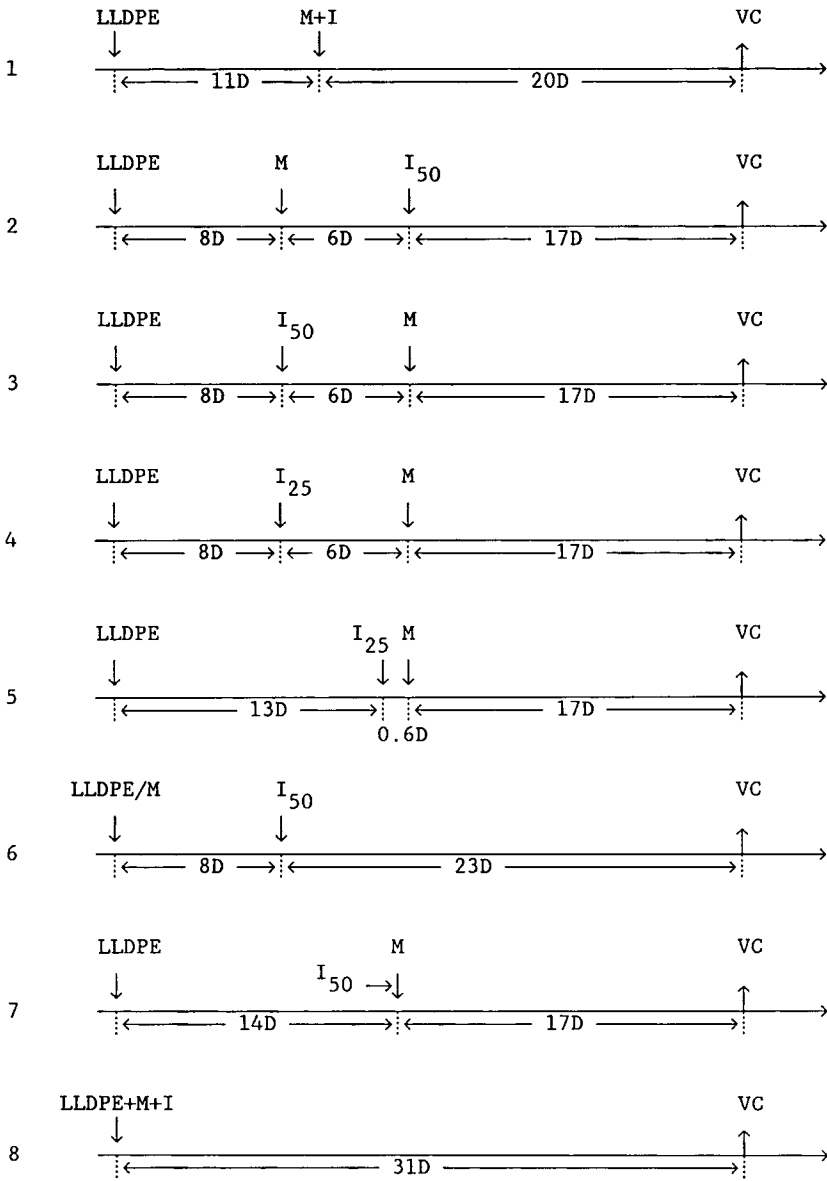
Sequential Addition of Monomer and Initiator

In order to achieve a higher degree of grafting with less homopolymerization and crosslinking, several modes of sequential addition of reactants were attempted and are schematically shown in Figure 7. In all cases, the LLDPE powder (*PE*) was fed through the hopper into the extruder. The residence time was controlled by changing the PE feed rate. When monomer and initiator were added separately, the initiator was diluted with mineral spirits in order (1) to reduce the metering error due to the very small amount of initiator needed and (2) to reduce the risk of explosion that might result from pumping pure peroxide into the extruder at a point of high temperature. The results of the sequential addition study are summarized in Table II for different conditions, α , as depicted in Figure 7.

Mode 1. The initiator was pre-dissolved in the monomer. The monomer/initiator solution was then injected into the LLDPE melt in the extruder. This mode has been described in Figure 1 and was used to obtain the results reported in the previous sections. The reaction conditions for runs 01–04 using this mode (Table I) were also used in other sequential addition experiments so that the different sequential addition arrangements could be compared.

Mode 2. The 50 wt % initiator in mineral spirits solution was injected 6D after the monomer addition. This mode gave both a lower degree of grafting and grafting efficiency than mode 1.

Mode 3. The 50 wt % initiator solution was injected 6D before the monomer injection. This sequential addition mode caused operating problem apparently because of extensive crosslinking. The problem became so severe at low monomer concentration that extruder operation went out of control (see Table II for the runaway phenomena). At high monomer concentration (run 70), the extruder was operable though the torque and the pressure were very high. The reaction product was a highly crosslinked material with $MFI < 0.01$, but the degree of grafting obtained was relatively high (2.0 wt %).

α 

D = 30 mm, the barrel inner diameter of the extruder.
 I = initiator, the subscript represent weight percent of initiator.
 M = monomer.
 VC = vacuum pumping out unreacted monomer.

Fig. 7. Sequential addition of monomer and initiator for the grafting extrusion. (Definition of α in Table II).

TABLE II
Influence of Sequential Addition of Reactants on the Functionalization of LLDPE
with DMAEMA in the Twin-Screw Extruder^a

Run #	α	θ (min)	T (°C)	RPM (rpm)	w_m (wt fraction)	w_I (wt fraction)	x (%)	DG (wt %)	GE (%)	w_h (wt %)	MFI (dg/min)
01	1	2.4	160	200	0.081	0.011	65	1.6	27	4.0	0.6
02	1	2.4	160	200	0.16	0.011	55	1.6	16	7.8	1.7
03	1	2.4	160	200	0.22	0.011	44	1.5	12	9.8	3.8
04	1	2.4	160	200	0.28	0.011	41	1.8	11	12	4.8
66	2	2.4	160	200	0.081	0.011	66	0.8	13	4.8	0.4
67	2	2.4	160	200	0.16	0.011	56	0.9	8.9	8.5	1.8
68	2	2.4	160	200	0.22	0.011	47	1.1	8.1	11	2.9
69	2	2.4	160	200	0.28	0.011	43	1.1	6.6	13	3.0
—	3	2.4	160	200	0.081	0.011	Runaway ^b				
—	3	2.4	160	200	0.16	0.011	Runaway				
—	3	2.4	160	200	0.22	0.011	Runaway				
70	3	2.4	160	200	0.28	0.011	65	2.0	8.2	18	0.00
72	4	2.4	160	200	0.28	0.0025	46	0.6	3.4	14	1.3
73	4	2.4	160	200	0.28	0.0053	50	1.5	7.9	15	0.3
74	4	2.4	160	200	0.28	0.0074	50	2.1	11	14	0.01
75	4	2.4	160	200	0.28	0.011	59	2.0	9.0	17	0.00
76	5	2.4	160	200	0.081	0.011	Runaway				
77	5	2.4	160	200	0.16	0.011	60	1.6	14	8.6	0.1
78	5	2.4	160	200	0.22	0.011	54	1.6	10	12	0.9
79	5	2.4	160	200	0.28	0.011	48	1.9	10	14	1.4
80	5	2.4	160	200	0.40	0.011	36	2.5	10	18	1.2
81	6	2.4	160	200	0.081	0.011	64	0.6	11	4.8	1.2
82	6	2.4	160	200	0.16	0.011	46	1.0	11	7.0	2.2
83	6	2.4	160	200	0.22	0.011	42	1.3	10	9.7	3.2
84	6	2.4	160	200	0.28	0.011	46	1.4	7.9	14	3.5
89	7	2.4	160	200	0.081	0.011	63	0.6	11	4.7	1.0
90	7	2.4	160	200	0.16	0.011	47	0.9	9.9	7.2	2.4
91	7	2.4	160	200	0.22	0.011	44	1.4	11	9.9	2.7
92	7	2.4	160	200	0.28	0.011	34	1.6	13	10	2.3
93	8	5.0	160	200	0.23	0.011	56	2.5	15	12	4.0
94	8	3.0	160	200	0.23	0.011	52	1.1	8.3	12	3.8

^a The reactant addition layout α is defined in Figure 7.

^b A runaway indicates that the reacting mixture inside the extruder became a powder and tended to block the vent port. At the same time, the torque and the pressure in the extruder exceeded the operating limits.

Mode 4. To take advantage of the higher DG observed in mode 3 while avoiding the extensive crosslinking, an initiator solution with lower concentration (25 wt %) was used and the reactions were run at lower initiator concentration in the reaction mixture while keeping the monomer concentration at high level (0.28). The results of run 75 with mode 4 are essentially the same as those of run 70 with mode 3 for the same reaction conditions, indicating little effect of diluting the initiator feed solution. When the initiator concentration in the reaction mixture was reduced, the extent of crosslinking decreased but the degree of grafting also decreased.

Mode 5. Mode 4 was modified by moving the initiator solution injection port as close to the monomer injection port as possible. This modification was

made with the goal of decreasing the residence time of the initiator and polymer alone together while effecting some premixing without the monomer. As expected, the crosslinking was greatly suppressed with such a modification although runaway conditions still occurred at very low monomer concentration. Reaction products (run 79) with relatively high DG (1.9 wt %) and acceptable crosslinking extent (MFI = 1.4 dg/min) were obtained at relatively high monomer concentration (0.28). This is further evident when a very high monomer concentration was used in run 80. The function of DMAEMA monomer to compete for the initiator radicals and to suppress the LLDPE crosslinking, which has been discussed previously, is well demonstrated with this modification of mode 4.

Mode 6. The monomer was injected through the hopper by preblending it with LLDPE. This modification of mode 2 was intended to improve the distribution of the monomer in the LLDPE melt in mode 2. Results similar to those with mode 2 were obtained, indicating that mixing of the monomer and the LLDPE melt before injection of the initiator in mode 2 was not responsible for the lower DG and GE obtained. Operation using mode 6 layout was sometimes difficult because the LLDPE powder, wetted by the liquid monomer, tended to block the hopper. Another disadvantage with mode 6 is greater experimental error caused by monomer loss through the hopper.

Mode 7. The initiator solution was injected into the monomer feeding tube close to the extruder and mixed with the monomer before entering the extruder. Mode 7 was essentially the same as mode 1 but provided the advantage of greater flexibility in altering feed ratio. The results obtained with mode 1 and mode 7 were essentially the same except at low monomer concentration. Greater metering error with mode 7 at low monomer concentration may be responsible for the differences.

Mode 8. LLDPE powder, the monomer, and the initiator of the required composition were premixed and stored in the K-Tron volumetric feeder for feeding through the hopper into the extruder. This feeding arrangement resembles most that used with the batch melt reactor (the Haake mixer). However, great experimental errors with mode 8 make it improper to compare the results obtained using mode 8 with those obtained in the batch mixer. The experimental errors resulted from composition non-uniformity of the reactant mixture in the feeding tank. The monomer/initiator solution that was not absorbed by the LLDPE powder tended to settle at the bottom of the feeding tank. Thus, the first experimental run with this mode (run 93) likely had higher monomer and initiator concentrations than shown. This may be responsible for the high DG obtained from run 93 shown in Table II. Besides great experimental errors, operation using mode 8 was difficult since the K-Tron volumetric feeder had difficulty to transporting the wet LLDPE powder and also the wet powder tended to bridge in the hopper. In fact, it was impossible to operate with mode 8 at high feeding rates and therefore short residence times.

To summarize the sequential addition investigation, modes 1 and 7 are preferable considering the goals of relatively high DG, low crosslinking and ease of operation. A higher DG can be obtained at the expense of higher crosslinking and homopolymerization with mode 5 and this can be extended with very high monomer concentration. When the monomer was added before injection of the

initiator, both low DG and GE resulted. Operating difficulties were met with modes 3, 6, and 8.

CONCLUSIONS

Relatively high degrees of grafting without excessive polyethylene crosslinking can be obtained using high monomer concentration and low initiator concentration (high M/I). A processing temperature between 130 and 160°C gives the maximum grafting efficiency observed but generally it does not exceed 25%. Too high a processing temperature will result in both lower grafting efficiency and degree of grafting. The degree of grafting does not increase when the mean reaction residence time exceeds a certain value beyond which primarily homopolymerization occurs and the grafting efficiency drops. The presence of DMAEMA homopolymer causes an increase in melt flow index of the reaction products. Values of the MFI for raw reaction products with high DMAEMA homopolymer content can even exceed that for the original LLDPE. Injecting the initiator into the extruder before the monomer gives high DG but with extensive crosslinking while injecting the monomer before the initiator resulted in both low DG and GE. Injection of pre-mixed monomer/initiator solutions into the extruder is preferable since relatively high DG with low crosslinking extent are obtained.

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