Search for Nonoxidative, Hydrogen-Abstracting Initiators Useful for Melt Grafting Processes

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SYNOPSIS

Using organic peroxide initiators in the melt grafting of monomers containing amino groups onto polyethylenes is known to cause serious discoloration of the resulting polymers. To eliminate the discoloration while preserving the controlled degree of grafting, a nonoxidative and hydrogen-abstracting initiator with appropriate thermal stability is needed. In this study, the hydrogen-abstracting capability of three azo initiators with suitable decomposition rates in the melt grafting temperature ranges was evaluated using polyethylene cross-linking and polypropylene degradation experiments (called "hydrogen-abstraction experiments"). Among the three azo initiators tested, only a phenylazo initiator, 2-phenylazo-2,4-dimethyl-4-methoxyl-valeronitrile (V-19), demonstrated strong hydrogen-abstracting capability from polymer backbones. These three azo initiators were used in the melt grafting of 2-(N,N-dimethylamino)ethyl methacrylate (DMAEMA) and 2-(N-t-butylamino)ethyl methacrylate (tBAEMA) onto a linear low-density polyethylene (LLDPE). In agreement with the results obtained from the hydrogen-abstraction experiments, only V-19 led to a considerable amount of grafting of both DMAEMA and tBAEMA onto LLDPE. As expected, polymers grafted with V-19 showed significantly reduced discoloration compared with those grafted with peroxide initiators. Further examination of the grafting results indicated that the initiator efficiency, defined as the number of grafted monomer units per radical generated from initiator decomposition, was higher with the phenylazo initiator than with peroxide initiators. The hydrogen-abstracting capability of the phenyl free radical generated from the decomposition of V-19 was estimated to be higher than peroxide and methyl free radicals produced in the decomposition of peroxide initiators. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Melt grafting of vinyl monomers containing polar or reactive groups onto commercially available polymers is now recognized as an economical and industrially practical way for obtaining new polymeric materials. Polymers functionalized by melt grafting are useful in the compatibilization of polymer blends. New polymer blends with improved properties may be made through reactive blending using functionalized polymers.[1]

In the 1960s, melt grafting of monomers with acidic and/or electrophilic functionalities such as maleic anhydride was the subject of numerous investigations.[2,3] However, few examples concerning the basic and/or nucleophilic functionalization of preformed polymers in the melt can be found in the literature. Only in recent years, advances have been made in the melt grafting of methacrylate-type monomers containing amino groups onto linear low-density polyethylene (LLDPE) with organic peroxide initiators.[4-7] However, oxidation of the amino groups by organic peroxides occurred at the elevated temperatures experienced in melt grafting processes (160–220°C). Direct evidence of this oxidation was the intense discoloration (from yellow to brown) of the grafted polymers, indicating the formation of amine oxides, the oxidation products of the amino functionalities. This oxidation reaction detracts from the principal merits of the melt grafting process, since strongly colored polymers are generally of little commercial value. In addition, the amine

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oxides have no basicity or nucleophilicity, rendering the grafted polymer inert in blending applications.

Trials have been performed by Simmons and Baker[4] on the melt grafting of 2-(N,N-dimethyl-amino)ethyl methacrylate (DMAEMA) onto LLDPE with azo initiators azobisisobutyronitrile (AIBN) and 2,2'-azobis(2-acetoxypropane) (LU-AZO AP). The LUAZO AP-type initiators were claimed to cause cross-linking of a number of polymers including polyethylene.[8] However, Simmons and Baker reported that no grafting occurred using AIBN and that LUAZO AP gave irreproducible results. Two possible explanations were given for these observations. First, the free radicals produced by the decomposition of AIBN are not capable of abstracting hydrogen atoms from LLDPE backbone to generate macroradical reactive sites, the first step for melt grafting. Second, AIBN has too short a half-life and LUAZO AP has too long a half-life at the reaction temperature. For example, the half-lives of AIBN and LUAZO AP at 160°C are estimated to be 2.3×10^{-16} and 3.9×10^{3} minutes, respectively.

Therefore, an ideal initiator for the melt grafting of amino-bearing monomers must meet the following criteria: nonoxidative, hydrogen-abstracting, and suitable thermal stability under melt grafting conditions. Azo initiators are potential candidates as they are nonoxidative. In this study, the hydrogen-abstracting capability of three azo initiators with the desired decomposition rates under melt grafting conditions was tested by polyethylene cross-linking and polypropylene degradation experiments (called "hydrogen-abstraction experiments"). As well, melt grafting of DMAEMA and tBAEMA monomers onto LLDPE with these azo initiators was conducted. Only one of the three azo initiators, 2-phenylazo-2,4-dimethyl-4-methoxylvaleronitrile (V-19), was found to abstract hydrogen atoms from polymer backbones and induce grafting reactions. The discoloration of grafted polymers was also monitored. The results of the melt grafting and the discoloration with the azo initiator V-19 were compared with those obtained with organic peroxide initiators.

EXPERIMENTAL

Materials

The linear low-density polyethylene (LLDPE) supplied by ESSO Chemical Canada (LL5103) is an ethylene-butene copolymer with a melt flow index of 12 dg/min, a density of 0.923 g/cm^3, a weight-average molecular weight of 58,000, and an M_w/M_n

of about 4. Proton NMR analysis indicated a co-monomer content of about 7 wt % butene. The polypropylene provided by Shell Canada Chemical Co. (GE6100) has a melt flow index of 1 dg/min.

The monomers, 2-(N,N-dimethylamino)ethyl methacrylate (DMAEMA) from Aldrich and 2-(N-t-butylamino)ethyl methacrylate (tBAEMA) from Pfaltz & Bauer were used without further purification.

The azo initiators, 2-phenylazo-2,4-dimethyl-4-methoxyl-valeronitrile (V-19), 2-(carbamoylazo) isobutyronitrile (V-30), and 1,1'-azobiscyclohexyl-nitrile (V-40), were kindly supplied by Wako Chemicals USA. V-19 is a transparent yellow liquid with a boiling point of 149–150°C/1 mmHg; V-30, a pale yellow crystal solid with a melting point of 76–78°C; and V-40, a white solid with a melting point of 113–115°C. The organic peroxide initiators, 2,5-dimethyl-2,5-di(t-butylperoxy)hexane(L101), 2,5-dimethyl-2,5-di(t-butylperoxy)hexyne-3 (L130), and 1,1-di-(t-butylperoxy)-3,3,5-trimethylcyclohexane (L231), kindly supplied by Atochem North America, are clear liquids. The decomposition half-life data of V-19, V-30, V-40, L101, L130, and L231 in the useful temperature range for melt grafting processes are listed in Table I.

Grafting Procedure

The melt grafting of DMAEMA and tBAEMA onto LLDPE was carried out on a Haake Buchler Rheomix 600 mixer, a batch-type internal intensive mixer with a capacity of about 50 cm^3. The mixer is interfaced with a microprocessor, which allows control of the processing variables such as processing time,

Table I Half-life Data of V-19, V-30, V-40, L101, L130, and L231 in the Temperature Range Useful for Melt Grafting Processes

Initiator	Temperature (°C)		
	160	180	200
		$t_{1/2}$ (min)	
V-19[a]	25.4	5.81	1.51
V-30[a]	1.7	0.29	0.06
V-40[a]	0.1	0.02	0.03
L101[b]	1.9	0.73	0.12
L130[b]	19.6	2.96	0.52
L231[b]	0.6	0.11	0.02

[a] Ref. 9.
[b] Ref. 10.

temperature, and rotor speed, as well as continuous recording of torque and temperature with time.

Prior to the melt grafting, 10 g of monomer and 0.25 g of initiator were added to 40 g of LL5103 and manually mixed until a homogeneous wet paste was obtained. This wet paste was fed into the preheated mixer and allowed to react for a specified processing time. The reaction temperature was varied between 160 and 200°C. The rotor speed and the reaction time were set at 60 rpm and 10 min, respectively, for all grafting experiments.

The hydrogen-abstraction experiments were performed by a similar procedure as in melt grafting, but without monomer. Cautions were taken so as to obtain reproducible torque value for each experiment.

Polymer Purification and Analysis

After the melt grafting, the grafted polymers were purified by drying them in a vacuum oven at 70°C to constant weight, dissolving the dried samples in refluxing toluene at a concentration of 0.04 g/cm^3 and precipitating the dissolved polymers in 10 volumes of methanol with stirring. The operation of dissolving in toluene and precipitating in methanol was repeated until no monomer or homopolymer remained in the purified polymers. The degree of grafting (D.G.) based on the mol % monomer bound to the LLDPE was measured by ^{1}H-NMR in toluene-d_8 at 90°C on a Bruker 400 MHz NMR spectrometer. The relative error of D.G. was determined by experiments at the 5% level.

The purified polymers were pressed into thin films at 180°C for 8 min under 14 MPa pressure. The thickness of the films was controlled between 0.1 and 0.2 mm. IR spectra of these films were obtained on a Bomen MB-120 FTIR spectrometer.

The colorimetric measurements of the grafted polymers were performed on a MacBeth 1500 ColorEye colorimeter using illuminant D_{65} with the UV component filtered out and with the specular component of the reflected light excluded. Injection-molded disk specimens of 1.5-in. diameter were used in the test.
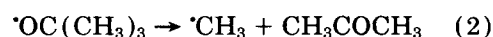
RESULTS AND DISCUSSION

Hydrogen-abstracting Capability of Phenyl Radical

Traditionally, organic peroxide initiators were believed to produce, upon their decomposition, strong hydrogen-abstracting free radicals,[11] while free radicals generated from the decomposition of conventional azo initiators were regarded as poor hydrogen abstractors.[12] These conclusions can be verified by considering the nature and reactions of the free radicals produced from the decomposition of the two types of initiators.

Table II presents the Gibbs free-energy changes (ΔG^0) of the homolysis reactions involving the free radicals of interest, which were estimated according to a standard method in statistical thermodynamics.[13] From the viewpoint of thermodynamics, the capability of a free radical to abstract a hydrogen atom from polymer backbones increases from the tertiary carbon radical to the phenyl radical (from the bottom to the top in Table II). The hydrogen-abstraction reactions involved in the functionalization of molten polyethylenes are those from primary, secondary, and tertiary carbons. The estimated equilibrium constants (K's) at 180°C for such hydrogen-abstraction reactions are compared in Table III. An equilibrium constant K larger than 1 indicates a thermodynamically favorable hydrogen-abstraction reaction. Hence, peroxide and methyl radicals are strong hydrogen abstractors with K's greater than 800 for hydrogen-abstraction reactions toward all the primary, secondary, and tertiary hydrogens. Peroxide and methyl free radicals are generated from the thermal decomposition of organic peroxide initiators such as L101, L130, and L231 [eq. (1)] and the rearrangement of the t-butyl peroxide radical [Eq. (2)]:

$$RO-OC(CH_3)_3 \rightarrow RO^{\bullet} + {}^{\bullet}OC(CH_3)_3 \quad (1)$$

$${}^{\bullet}OC(CH_3)_3 \rightarrow {}^{\bullet}CH_3 + CH_3COCH_3 \quad (2)$$

Therefore, organic peroxide initiators are good hydrogen-abstracting agents. However, the conven-

Table II Free Energy Changes (ΔG^0) of Some Homolysis Reactions^a

Reaction	ΔG^0 (kJ/mol)
PhH $\rightarrow$ H$^{\bullet}$ + Ph$^{\bullet}$	508
ROH $\rightarrow$ H$^{\bullet}$ + RO$^{\bullet}$	473
CH$_4$ $\rightarrow$ H$^{\bullet}$ + CH$_3^{\bullet}$	451
RCH$_3$ $\rightarrow$ H$^{\bullet}$ + RCH$_2^{\bullet}$	444
(R)$_2$CH$_2$ $\rightarrow$ H$^{\bullet}$ + (R)$_2$CH$^{\bullet}$	431
(R)$_3$CH $\rightarrow$ H$^{\bullet}$ + (R)$_3$C$^{\bullet}$	415

^{a} Estimated according to a standard method in statistical thermodynamics.[13]

Table III   Estimated Equilibrium Constants (K's) for Hydrogen-abstraction Reactions at 180°C

Radical	Hydrogen Type		
	Primary	Secondary	Tertiary
Ph·	6×10^6	2×10^8	1×10^{10}
RO·	1×10^3	7×10^4	6×10^6
CH·$_3$	8×10^2	2×10^4	2×10^6
RCH·$_2$	1	3×10^1	2×10^3
(R)$_2$CH·	4×10^{-2}	1	9×10^1
(R)$_3$C·	4×10^{-4}	1×10^{-2}	1

tional azo initiators such as AIBN produces only tertiary carbon radicals that have no hydrogen-abstracting capability.[12] In addition, the half-lives of commonly used azo initiators are too short[14] to be useful in the melt grafting temperature ranges.

According to the ΔG^0 values in Table II and K values in Table III, phenyl free radicals should have even higher hydrogen-abstracting capability than that of peroxide and methyl free radicals. In fact, kinetic studies on the hydrogen-abstraction reactions of phenyl free radical in both the gas phase[15] and solution[16] were reported since the early 1960s. Comparison of the data obtained in the gas phase shows that the activation energy of the hydrogen-abstraction reaction from cyclopropane by the phenyl free radical is 18.4 kJ/mol less than with the methyl free radical.[17] Thus, from the point of view of both thermodynamics and kinetics, the hydrogen-abstraction reaction with a phenyl radical is more favorable than with other radicals. However, to the authors' best knowledge, the use of phenyl radical as hydrogen abstractor in polymer modification has not been reported in the literature.

The phenylazo initiator V-19 decomposes in a two-step process [Eq. (3)],[18] yielding two types of radicals:

$$
\begin{array}{ccc}
 & CH_3 & CH_3 \\
 & | & | \\
Ph-N=N-C-CH_2-C-CH_3 & \rightarrow \\
 & | & | \\
 & CN & OCH_3 \\
\end{array}
$$

$$
\begin{array}{ccc}
 & CH_3 & CH_3 \\
 & | & | \\
Ph-N=N· + ·C-CH_2-C-CH_3 & (3) \\
 \downarrow & | & | \\
 & CN & OCH_3 \\
Ph· + N_2 & &
\end{array}
$$
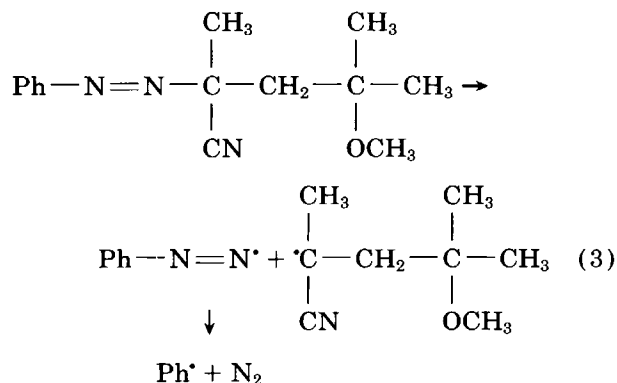
The tertiary carbon radical produced in the first step cannot easily abstract hydrogen,[12] but the phenyl radical can. Moreover, due to the stepwise nature of its decomposition, the tertiary carbon radicals may escape the solvent cage before the formation of phenyl radicals. Thus, radical recombination within the solvent cage may be reduced. This may result in an enhanced initiator efficiency. This is particularly interesting for the melt grafting processes, since polymer melts are generally highly viscous and the cage effects are likely to be very important.

Hydrogen-abstraction Experiments

As mentioned in the Introduction, the first step in the melt grafting process via the free-radical mechanism is the abstraction of hydrogen atoms by initiating free radicals from polymer backbones to create macroradicals, the sites of the grafting reactions. However, in the absence of any monomer molecules, radical recombination, disproportionation, and/or β-scission may occur, resulting in changes in polymer molecular weight depending on the nature of the particular polymer involved. For polyethylenes, cross-linking is the dominating reaction,[19] whereas for polypropylenes, degradation predominates.[20] Since changes in the polymer molecular weight have a direct influence on the viscosity of the polymer melt,[21] the torque exerted by the motor on the polymer melt will vary accordingly in order to maintain the rotor speed constant. Therefore, the cross-linking of polyethylenes and the degradation of polypropylenes may be observed from torque traces recorded during the hydrogen-abstraction experiments. The cross-linking of polyethylenes will be indicated by a torque increase, and the polypropylene degradation, by a torque decrease.

Figure 1 compares the torque variations with time during the processing of LL5103 alone and with 0.9 wt % of azo initiator V-30 at 160°C for 6 min. It can be seen that the torque values were not increased by the addition of V-30 into LL5103. Instead, a slight torque decrease was observed. V-40 was shown to have a similar effect on torque values for the processing of the same LLDPE. Thus, the free radicals produced from the decomposition of V-30 and V-40 are not capable of abstracting hydrogen atoms from the LLDPE backbone. The small torque decreases can be explained by the plasticizing effect of the small molecules of the added initiators and their decomposition products. However, Figure 2 clearly demonstrates that the addition of 0.9 wt % of V-19 into LL5103 resulted in ca. a 60% torque increase after processing at 180°C for 6 min. This is the first

evidence that the free radicals generated from the phenylazo initiator V-19 can abstract hydrogen atoms from LLDPE, resulting in cross-linking of LLDPE. Comparable experiments using organic peroxide initiators L101, L130, and L231 also showed torque increases, indicating cross-linking of the polyethylene. This is in agreement with other authors' findings that organic peroxide initiators are good hydrogen abstractors.[22] However, the polyethylene cross-linking reactions are not sensitive enough to allow discrimination of the hydrogen-abstracting capabilities of V-19 and the organic peroxides.

It is well known that polypropylenes are more sensitive to the attack of hydrogen-abstracting free radicals than are polyethylenes.[20] Thus, it could be possible to differentiate the hydrogen-abstracting capability of V-19 from that of the organic peroxides by comparing torque decreases during the processing of molten polypropylene to which the particular initiator was added. Among the three organic peroxide initiators used, L130 is the one with the smallest difference in thermal stability relative to the azo initiator V-19. L130 was, hence, used in the experiments designed for the purpose mentioned above. The results are presented in Figure 3. It is clearly shown that the torque values for the processing of polypropylene GE6100 melt at 180°C were reduced from 9.0 to 1.7 and 0.1 N-m by 0.5 wt % of V-19 and L130, respectively. L130 seems to be more efficient in abstracting hydrogen atoms from the polypropylene backbone than is the phenylazo initiator V-19. However, one must consider that (a) 1 mol of L130 produces in total 4 mol of peroxide and methyl
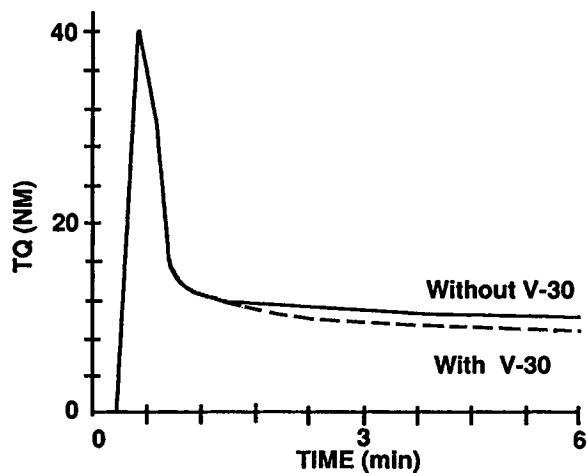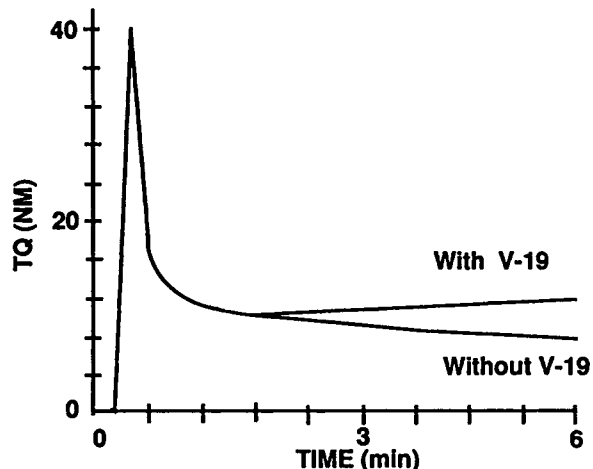

Figure 2 Effect of added V-19 on torque during processing of LL5103. Conditions: 190°C, 100 rpm, 0.9 wt % initiator.

radicals, but 1 mol of V-19 can generate only 1 mol of phenyl radical [Eq. (3)]; and (b) the decomposition of L130 is twice as fast as that of V-19 at 180°C (Table I). Therefore, the hydrogen-abstracting capability of V-19 is at least comparable to that of L130 if the same amount of hydrogen-abstracting radicals were involved.

Characterization of Grafts

The azo initiators V-19, V-30, and V-40 were also used in the melt grafting of DMAEMA and tBAEMA onto LL5103. Figures 4 and 5 present typ-
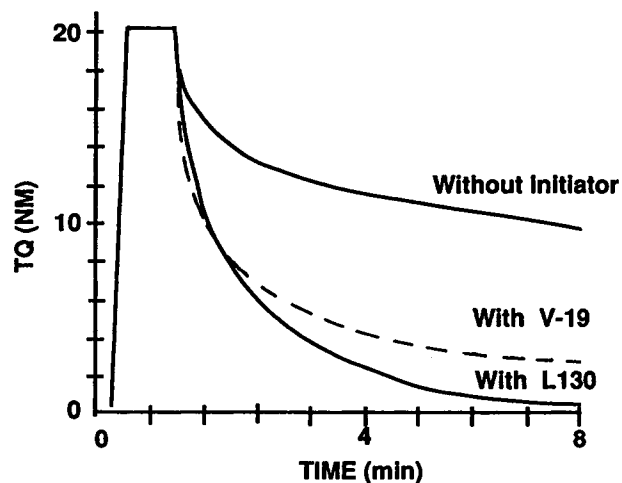

Figure 1 Effect of added V-30 on torque during processing of LL5103. Conditions: 160°C, 100 rpm, 0.9 wt % initiator.

Figure 3 Effect of added V-19 and L130 on torque during processing polypropylene GE6100. Conditions: 190°C, 100 rpm, 0.5 wt % initiator.
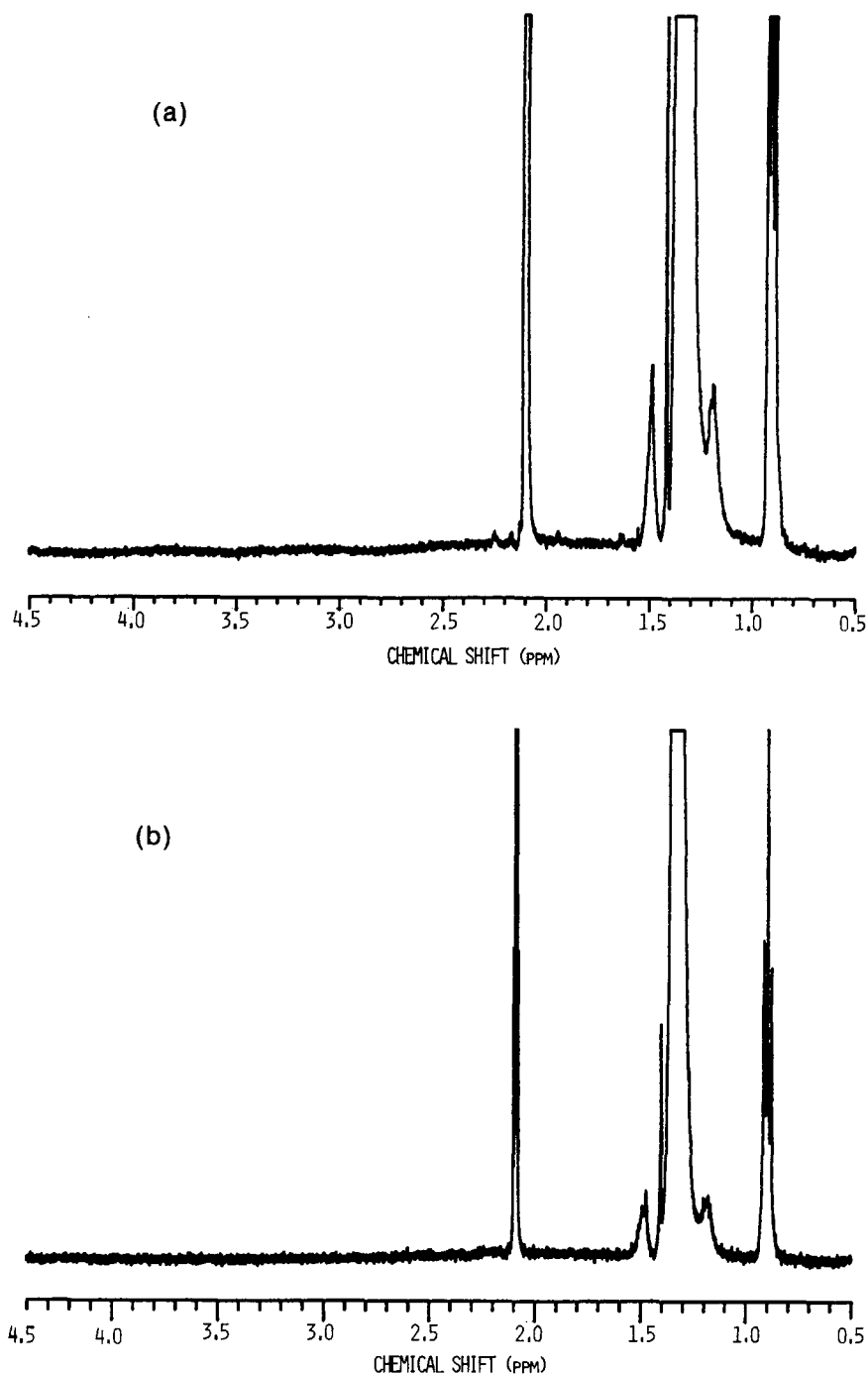
Figure 4 Comparison of ^{1}H-NMR spectra of virgin and purified grafted LLDPE: (a) virgin LL5103; (b) grafted with DMAEMA using V-30; (c) grafted with DMAEMA using V-19; (d) grafted with tBAEMA using V-19.

ical ^{1}H-NMR and IR spectra of virgin LL5103 and purified samples of grafted LL5103. As shown in Figure 4(b), the ^{1}H-NMR spectrum of LL5103 grafted with DMAEMA using V-30 is not different from that of the virgin LLDPE [Fig. 4(a)]. In ad-

dition, the IR spectrum of the same purified sample [Fig. 5(a)] shows the absence of ester carbonyl absorption at around 1730 cm^{-1}. Similar ^{1}H-NMR and IR studies on the purified LL5103 samples processed with DMAEMA and V-40, or tBAEMA and V-30

(c)
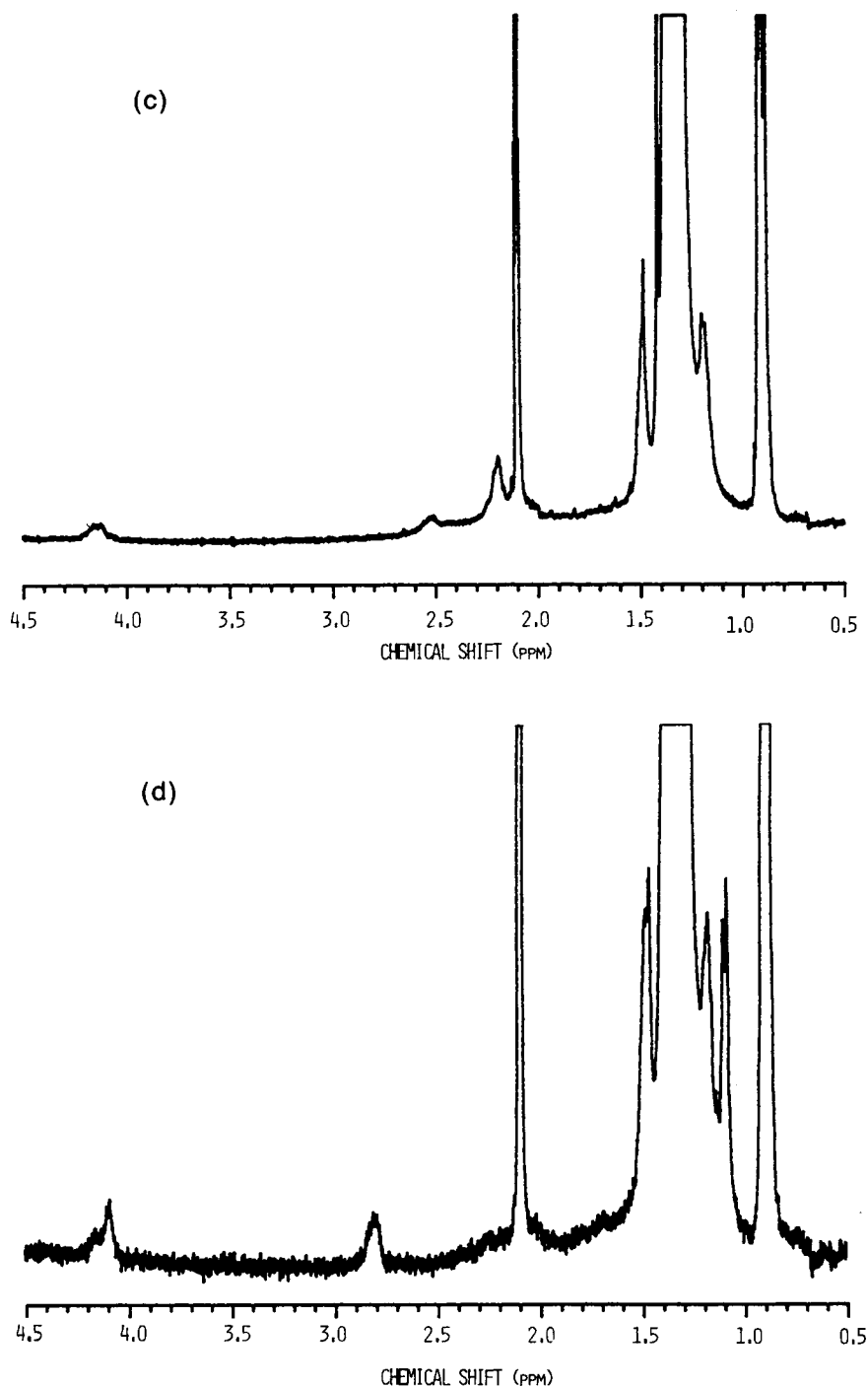
CHEMICAL SHIFT (PPM)

(d)

CHEMICAL SHIFT (PPM)

Figure 4. *(Continued from the previous page)*

or V-40, did not show any evidence of grafting either. These results clearly demonstrate that the azo initiators V-30 and V-40 are not capable of initiating grafting reactions of DMAEMA or tBAEMA onto LLDPE. This observation is in agreement with the results obtained in the hydrogen-abstraction exper-iments, in which the V-30 and V-40 are shown not to be capable of abstracting hydrogen atoms from polymer backbones.

The observation that V-40 cannot abstract hydrogen atoms from polymer backbones and initiate grafting reactions can be explained by the fact that
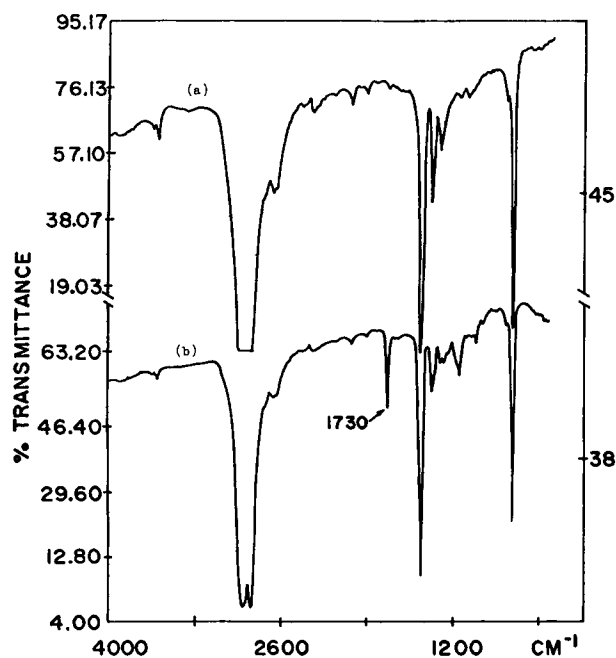
Figure 5 IR spectra of purified grafted LL5103 films: (a) grafted with DMAEMA using V-30; (b) grafted with DMAEMA using V-19.

its decomposition results in the formation of 1-cyanocyclohexyl radical. The latter is a tertiary radical not capable of abstracting hydrogen atoms from polymer backbones (Tables II and III). In the case of V-30, one of the two radicals generated from its decomposition is a tertiary butyl radical, a nonhydrogen-abstracting radical as well. The other, the carbamoyl radical, is unstable and decomposes easily, yielding CO, CO_2, N_2, NH_3, etc.[12] Therefore, both V-30 and V-40 were shown not capable of abstracting hydrogen atoms from polymer backbones and initiating grafting reactions.

However, the ^{1}H-NMR spectra of the purified grafted LL5103 with DMAEMA and tBAEMA using V-19 [Fig. 4(c) and (d)] obviously show new peaks not seen in the pure LLDPE [Fig. 4(a)]. The broad peaks at 4.05–4.25 and 2.50–2.90 ppm indicate, respectively, the methylene protons adjacent to ester oxygen and amino nitrogen in the graft chains. In the case of DMAEMA grafts, the six methyl protons have resonance at ca. 2.15 ppm [Fig. 4(c)]. The nine t-butyl protons should resonate at ca. 1.2 ppm, but they are masked by the large ethylene proton peaks of LLDPE [Fig. 4(d)]. In the IR spectrum [Fig. 5(b)], the ester carbonyl group of DMAEMA graft is shown by its characteristic absorption at 1730 cm^{-1}. Similar IR spectrum was obtained from purified samples of LLDPE grafted with tBAEMA. Hence, grafts of DMAEMA and tBAEMA on

LL5103 were identified and grafting of DMAEMA and tBAEMA onto LLDPE was realized with the phenylazo initiator V-19.

Using the same techniques, grafts of DMAEMA and tBAEMA onto LL5103 with peroxide initiators L101, L130, and L231 were characterized. The ^{1}H-NMR and IR spectra of LLDPE grafted with these peroxide initiators were shown to be identical to those grafted with V-19. The results of these spectroscopic investigations were also in agreement with the characterization of the same grafts reported previously.[4–7]

Comparison of Grafting with V-19, L101, L130, and L231

Since the azo initiators V-30 and V-40 cannot initiate the grafting reactions of DMAEMA and tBAEMA onto LLDPE, it is only possible to compare the grafting results obtained using initiators V-19, L101, L130, and L231.

The degree of grafting (D.G.) of DMAEMA and tBAEMA onto LLDPE with V-19 was compared to that with L101, L130, and L231 in Table IV. The first interesting feature of the melt grafting of DMAEMA and tBAEMA onto LLDPE is that under identical grafting conditions with the same initiator D.G.s show no difference within experimental error between the two monomers. This indicates that the presence of different amino groups (tertiary vs. secondary) has no significant effect on the D.G. It is understandable since the amino groups are two carbons away from the polymerizing double bond and should not affect the grafting initiation and propagation rates.

Under similar conditions, the grafting with V-19 yields comparable D.G.s with those using L101 and L130. At 160°C, the peroxide initiator L231 demonstrates ca. 70% higher D.G. than does V-19. However, L231 decomposes more than 40 times as fast as does V-19 (Table I). In fact, according to the half-life data in Table I, L231 can reach essentially 100% decomposition at 160°C for 10 min, whereas V-19 decomposes only 24%.

One can more fairly evaluate the efficiency of the initiators by taking into account the number of initiating radicals involved in the grafting process. We define here the initiator efficiency (I.E.) as follows:

$$I.E. = \frac{\text{Grafted monomer (moles)}}{\text{Appropriate radicals produced (moles)}}$$

$$= \frac{D.G.}{c_i \times a_i} \tag{4}$$

where D.G. is the degree of grafting; c_i represents

Table IV   Summary of D.G.s (mol %) for Melt Grafting of DMAEMA and tBAEMA onto LLDPE with V-19, L101, L130, and L231

Initiator	Monomer	160°C	180°C	200°C
V-19	DMAEMA	0.34	0.17	0.11
	tBAEMA	0.34	0.16/0.17[a]	0.07
L101	DMAEMA	0.35	0.18	0.11
	tBAEMA	0.37	0.32	0.13
L130	DMAEMA	0.35		
	tBAEMA	0.38/0.41[a]		
L231	DMAEMA	0.57		
	tBAEMA	0.69		

[a] Results of two independent runs.

the initiator concentration; and a_i is the initiator conversion estimated from $t_{1/2}$, processing time, and temperature.

Table V compares the I.E.s of V-19 with those of L101, L130, and L231 at 160°C based on the results shown in Table IV and the decomposition rates in Table I. Hence, V-19 has I.E.s of ca. 20, whereas those of peroxide initiators range from 3.3 to 11.4 at 160°C. Since the grafting reactions were conducted under identical conditions and, in the case of V-19 and L130, the concentration of free radicals available for the graft chain termination is about the same, it can be concluded that the graft chain are about the same length. In this case, it can be argued that the higher I.E.s obtained with V-19 indicate that more graft chains were obtained with the azo initiator than with the organic peroxides. Therefore, the unusually high hydrogen-abstracting capability of phenyl radical generated from V-19 is unambiguously demonstrated by the grafting results. This could be primarily due to the high reactivity of phenyl radical in the hydrogen-abstraction reaction. This observation is in agreement with the conclusions drawn from the kinetic studies in free-radical chemistry. In addition, the stepwise decomposition may be a complementary factor contributing to the high I.E. of the phenylazo initiator V-19.

Table V   Comparison of I.E.s for Melt Grafting of DMAEMA and tBAEMA onto LLDPE at 160°C

Initiator	Monomer	
	DMAEMA	tBAEMA
V-19	20.1	20.1
L101	3.3	3.5
L130	10.4	11.4
L231	4.9	6.0

Colorimetric Measurements

The goal of using an azo initiator instead of an organic peroxide is not limited to effecting grafting onto polyethylene but, more importantly, to reducing the discoloration of the grafted polymers. Thus, colorimetric measurements were performed on samples grafted with V-19 and the peroxide initiators. Typical results (color indices) are listed in Table VI.

It is clearly shown that the lightness and red/green indices of the grafted polymers were improved by using V-19 instead of organic peroxide initiators. In fact, the indices for polymers grafted with V-19 were very close to those of virgin LLDPE. However, addition of L101, L130, or L231 reduces the lightness and increases the redness of the polyethylene, which is consistent with the proposed formation of amine oxides, a red species. The blue/yellow index changes from −7 for unprocessed LLDPE to 29 ± 1 for polymers grafted with all the initiators studied.

It must be mentioned that the oxidation of amines by molecular oxygen at high temperatures such as

Table VI   Comparison of Color Indices of DMAEMA-grafted LLDPE with V-19, L101, L130, and L231 at 160°C

	Color Index[a]		
	L	A	B
V-19	61	0	29
L101	56	5	30
L130	55	4	28
L231	54	4	30
LLDPE	64	−1	−7

[a] L: (100) light/dark (0); A: (+) red/green (−); B: (+) blue/yellow (−).

those under the melt grafting conditions can also contribute to the discoloration of polymers. The operation on the Haake mixer does not allow easy prevention of oxygen in the air from contacting the hot polymer melts. If this can be further eliminated, less discoloration should be observed.

CONCLUSIONS

Hydrogen-abstraction reactions observed through polyethylene cross-linking and polypropylene degradation experiments demonstrated that the free radicals produced from the decomposition of the azo initiators V-30 and V-40 cannot abstract hydrogen atoms from the polymer backbones. The grafting experiments conducted with LLDPE (LL5103) and monomers DMAEMA and tBAEMA have confirmed this observation by showing that no grafting was realized with these two azo initiators. However, the phenylazo initiator V-19 was revealed to have a remarkable capability to abstract hydrogen atoms from polymer backbones and to initiate the grafting of both DMAEMA and tBAEMA onto LLDPE. Colorimetric measurements demonstrated that the discoloration of grafted polymers with V-19 was significantly reduced compared to those functionalized with organic peroxide initiators. Further examination of the melt grafting results shows that the phenyl free radical generated from the decomposition of V-19 is a stronger hydrogen abstractor than are organic peroxide and methyl free radicals produced from the decomposition of organic peroxides. Therefore, V-19 demonstrated not only the nonoxidative property in preventing the discoloration of basic functionalized polymers, but also a higher initiating efficiency than that of organic peroxide initiators. The experimental results clearly indicate that the phenylazo initiator V-19 can be used as an improved initiator for the melt grafting of aminobearing monomers onto polyethylenes. These advantages could extend the usefulness of the phenylazo-type initiators into various other applications involving fragile or oxidizable functionalities, such as aldehydes, thiols, etc.

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