Polymer 51 (2010) 153–163

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Thermoreversible crosslinking of polyethylene enabled by free radical initiated functionalization with urethane nitroxyls

Bharat Indu Chaudhary [a,*], Thomas H. Peterson [b], Eric Wasserman [a], Stéphane Costeux [b], John Klier [b], Andrew J. Pasztor Jr. [b]

[a] *The Dow Chemical Company, 171 River Road, Piscataway, NJ 08854, USA*
[b] *The Dow Chemical Company, Midland, MI 48674, USA*

ARTICLE INFO

Article history:
Received 28 July 2009
Received in revised form
17 November 2009
Accepted 18 November 2009
Available online 26 November 2009

Keywords:
Thermoreversible
Crosslinking
Polyethylene

ABSTRACT

This paper describes the functionalization of polyethylene with urethane derivatives of 2,2,6,6-tetramethylpiperidinyloxy (TEMPO), resulting in thermoreversible crosslinking of the polymer, which exhibits thermoplastic characteristics at sufficiently elevated temperatures. The urethane TEMPO adducts were synthesized by the reaction of 4-hydroxy TEMPO with various diisocyanates using appropriate catalysts, and were subsequently grafted to polyethylene using free-radical chemistry. A model study conducted on urethane isopropanol adducts confirmed that endothermic urethane reversion occurred with aromatic and alkyl diisocyanates at temperatures greater than 170 °C, and no exothermic urethane decomposition was observed. In contrast, urethane TEMPO adducts underwent exothermic decomposition at elevated temperatures, probably because of participation of the free nitroxyl species in urethane decomposition. Hence, the urethane TEMPO adducts were most effective when used as crosslinkers below their decomposition points.

1. Introduction

Polyolefins such as ethylenic polymers are often crosslinked in order to increase resistance to flow and high temperature deformation, as well as to enhance other properties. The methods used to crosslink polyolefins include the use of organic peroxides at elevated temperatures which generate polymer radicals that subsequently combine to form carbon–carbon bonds [1–9].

For the specific case of polyethylene, it has been demonstrated that crosslinking via peroxides can be controlled through the reaction of carbon-centered radicals with persistent nitroxyl radicals such as 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) and its derivatives which, if additional functionality is present, also enables functionalization of the polymer [10]. The mechanism through which crosslinking or “cure” is influenced by persistent radicals derives from their ability to intercept incipient polymeryl radicals formed via hydrogen atom abstraction by peroxides to yield polymeryl alkoxyamines [10]. When persistent radicals comprising more than one nitroxyl (such as PROSTAB® 5415, also known as “bis-TEMPO”) are used, crosslinks result and the polymer is transformed from a thermoplastic to a thermoset.

A key disadvantage of peroxide-based crosslinking (as well as other conventional crosslinking chemistries, including silane and radiation technologies) is that the materials become thermoset, and cannot be processed as thermoplastics after manufacture. Therefore, it would be advantageous to identify and develop a strategy that enables polymer crosslinking in a reversible manner wherein the subsequent application of a chemical or physical stimulus permits controlled reversion of the thermoset back to its antecedent thermoplastic form. This strategy may take advantage of a variety of chemistries, for instance, by incorporating a reactive group into the polymer architecture through grafting or copolymerization of a functional comonomer and subsequently coupling with difunctional crosslinking agents that react in a reversible manner. For the case of thermoreversible crosslinking, reversion to the non-crosslinked thermoplastic state may be achieved by the application of high temperatures wherein the entropic gains of decrosslinking overcome the enthalpic driving force of crosslinking. Entropy values typical for fragmentation reactions are in the range of 20–30 cal mol^{-1}. Thus, by a judicious choice of the crosslinking chemistry, one can, in theory incorporate reactions where the entropic/enthalpic balance effects decrosslinking in a temperature range useful for polymer processing.

In this paper, we describe a novel approach toward thermoreversible crosslinking by taking advantage of the reversibility of the reactions of isocyanates with alcohols that can be grafted to the

---

* Corresponding author. Tel.: +1 732 563 5137; fax: +1 732 563 5218.
E-mail address: bichaudhary@dow.com (B.I. Chaudhary).

0032-3861/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2009.11.039

polymer backbone through radical-mediated nitroxyl coupling. Specifically, we have synthesized diurethane crosslinking agents that are end-capped with graftable nitroxyl groups. The urethane linkage, derived from reactions of isocyanates with polyols, is known to be thermoreversible at temperatures between 120 °C and 250 °C, depending on the nature of the alcohol and isocyanate precursors [11]. In the present work, urethane TEMPO adducts were synthesized by reactions of 4-hydroxy TEMPO with various diisocyanates, and these were grafted to polyethylene to impart thermoreversibility to the crosslinked polymer. A schematic of such thermoreversible crosslinking with urethane bis-TEMPO (UBT) derivatives is shown in Fig. 1. Although this concept has been demonstrated with polyethylene and peroxides, it is potentially adaptable to other polymers (such as propylene polymers) and with other free-radical generators (such as electron beam radiation).

2. Experimental materials and procedures

2.1. Polymer

The polymer used in this investigation was low-density polyethylene (LDPE). It was additive-free, to start with, and its properties were as follows: Melt index (measured in accordance with ASTM D-1238; 190 °C: I_2 with 2.16 kg load) of 2.4 dg/min; density (determined according to ASTM D-792) of 0.9200 g/cc. Detailed characterization of this polymer was published in a previous paper [10].

2.2. Synthesis of urethane TEMPO adducts

2.2.1. General

Unless otherwise indicated, all reactions were performed under nitrogen in a dry box or on a vacuum line. Anhydrous solvents used were purchased from Honeywell, Burdick and Jackson or Aldrich and were further purified through an in-house solvent clean-up system. Hexamethylene diisocyanate (HMDI), methylenediphenylisocyanate (MDI), triethylamine and dibutyltin dilaurate (DBTDL) were obtained from Aldrich. PAPI® 901 (polymeric MDI) was obtained from The Dow Chemical Company. 4-Hydroxy TEMPO refers to 4-hydroxy-2,2,6,6-tetramethyl-1-piperidinyloxy, obtained from AH Marks or Aldrich. The urethane nitroxyls synthesized (HMDI UBT, MDI UBT, and PAPI-TEMPO adducts) are illustrated in Fig. 2. Infrared spectroscopy of HMDI UBT, MDI UBT and PT adducts was performed using a Mattson Galaxy 5000 spectrometer.

2.2.2. Synthesis

Preparation of HMDI UBT. To a stirred solution of HMDI (8.00 g, 49.7 mmol) in methylene chloride (100 mL) was added 4-hydroxy TEMPO (17.55 g, 101.9 mmol, 2.05 equiv). The mixture was stirred for 2 h at room temperature and DBTDL (100 µL, 0.174 mmol, 0.0035 equiv) was added. Stirring was continued at room temperature for an additional 48 h. After that time, the solvent was removed under reduced pressure to yield a viscous orange oil. The oil was macerated with a metal spatula while repeatedly washing the resulting paste with hexanes until a peach-tan colored solid was obtained. The solid was vigorously stirred with hexanes overnight and filtered under vacuum. The solid was then dried under vacuum to give a pale peach-colored powder (23.62 g) in 93% yield. Infrared spectroscopic analysis of the solid indicated complete disappearance of the –NCO band at 2262 cm^{-1}, hence complete consumption of the isocyanate residues in the sample. IR (Thin Film) 3332 (N–H), 2930 (C–H), 1703 (C=O), 1520 cm^{-1}. HRMS: Calc. 514.3730, Anal. 514.3796 **HMDI UBTH$_2$:** HMDI UBT was characterized as its diamagnetic reduced derivative by heating a toluene solution of HMDI UBT and 1.05 equiv of 9,10-dihydroanthrcene overnight at 100 °C (Fig. 3). The orange-peach color of the HMDI

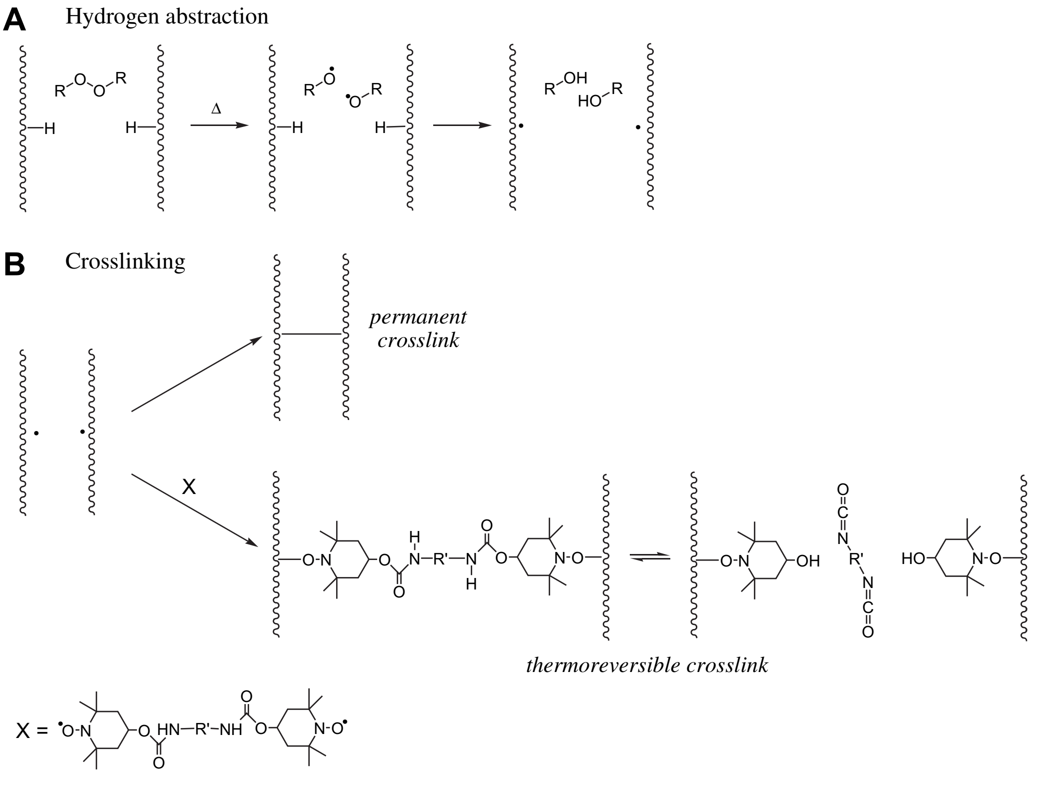


Fig. 1. Schematic of thermoreversible crosslinking with urethane chemistry.

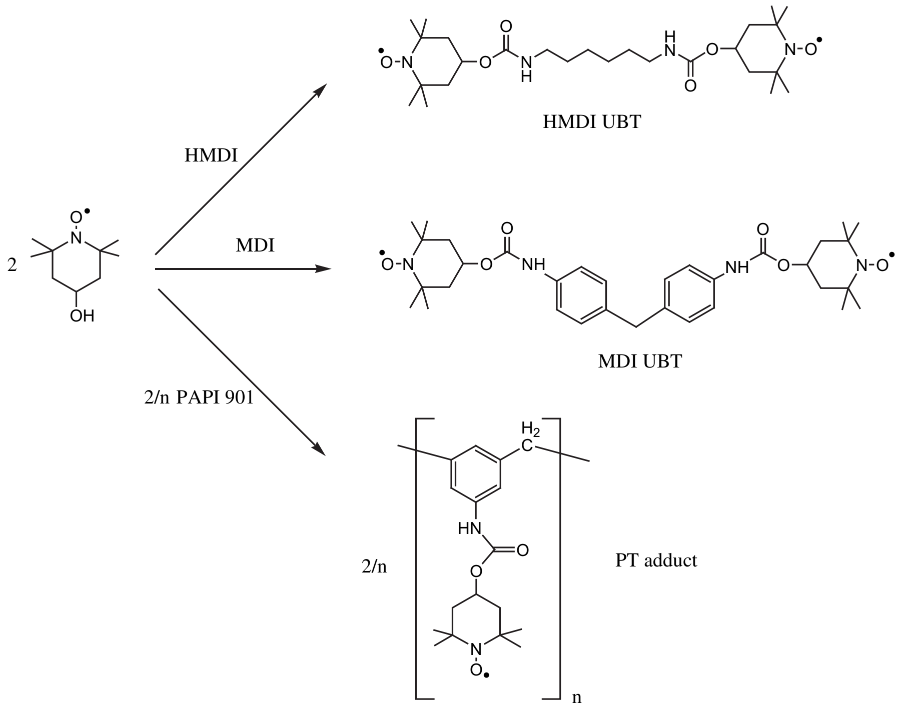


Fig. 2. Chemical structures of HMDI UBT, MDI UBT and PAPI-TEMPO adduct.

UBT solution bleached during reaction resulting in a colorless solution at the conclusion of reaction. HMDI UBTH$_2$ was isolated as a white powder and was purified by recrystallization from a hot toluene solution. The derivatization was determined to be quantitative by ^{1}H NMR analysis. ^{1}H NMR (THF-d_8) δ 1.13 (*s*, 12 H), 1.14 (*s*, 12 H), 1.26–1.55 (*m*, 12 H), 1.86 (*m*, 4 H), 3.04 (AB q, $J = 6.6$ Hz, 4 H), 4.87 (*m*, 2 H), 6.11 (br s, 2 H), 6.53 (*s*, 2 H) ppm. ^{13}C NMR (THF-d_8) 20.90, 27.61, 31.22, 33.19, 41.61, 45.83, 59.55, 156.75 ppm. HRMS: Calc. 512.3574, Anal. 512.3647.

Preparation of MDI UBT. A solution of 4-hydroxy TEMPO (15.56 g, 90.31 mmol, 2.26 equiv) in 3:1 v:v Et$_2$O-toluene (100 mL) was added to a solution of MDI (10 g, 40.0 mmol) in toluene (30 mL). After 45 min of stirring at room temperature, dibutyltin dilaurate (100 µL, 0.167 mmol, 0.0042 equiv) was added via syringe. Stirring was continued for 6 h at room temperature after which the addition of pentane caused the separation of a viscous orange oil. The supernatant was decanted and set aside and the oil was twice washed with diethyl ether, followed by pentane, resulting in precipitation of a beige solid. The solid was washed with ether and dried *in vacuo* to afford 16.2 g of a pale peach-colored powder. An additional 3.0 g of material was recovered from the wash supernatants by addition of pentane, giving a total yield of 19.2 g (80%). Infrared spectroscopic analysis of the solid indicated complete disappearance of the –NCO band at 2274 cm^{-1}, IR (thin Film) 3295 (N–H), 2967 (C–H), 1715 (C=O), 1533 cm^{-1}. HRMS: Calc. 594.3417, Anal. 594.3486. **HMDI UBTH$_2$:** MDI UBT was characterized as its

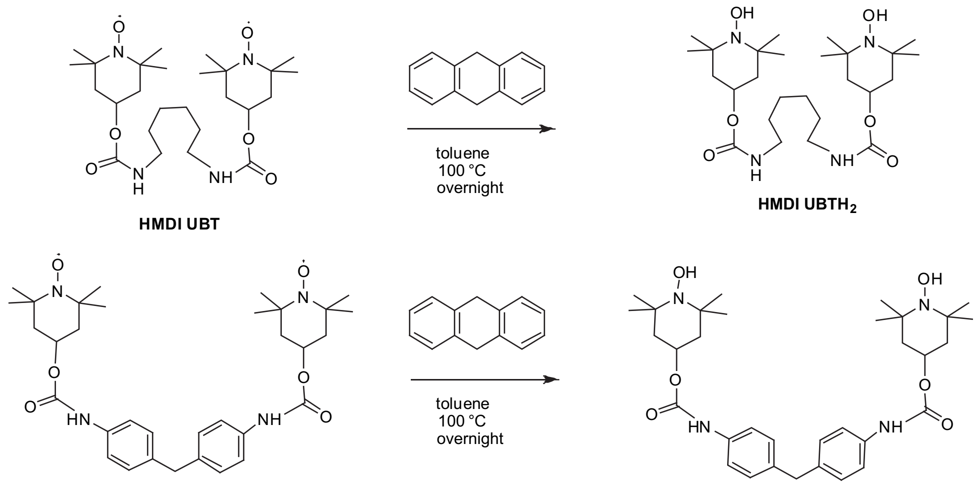


Fig. 3. Derivatization of HMDI UBTH$_2$ and MDI UBTH$_2$.

diamagnetic reduced derivative by heating a toluene solution of MDI UBT and 1.05 equiv of 9,10-dihydroanthrcene overnight at 100 °C (Fig. 3). The orange-red color of the HMDI UBT solution bleached during reaction resulting in a pale-yellow solution at the conclusion of reaction. MDI UBTH$_2$ was isolated as a white powder and was purified by recrystallization from a hot toluene solution. The derivatization was determined to be quantitative by ^{1}H NMR analysis. ^{1}H NMR (THF-d_8) 1.15 (*s*, 12 H), 1.18 (*s*, 12 H), 1.48 (*t*, $J = 12.3$ Hz, 4 H), 1.93 (dt, $J = 12.3$, 1.4 Hz, 2 H), 1.97 (dt, $J = 12.3$, 1.4 Hz, 2 H), 3.83 (*s*, 2 H), 5.00 (*m*, 2H), 6.58 (*s*, 2H), 7.02 (AB *q*, $J = 8.5$ Hz, 4 H), 7.34 (AB *q*, $J = 8.5$ Hz, 4 H), 8.50 (*s*, 2 H) ppm. ^{13}C NMR (THF-d_8) 20.58, 33.09, 41.31, 45.50, 59.42, 119.01, 129.86, 136.39, 138.74, 153.94 ppm. HRMS: Calc. 596.3574, Anal. 596.3639.

Preparation of PAPI-TEMPO adduct (PT adduct). A mixture of PAPI® 901 (5 mL, 46.2 mmol of isocyanate equivlants) and 4-hydroxy TEMPO (9.95 g, 57.8 mmol, 1.25 equiv) in 50 mL THF was refluxed for 23 h. After cooling to room temperature, the volatile materials were removed under reduced pressure to yield a viscous brown liquid. The liquid was repeatedly washed with diethyl ether and then with hexanes to yield a granular solid. Filtration and drying *in vac*uo produced a pale tan solid (10.5 g) representing a 75% yield. IR (Thin Film) 3311 (N–H), 2988 (C–H), 1722 (C=O), 1533 cm^{-1}.

2.3. Thermal studies of urethane TEMPO adducts

Thermal transitions of the PT adduct and HMDI UBT were determined by differential scanning calorimetry (DSC) in a closed pan, using Thermal Analysis (TA) Model 2920. The sample was heated from −50 °C to 150 °C at a rate of 10 °C/min (1st heat); cooled to −50 °C at a rate of 10 °C/min; and heated to 300 °C at a rate of 10 °C/min (2nd heat).

The thermal stability of the PT adduct was investigated by Thermal Gravimetric Analysis (TGA) using TA Instruments High Resolution TGA 2950 version 5.4A. TGA testing was conducted under nitrogen by raising the temperature from 20 °C to 800 °C at a rate of 10 °C/min, to determine the weight loss as a function of temperature.

The thermal stability of the PT adduct was also studied by hot cell FT-IR. Samples were analyzed via transmission between 25 mm round KBr disks. Hot cell FT-IR data were collected on a Nicolet Magna 750 FT-IR spectrometer running on Omnic E.S.P. software and fitted with a Thermo Electron Model 0019-200 heated cell and a DTGS detector. Temperature was controlled using a Scientific Instrument Inc (SIS) Model CT-101 temperature controller. The assembled cell, including clean KBr disks was placed in the nitrogen purged sample compartment, heated to 150 °C and used as the background spectrum. Acquisition parameters were set at 64 co-added scans, 4 cm^{-1} resolution and triangular apodization was employed. The cell was removed, partially disassembled, sample inserted, reassembled, and placed back in the spectrometer. Spectral collection for the PT adduct started at 150 °C and raised in 10 °C increments to 280 °C. Samples were given 5 min at each temperature to equilibrate prior to spectral collection. All data were plotted in absorbance relative to the empty cell.

2.4. Model studies of urethane adducts with isopropanol (iPrOH)

Preparation of HMDI-iPrOH. A 100 mL RBF equipped with a magnetic stir bar was charged with isopropanol (30 mL). Hexamethylene diisocyanate (2.04 g, 2.00 mL 12.2 mmol) and dibutyltin dilaurate (DBTDL) (25 μL, 0.0425 mmol, 0.0035 equiv) were added successively. The mixture was stirred 48 h at ambient temperature. After 48 h, the volatile materials were removed *in vacuo* to provide a white powder. The powder was dissolved in 20 mL of CH$_2$Cl$_2$ and the solution was layered with hexanes. Long fibrous crystals were formed over the course of several days. The crystals were collected on a frit and dried *in vacuo* to give 2.65 g of product in 76 % yield. ^{1}H NMR (CDCl$_3$) δ 1.23 (d, $J_{\text{H–H}} = 6.2$ Hz 12 H), 1.34 (*m* 4 H), 1.50 (*m* 4 H), 3.16 (br *m* 4 H), 4.65 (br *s* 2 H), 4.91 (septet, $J_{\text{H–H}} = 6.2$ Hz 2 H) ppm. ^{13}C {^{1}H} NMR (CDCl$_3$) δ 22.45, 26.59, 30.23, 40.90, 68.96, 156.44 ppm. HRMS: Calc. 288.2049, Anal. 288.2128.

Preparation of MDI-iPrOH. In a 100 mL RBF equipped with a magnetic stir bar methylenediphenyldiisocyanate (2.00 g, 7.99 mmol) and dibutyltin dilaurate (DBTDL) (25 μL, .044 mmol, 0.0035 equiv) were dissolved in isopropanol (30 mL). The MDI had only partial solubility in isopropanol and the slurry was stirred 48 h at ambient temperature. After that time the volatile materials were removed *in vacuo* to provide a white powder. The powder was dissolved in 20 mL of CH$_2$Cl$_2$ and was layered with hexanes. Long fibrous crystals formed over the course of several days. The white solid was collected on a frit and was dried *in vacuo* to give 0.67 g of desired product in 23% yield from a single crop. ^{1}H NMR (CDCl$_3$) δ 1.32 (*d*, $J_{\text{H–H}} = 6.2$ Hz 12 H), 3.91 (br *s* 2 H), 5.04 (septet, $J_{\text{H–H}} = 6.2$ Hz 2 H), 6.66 (br *s*, 2 H), 7.12 (AB quartet, $J_{\text{H–H}} = 8.7$ Hz 4 H), 7.32 (AB quartet, $J_{\text{H–H}} = 8.6$ Hz 4 H),ppm. ^{13}C {^{1}H} NMR (CDCl$_3$) δ 22.31, 40.76, 68.82, 100.11, 119.00, 136.22, 136.27, 153.40 ppm. HRMS: Calc. 370.1893, Anal. 370.1968.

2.5. Thermal investigation of HMDI-iPrOH and MDI-iPrOH model compounds

Thermal transitions of these urethane adducts were investigated by closed capillary DSC. A method for using glass capillaries to prevent sample loss has been previously described [12,13]. A portion of the sample was placed in a glass capillary and while the sample was frozen (using a cold finger at liquid nitrogen temperatures) the glass capillary was flame sealed. Special silver capillary holders were used for the measurement as well as temperature and heat flow calibration. The sample was re-weighed after the DSC scan to assure that no sample mass was lost.

TGA/DSC/MS experiments on the model compounds were conducted in open pans using TA Instruments 2960 SDT running operating system V3.0F and with a MS interface via a heated sample line. After loading, the sample was ramped rapidly to 160 °C under a stream of nitrogen where it was held in isothermal mode for a period of 6 h during which mass change, heat flow and selected ions were monitored.

2.6. Melt blending of peroxides and urethane TEMPO adducts with polyethylene

Peroxides and/or urethane TEMPO adducts (ranging in concentration from 1 wt% to 4 wt%) were blended with polyethylene using a Brabender mixing bowl. The polymer and nitroxyls (except peroxide) were mixed for 3 min at 125 °C, followed by additional 4 min mixing with peroxide at that temperature, in the mixing bowl. The temperature was low enough to avoid significant decomposition of the peroxide, while still melting the polymer. The free-radical generators studied were: 2,5-bis(tert-butylperoxy)-2,5-dimethylhexane [Luperox® 101 (L101)] and 2,5-bis(tert-butylperoxy)-2,5-dimethyl-3-hexyne [Luperox® 130 (L130)]. These two peroxides were used (instead of more commonly available dicumyl peroxide) in order to minimize the amounts of methyl radicals spontaneously generated from peroxide decomposition, since these can also be trapped by nitroxyls thereby leading to decreased nitroxyl trapping of carbon-centered polymer radicals [10]. The nitroxyls evaluated were HMDI UBT, MDI UBT, and PT adduct (Fig. 2).

2.7. Crosslinking kinetics and solid/melt state properties of crosslinked polyethylene

The kinetics of free-radical (peroxide) grafting of urethane TEMPO adducts to polyethylene were studied at temperatures of 160 °C, 180 °C and 200 °C using a Moving Die Rheometer from Alpha-Technologies (Model MDR 2000), set at 100 cycles/min and deformation amplitude of 0.5°. Details of the experimental procedure have been described elsewhere [10]. Comparisons were made with peroxide crosslinked polyethylene without any urethane TEMPO adducts in the composition. The products from the MDR experiments were subjected to extraction in boiling decalin or cyclohexane in order to measure the gel fraction. This method, ASTM D-2765, Method A, determines the percentage of a sample that is soluble in decalin (190 °C boiling point) or cyclohexane (80 °C boiling point) over 6 h. The material which is insoluble, and therefore does not pass through a 120 mesh screen, is the crosslinked portion of the material (and is reported as the gel content).

Specimens were prepared for the following property evaluations by compression molding at 160 °C until complete decomposition of peroxide, followed by aging for 1 week at room temperature, to fully crosslink those compositions that contained peroxide and/or urethane TEMPO adducts.

Dynamic modulus was measured as a function of temperature using a dynamic mechanical spectrometer (DMS). The DMS testing on samples (prepared by compression molding at 160 °C for 120 min) was performed on an ARES controlled strain rheometer (TA Instruments) equipped with dual cantilever fixtures for torsion testing. A 1.5 mm plaque was pressed and cut into a bar of dimensions 32 mm × 12 mm. The sample was then clamped at both ends between the fixtures separated by 10 mm (grip separation ΔL) and subjected to successive temperature steps from 30 °C to 220 °C (2 °C per step). At each temperature, the torsion moduli G' and G'' were measured at an angular frequency of 10 rad/s, the strain amplitude being maintained between 0.1% and 3% to ensure that the torque was sufficient and that the measurement remained in the linear regime. The tangent of the loss angle, tan(δ), was obtained as G''/G' at every temperature. An initial static force of 10 g was maintained (auto-tension mode) to prevent slack in the sample when thermal expansion occurred. As a consequence, the grip separation ΔL increased with temperature, particularly above the melting or softening point. The test stopped at the maximum temperature or when the gap between the fixtures reached 65 mm.

Temperature-dependent probe penetration experiments were performed using a TA instrument Thermo-Mechanical Analyzer (TMA) on samples (prepared by compression molding at 160 °C for 120 minutes). The sample was cut into an 8 mm disk (thickness = 1.5 mm). A 1 mm diameter cylindrical probe was brought to the surface of the sample and a force of 1 N (102 g) was applied. As the temperature was varied from 30 °C to 220 °C at a rate of 5 °C/min, the probe penetrated into the sample due to the constant load and the rate of displacement was monitored. The test ended when the penetration depth reached 1 mm.

Dynamic oscillatory shear measurements were conducted using a Weissenberg Rheogoniometer on samples (prepared by compression molding at 160 °C for 100 min) at temperatures ranging from 140 °C to 220 °C, to determine if the urethane-crosslinked compositions would flow at elevated temperatures and to compare melt rheological properties with those of uncrosslinked polyethylene. Each frequency sweep from 0.1 to 100 rad/s took about 15 min to complete (including about 3 min initially to equilibrate at test temperature). The data were then fit by the commercial IRIS™ software using the method of Baumgaertel and Winter [14] to determine the discrete relaxation spectrum (g_i, λ_i) by fitting the dynamic moduli G' and G'' over the range of frequency ω:

$$G'(\omega) = \sum_{i=1}^{N} g_i \frac{(\omega\lambda_i)^2}{1+(\omega\lambda_i)^2} \quad \text{and} \quad G''(\omega) = \sum_{i=1}^{N} g_i \frac{\omega\lambda_i}{1+(\omega\lambda_i)^2}$$

The Relaxation Spectrum Index [15], a measure of the breadth of the relaxation index, was calculated as the ratio of the first two moments of the relaxation spectrum:

$$\mathrm{RSI} = \lambda_{\mathrm{II}}/\lambda_{\mathrm{I}}, \quad \text{where } \lambda_{\mathrm{I}} = \sum_{i=1}^{N} \frac{g_i}{g_i/\lambda_i} \text{ and } \lambda_{\mathrm{II}} = \sum_{i=1}^{N} \frac{g_i\lambda_i}{g_i}$$

3. Results and discussion

3.1. Synthesis of urethane TEMPO adducts

The synthesis of the targeted urethane TEMPO adducts was effected using standard procedures developed for isocyanate-alcohol coupling reactions. In general, secondary alcohols could be efficiently reacted with aliphatic isocyanates using dibutyltin dilaurate as a catalyst. Aromatic isocyanates could be reacted using triethylamine as a catalyst, though reactions are generally faster with the tin catalyst. Molecular characterization of the urethane nitroxyls was attempted by NMR, but the species are paramagnetic and so the NMR spectra could not be used to characterize structure. Instead, the paramagnetic urethane TEMPO adducts derived from HMDI and MDI were converted to diamagnetic species by reaction with 9,10-hydroanthracene. Heating toluene solutions of HMDI UBT or MDI UBT at 100 °C overnight with a slight excess of 9,10-dihydroanthracene afforded hydrogen atom transfer and quantitative conversion to the corresponding TEMPOH species, permitting characterization by ^{1}H and ^{13}C NMR spectroscopy.

For the polymeric aromatic system PAPI 901, 3 h reaction time with triethylamine as the catalyst was insufficient to achieve complete conversion of the starting materials (at an initial concentration of approximately 1 M). Infrared spectroscopy provided a convenient means of monitoring the progress of the reaction. After 3 h, a significant quantity of PAPI 901 remained, as was evident from the intense band at 2266 cm^{-1}, and so the reaction was maintained for 20 h whereupon a second sampling indicated complete conversion (Fig. 4). The product was isolated from the reaction mixture as a viscous oil. However, as with its two congeners, the initially isolated product could be induced to solidify by maceration of the oil with a non-solvent (e.g., ether or alkane). This procedure also permitted the removal of unreacted 4-hydroxy TEMPO from the reaction mixture. Infrared analysis of the resin purified in this manner indicated that no unreacted TEMPO or isocyanate functionality remained (Fig. 5).

An initial attempt to prepare the analogous product between MDI and 4-hydroxy TEMPO was made without a catalyst; however, when no reaction was evident after a period of 45 min, dibutyltin dilaurate was added. The addition of the tin catalyst led to immediate reaction as indicated by a rise in the pot temperature. After 6 h of stirring without the application of an external heat source, the reaction was complete by IR spectroscopy. In contrast to the PAPI 901 adduct, the MDI adduct remained soluble in the reaction medium. The addition of pentane induced precipitation of the crude product as a viscous oil that could be treated similarly to the PAPI adduct to obtain a purified solid product.

The adduct derived from the aliphatic isocyanate HMDI also required the use of the tin catalyst for its preparation. Stirring HMDI and 4-hydroxy TEMPO together in methylene chloride solution with 0.35 mol percent tin catalyst for a period of 96 h effected complete conversion. In subsequent experiments, we found that the reaction is essentially complete within 48 h. In contrast to the work of Lizzotte et al. [16], the HMDI urethane bis-TEMPO could be

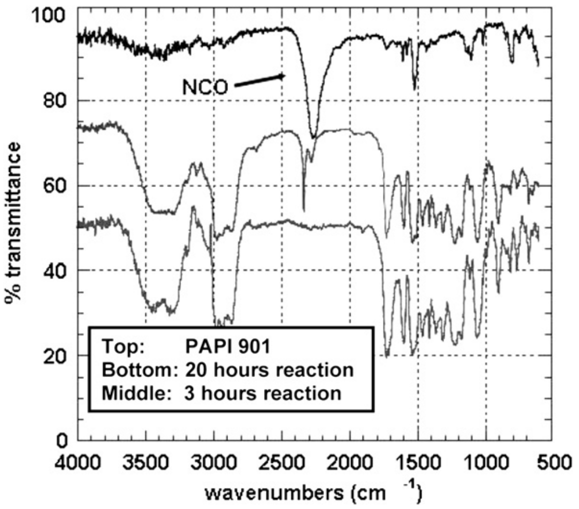


Fig. 4. Infrared spectral monitoring of the reaction between PAPI 901 and 4-hydroxy TEMPO.

isolated as a solid when the oil was washed exhaustively with a non-solvent.

3.2. Thermal stabilities of urethane TEMPO reagents and model studies

In order to gain insight into the thermochemical attributes of the urethane-based crosslinking agents, we examined the thermal stabilities of the urethane TEMPO adducts and urethane model compounds using DSC and TGA/DSC/MS techniques. DSC analysis of HMDI-TEMPO (2nd heat) indicated an endothermic feature at 122 °C corresponding to the melt of the crystalline solid followed by two large exotherms (74 kcal mol^{-1}) with an onset at 190 °C and peak temperatures of 237 and 250 °C. Since the thermal reversion of a urethane group would be manifest as an *endothermic* feature (ca. 20 kcal mol^{-1}), we have interpreted the large exotherm therefore to correspond to an unknown decomposition of the HMDI-TEMPO agent. Support for this assertion was obtained from the corresponding cooling cycle which showed irreversibility by the lack of the expected exo- and endotherm features.

For the reagents derived from aromatic isocyanates, MDI-TEMPO and PAPI-TEMPO, slightly different behavior was observed. The MDI-TEMPO exhibited a melt feature at 145 °C and a minor endotherm with an onset at 170 °C. Continued heating above 190 °C led to two large exothermic events with peak temperatures identical to that for the HMDI-TEMPO adduct. Similarly, the PT adduct showed a melt transition at 93 °C followed by large exotherm of (259.7 J/g) with onset and peak temperatures of 180 °C and 232 °C, respectively. As before, we interpret the exothermic thermal event to correspond to a decomposition reaction involving the urethane functional group.

In order to determine if the potentially reactive nitroxyl group was contributing to the decomposition reaction, we also prepared and examined model compounds (Fig. 6) derived from the reaction of isopropanol (iPrOH) with HMDI and MDI. In contrast to the urethane TEMPO agents, the urethane-iPrOH agents did not exhibit exothermic decomposition up to 250 °C (Fig. 7). HMDI-iPrOH exhibited two reversible melt features at 85 °C and 105 °C. Beginning at 179 °C, the onset of an endothermic event (24.1 kcal mol^{-1}) was observed continuing with a peak temperature of 234 °C. For MDI-iPrOH, a single melt feature at 152 °C was accompanied by the endothermic reversion (33 kcal mol^{-1}) with onset and peak temperatures of 230 °C and 273 °C, respectively. With consideration of the putatively greater stability of urethanes based on aliphatic isocyanates in comparison to urethanes derived from aromatic isocyanates, we were somewhat surprised that endothermic reversion of HMDI-iPrOH occurred at a lower temperature than that of MDI-iPrOH. However, further support for the greater lability of iPrOH in HMDI-iPrOH in comparison to MDI-iPrOH was obtained through TGA/DSC/MS studies of the model compounds. In these experiments, the samples were ramped to 160 °C and held for 6 h while heat flow, mass loss and selected masses were monitored. Mass spectral data during the experiment indicated that mass loss was occurring by loss of iPrOH. Unfortunately, at 160 °C, the low rate of reversion precluded detection of any change in the heat load of the sample. After 6 h, the HMDI-iPrOH sample experienced a 36% mass loss compared to only 4% mass loss for the iPrOH-MDI compound. The theoretical mass loss for HMDI-iProH and MDI-iPrOH arising from reversion and iPrOH volatilization were 42% and 32%, respectively. Therefore, despite literature claims concerning relative stabilities, reversion in the aliphatic urethane of our system appears more facile than reversion in the aromatic system.

The reason for the discrepancy in DSC behavior between the TEMPO adducts and model compounds became apparent when 4-hydroxy TEMPO itself was analyzed by DSC. Following a melt at 52 °C, 4-hydroxy TEMPO exhibited two large exothermic events with an initial onset temperature of 178 °C. These decomposition events were superimposable with those observed for the urethane TEMPO adducts indicating that the nitroxyl functionality was responsible for the discrepancy in thermal behavior between the urethane TEMPO adducts and the urethane-iPrOH model compounds. Note that, since the DSC scans were done in sealed glass capillaries to prevent weight loss (and none was found), sublimation of the sample can be excluded. This result places a practical constraint on the application of urethane TEMPO agents

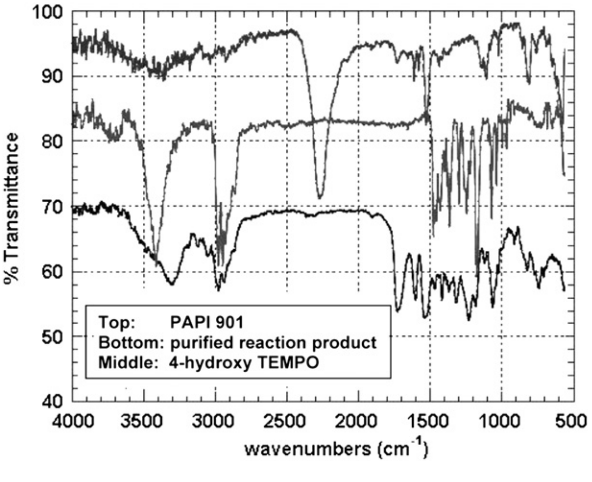


Fig. 5. Infrared spectral analysis of the purified reaction product (PT adduct) between PAPI 901 and 4-hydroxy TEMPO.

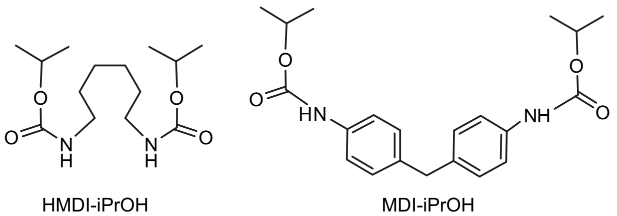


Fig. 6. Model compounds (MDI-iPrOH and HMDI-iPrOH) synthesized from isopropanol and diisocyanates.

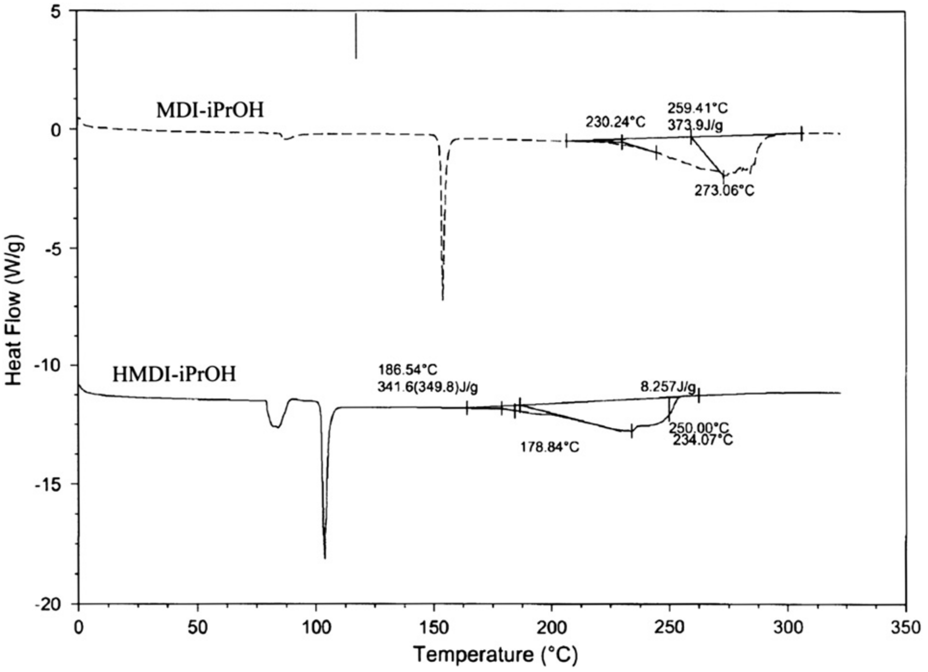


Fig. 7. Closed capillary DSC studies of model compounds MDI-iPrOH and HMDI-iPrOH.

for grafting and crosslinking applications requiring that the grafting step must be conducted at temperatures below 180 °C to avoid significant TEMPO decomposition. It should be noted that DSC data was obtained under "artificially-concentrated" conditions and that similar decompositions may not be relevant under the relatively dilute concentrations of urethane TEMPO encountered in polymer processing. Nevertheless, when interpreting the rheological data that follow, one must consider that some free nitroxyl-bearing species may exist at elevated temperatures, leading to decomposition and an overall reduction in crosslinking efficiency.

Testing of the PT adduct by hot cell FT-IR, in which the temperature was varied from 160 °C to 260 °C in 10 °C increments, showed a decrease in urethane linkages starting from 180 °C and the appearance of what could be interpreted as an isocyanate band starting around 200 °C, thus providing qualitative evidence of urethane reversion at these elevated temperatures (Fig. 8).

3.3. Peroxide and urethane crosslinking of LDPE

An important consideration in the crosslinking of polymers with nitroxyl-bearing species, especially in light of nitroxyl decomposition, is the stability of the graft, since thermal reversion and/or decomposition of the resulting alkoxyamine is known to occur under certain conditions. For example, Otsuka et al. have exploited the lability of nitroxyl-benzylic carbon bonds in styrenic polymers wherein reversible homolysis of the C–O bond provided the basis for macroinitators [17], molecular weight control [18] and crosslinking [19]. However, without sufficient stabilization of incipient carbon radical, C–O bond homolysis does not appreciably occur at temperatures below 200 °C. While the homolytic bond dissociation energies (BDE) of benzylic-TEMPO bonds have been measured to range from 25–31 kcal mol^{-1} enabling homolysis at temperatures as low as 100 °C [20], computational estimates of bond dissociation energies for primary and secondary alkoxyamines derived from TEMPO fall in the range of 40–44 kcal mol^{-1} [21]. In contrast, calculations for tertiary alkoxyamines predicted significantly less stability (BDE = 33 kcal mol^{-1}). Therefore, while the half-life for homolysis of a benzylic-TEMPO bond (BDE = 30 kcal mol^{-1}) would be 9 h at 100 °C, the half-life for homolysis of a secondary carbon-TEMPO bond would be 57 h at 200 °C. Since LDPE possesses primary, secondary and tertiary C–H bonds through which peroxide-mediated grafting of TEMPO reagents may occur, it is possible to generate all three types of alkoxyamines in the present studies. However, in model compound studies, we have determined that with the use of Luperox® 101 and Luperox® 130 as initiators, greater than 95% of the TEMPO grafts reside at the more thermally stable primary or secondary positions on the polymer

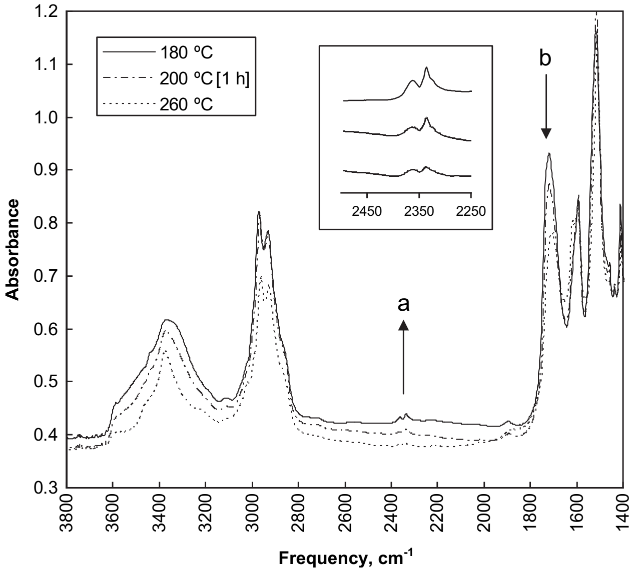


Fig. 8. FTIR spectra of PAPI-TEMPO adduct taken at various temperatures. The spectrum at 200 °C was acquired after holding the sample for 1 h at that temperature. The feature marked "a" indicates increased absorbance attributed to the concentration of isocyanate groups, while "b" marks the loss of absorbance at the frequency characteristic of the carbamate (urethane) C=O stretch.

chain (unpublished results). Consequently, polymer processing at temperatures below 200 °C should not result in graft loss from alkoxyamine decomposition [10].

Unless otherwise noted, the crosslinking experiments in the moving die rheometer (MDR) were conducted at a temperature of 160 °C in order to minimize exothermic decomposition and urethane reversion of the TEMPO adducts at higher temperatures. Under these conditions, decompositions of the PT adduct, MDI UBT and HMDI UBT are unlikely to have occurred, based on the DSC results in which exothermic activity was not observed below 170–190 °C. The results of moving die rheometer experiments conducted at 160 °C to evaluate the effectiveness of grafting and crosslinking with the PT adduct are plotted in Fig. 9. The addition of 4 wt% PT adduct (to polymer compositions containing 1.0 wt% L130 peroxide and 1.5 wt% L130 peroxide) resulted in an unusual flat induction period. As shown previously [10], the induction period corresponds to the initial trapping of polymeryl radicals (and adventitious methyl radicals generated from secondary peroxide decomposition reactions) by the PT adduct generating grafted urethane TEMPO moieties. Once the concentration of free urethane TEMPO reagent is depleted, the pendant grafted nitroxyl group can participate in radical trapping, leading to crosslinking and an expected rise in torque. In the present case, no crosslinks were formed in the initial 25–30 min. Thereafter, radical trapping was increasingly due to the pendant nitroxyl moieties on polymer-bound PT adduct, leading to an increase in MDR torque.

The ultimate degree of crosslinking was measured by the final MDR torque as well as the gel content measured by extraction in boiling decalin or cyclohexane (Table 1). The gel contents were not significantly different with and without PT adduct, at a fixed concentration of peroxide. This indicates that the PT adduct functioned as a crosslinker and did not just inhibit carbon–carbon crosslinking. Of course, it is possible that some of the PT adduct may have been lost during mixing by mechanical promoted degradation and/or volatilization. Noteworthy is the observation that in the presence of PT adduct, the ultimate torques were less than those obtained with peroxide alone. The reason for this is not clear, but it is possible that with the use of a polyfunctional crosslinking agent, the ultimate crosslink architecture (e.g. star-type polymers) could look very different from what would result from simple peroxide carbon-carbon crosslinking or even a dimeric TEMPO adduct. This difference may manifest itself in a lower overall crosslink density as measured by ultimate MDR torque.

Table 1
Gel contents (weight percent) of crosslinked polyethylene.

	Weight percent gels (decalin extraction)	Weight percent gels (cyclohexane extraction)
160 °C/4 h in MDR		
1.0 wt% L130	82	Not available
1.5 wt% L130	87	Not available
1.0 wt% L130 + 4 wt% PT adduct	74	Not available
1.5 wt% L130 + 4 wt% PT adduct	86	91
160 °C/80 min in MDR		
1.25 wt% L101	91	85
1.25 wt% L101 + 3 wt% HMDI UBT	1	63
1.25 wt% L101 + 3 wt% MDI UBT	61	79

The crosslinking of LDPE with L101 peroxide and various urethane bis-TEMPO derivatives at 160 °C is shown in Fig. 10, and the corresponding gel contents are given in Table 1. The theoretical molecular weights of the HMDI UBT and MDI UBT were 512 g/mol and 595 g/mol, respectively. Since the UBT reagents were used at equal weight percent, the molar concentration of nitroxyl varied slightly. The flat induction period observed with PT adduct (Fig. 9) was absent with MDI UBT and HMDI UBT, probably due in part to the faster decomposition rate of L101 in comparison to L130. Despite the fact that both MDI UBT and PAPI-TEMPO effect crosslinking through aromatic/aliphatic urethane linkages, they differed significantly in their crosslinking behavior. Unlike PAPI-TEMPO, the MDI UBT yielded approximately the same ultimate torque as the composition with peroxide alone (Fig. 10). In contrast, the gel content determined by extraction in boiling decalin was substantially lower with MDI UBT as crosslinker. This is consistent with urethane reversion during the elevated temperatures of the extraction procedure and that lower extractables from polymers crosslinked with PAPI-TEMPO derived from inherently more stable crosslinks.

Surprisingly, HMDI UBT yielded very different crosslinking results, exhibiting ultimate torque values less than half of those of its aromatic congeners (Fig. 10). Enthalpic considerations would not have predicted this, since the literature reports that urethanes derived from aliphatic alcohols and aliphatic isocyanates are stable to 250 °C while urethanes derived from aliphatic alcohols and aromatic isocyanates are only stable to about 200 °C [11]. In contrast, the lower degree of crosslinking achieved at 160 °C using HMDI UBT is supported by our model compound studies which showed that reversion occurred at a lower temperature and with a lower net enthalpy for the urethane formed from a secondary alcohol and an aliphatic isocyanate in comparison to the urethane derived from an aromatic isocyanate, However, the degree of reversion that must have occurred at 160 °C is somewhat surprising if bond thermodynamics is the lone consideration, since even the HMDI-iPrOH model compound did not show reversion onset until

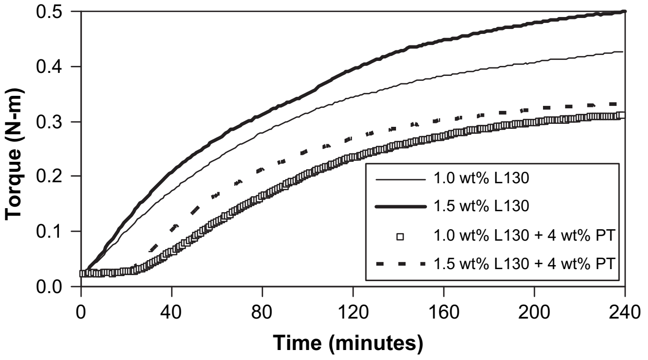


Fig. 9. Crosslinking of LDPE with PT adduct at 160 °C (with L130 peroxide).

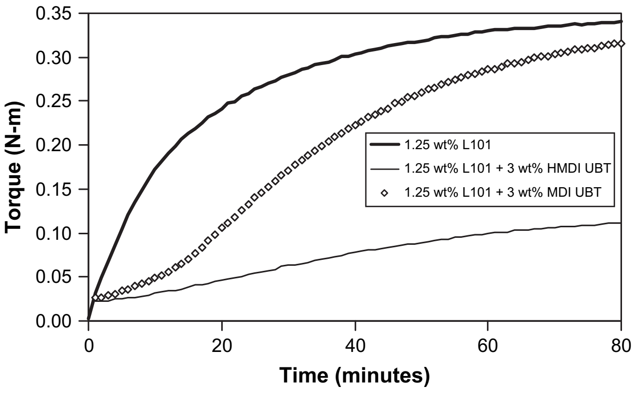


Fig. 10. Crosslinking of LDPE with urethane bis-TEMPO derivatives at 160 °C (with L101 peroxide).

nearly 180 °C. One possible explanation is that urethane reversion at elevated temperature results in free HMDI or MDI that can evaporate from the melt pool resulting in an irreversible loss of crosslinking density. Given the comparatively lower reversion temperature and greater volatility of HMDI, it is reasonable to suppose that it would evaporate faster than the MDI from the melt pool leading to lower torque values.

It is interesting to note that the composition containing PT adduct and L130 peroxide crosslinked at approximately the same rate, and to the same ultimate torque, as one containing HMDI UBT and L130 peroxide (Fig. 11). Since HMDI UBT led to slower and less effective crosslinking than MDI UBT, it can be inferred that the PT adduct was also slower and less efficient than MDI UBT at crosslinking the polymer. This may be due to slower diffusion of the bulkier PT adduct, particularly after its “free” concentration was depleted due to grafting to the polymer, such that the pendant nitroxyls on polymer-bound adduct were not as readily accessible.

The gel contents of fully crosslinked specimens out of MDR, as determined by 6 h extraction in boiling decalin (190 °C) or cyclohexane (80 °C), are plotted in Fig. 12. The tests were also conducted on the uncrosslinked polyethylene (“no peroxide, no TEMPO”). The crosslinking temperatures in the MDR were 160 °C, 180 °C or 200 °C. As expected, the gel content of the uncrosslinked polyethylene was measured as zero in both solvents. The compositions crosslinked with peroxide alone yielded similar gel contents after extraction in both solvents and the gel contents did not vary significantly with MDR test temperature. This confirms that permanent (stable) crosslinks were obtained with peroxide alone. On the other hand, the addition of the PT adduct or urethane bis-TEMPO derivatives generally led to lower values of gel content measured by decalin extraction in comparison with the measurements obtained by cyclohexane extraction, showing that many of the crosslinks that were present at 80 °C had broken over the long period of time at 190 °C, further substantiating the observation that urethane reversion occurred at elevated temperatures. In particular, the difference in gel contents with the two solvents was dramatically different with HMDI UBT, presumably due to the relatively higher amounts of the aliphatic isocyanate generated upon urethane reversion and the associated drive in the equilibrium towards more urethane reversion. The fact that the gel contents of HMDI UBT crosslinked polyethylene measured by decalin extraction were only 1wt% indicates that it contained very few (if any) carbon–carbon crosslinks. This further suggests that the nitroxyls were extremely efficient at trapping polymer radicals and functionalizing the polymer. With the PT adduct and MDI UBT, the crosslinking temperature had an effect on the measured gel contents, with the lowest gel contents obtained at a MDR temperature of 200 °C. This is consistent with any decomposition of the nitroxyls that might have occurred at this temperature (as shown before in the DSC analyses), prior to grafting to the polymer, as well as loss of diisocyanates at the elevated temperatures in MDR. Although the PT adduct had earlier been observed to be a less efficient crosslinker than MDI UBT, the resulting crosslinks did appear to be more thermally stable as evidenced by the results plotted in Fig. 12.

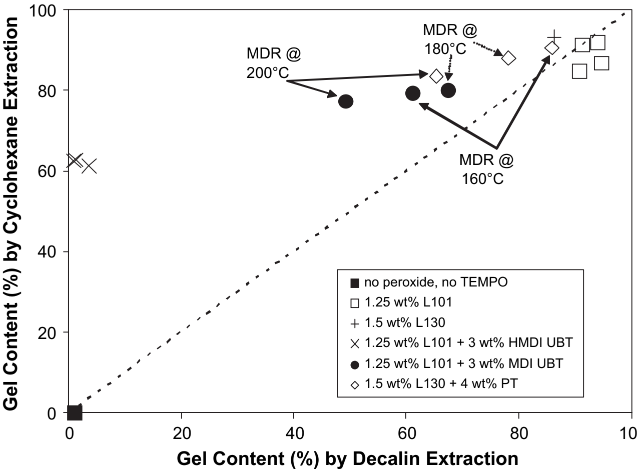


Fig. 12. Effect of extraction solvent (temperature) on gel content of uncrosslinked and crosslinked LDPE.

The results of DMS testing and rate of probe penetration (by TMA) testing are presented in Figs. 13–15. Note that the gel contents reported in these figures are from cyclohexane extraction after 80 min in MDR at 160 °C. Interestingly, the modulus of LDPE crosslinked with MDI UBT decreased to a plateau above the melting point of the polymer, and only started decreasing again above 200 °C, indicating that this was the onset temperature for significant urethane reversion. This reversion temperature was consistent with that observed in model compound studies. No such reversion was observed in the LDPE sample crosslinked with L101 peroxide alone, confirming that the reversion was not due to polymer degradation. The expected decrease in elasticity of the LDPE crosslinked with MDI UBT during reversion was confirmed by the increase in tan(δ) (Fig. 14). The HMDI UBT crosslinked specimen did not show evidence of a plateau above the crystalline melting point, but instead showed a continuous linear decline in modulus up to

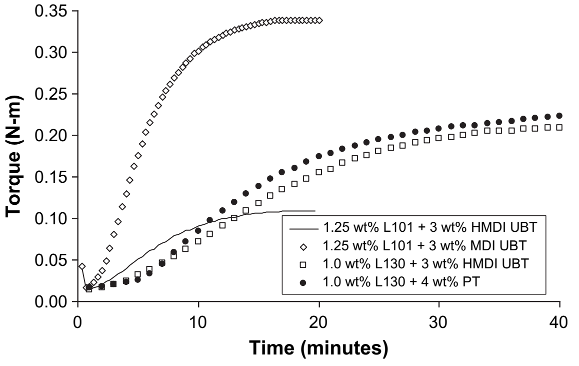


Fig. 11. Crosslinking of LDPE with PT Adduct and urethane bis-TEMPO derivatives at 180 °C.

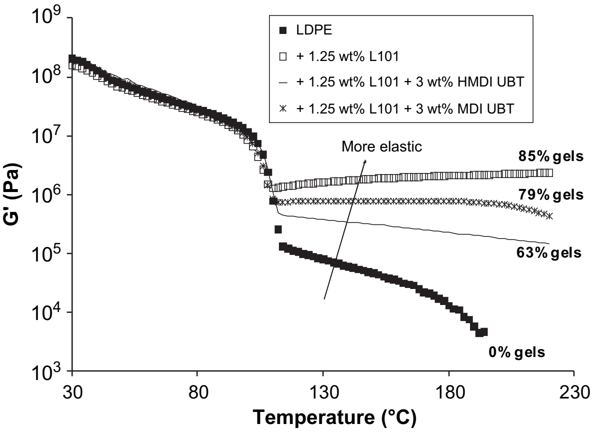


Fig. 13. Temperature-dependent dynamic storage modulus (G') of uncrosslinked and crosslinked LDPE.

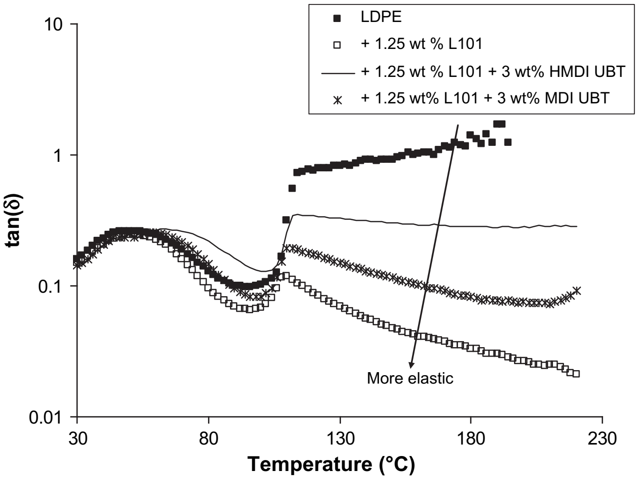


Fig. 14. Temperature-dependent dynamic tan(δ) of uncrosslinked and crosslinked LDPE.

230 °C. The decreasing modulus and absence of a plateau indicates significant urethane reversion up to the maximum test temperature of 220 °C, in agreement with greater reversion of the aliphatic urethane predicted by model compound studies. Of course, it is reasonable to assume that some carbon-carbon crosslinks may also have been present, in addition to the urethane crosslinks. The results on rate of probe penetration (Fig. 15) followed the same order as the dynamic modulus data (Fig. 13).

The shear-thinning behavior determined from dynamic oscillatory shear measurements is given in Fig. 16. Except for uncrosslinked LDPE (which was tested at two different temperatures), all others were only run at 220 °C. The specimen crosslinked with L101 peroxide (with 85% gels in cyclohexane) could not be run since it was thermoset. The composition crosslinked with MDI UBT (with 79% gels in cyclohexane and remarkably high modulus up to about 190 °C) showed considerable shear-thinning at 220 °C, such that the high-shear viscosity of this composition approached that of uncrosslinked LDPE at 220 °C (even though its low-shear viscosity was close to that of uncrosslinked LDPE at 140 °C). That is, this crosslinked composition behaved like a thermoplastic above 200 °C, confirming that urethane reversion had occurred. The composition crosslinked with HMDI UBT exhibited lower viscosity and less shear thinning than that crosslinked with MDI UBT, consistent with its relatively lower gel content. Both crosslinked compositions showed evidence of polymer chain coupling, which is a desirable means of improving melt strength (a key requirement for extrusion foaming, blow molding, thermoforming and other plastic processing). The oscillatory shear data were transformed into relaxation spectra, which in turn were used to compute values of relaxation spectrum index (RSI) [15]. The higher RSI values and shear-thinning characteristics of urethane-crosslinked LDPE were indicative of rheology modification of the polymer through coupling of polymer chains, leading to a broadening of the distribution of relaxation times towards long times.

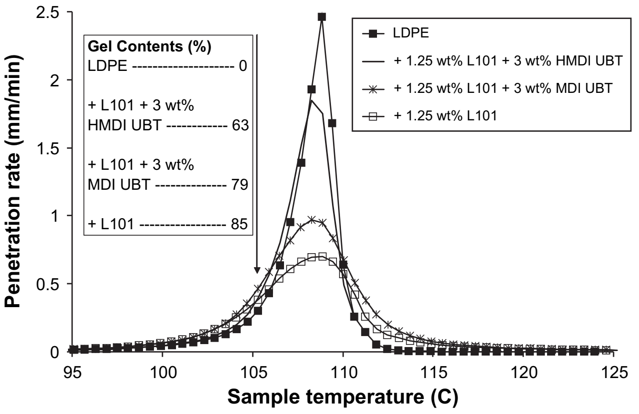
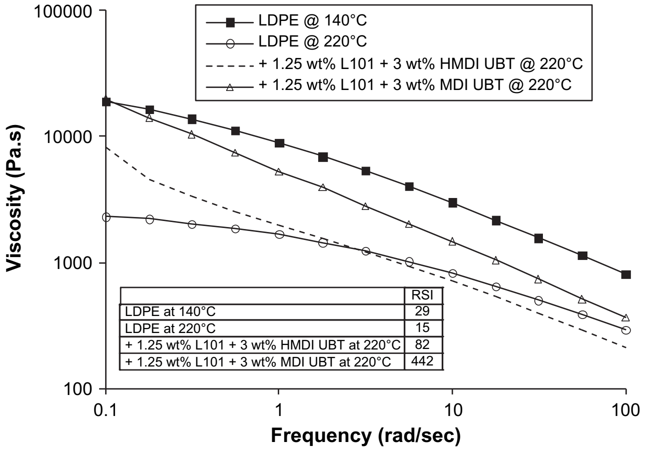


Fig. 15. Temperature-dependent rate of probe penetration in uncrosslinked and crosslinked LDPE.



	RSI
LDPE at 140°C	29
LDPE at 220°C	15
+ 1.25 wt% L101 + 3 wt% HMDI UBT at 220°C	82
+ 1.25 wt% L101 + 3 wt% MDI UBT at 220°C	442

Fig. 16. Melt viscosity and relaxation spectrum index (RSI) of uncrosslinked and crosslinked LDPE.

4. Conclusions

Three carbamate-linked dinitroxyl or polynitroxyl compounds were synthesized and subsequently used for free-radical initiated functionalization of polymers. The syntheses were effected simply by the reaction of 4-hydroxy TEMPO with various diisocyanates using triethylamine or a tin compound as catalyst. The reactions were monitored by infrared spectroscopy and the products were isolated as tan or peach-colored powders in good yields (75–93%).

The di- or polynitroxyl urethanes were used in combination with peroxide to couple or crosslink polyethylene in the molten state. The mechanism involved peroxide-induced formation of a polymer radical, followed by rapid trapping of the radical via the nitroxyl end group. In this way the bifunctional or polyfunctional nitroxyl adducts were able to provide crosslinking sites, in addition to carbon-carbon crosslinking arising from combination of polymer radicals generated as a consequence of peroxide-induced hydrogen abstraction. Urethane reversion was detected in the adducts as well as the crosslinks at elevated temperatures. The types of urethane groups in the crosslinks were observed to influence the rate and degree of crosslinking, as well as kinetics of urethane reversion. Remarkably high plateau modulus was achieved in aromatic/aliphatic urethane-crosslinked polyethylene up to a temperature of about 190 °C. This urethane-crosslinked polyethylene, as well as another crosslinked to lesser extent, both behaved like thermoplastics at sufficiently elevated temperatures. Thus, not only were thermoset-like properties achieved with urethane-crosslinked compositions, but the high degree of shear-thinning in the thermoplastic state was indicative of polymer chain coupling, which is a desirable means of improving melt extensional properties. It is anticipated that di- or polynitroxyl urethanes can also be used to reversibly couple or crosslink propylene polymers and other polymers. Although thermoreversible crosslinking has been demonstrated, the ability of the systems to withstand multiple heating and cooling cycles has not been ascertained.

This work also demonstrates that polymers can be functionalized with nitroxyls in the presence of free-radical generators, thus providing the ability to graft functional groups onto a variety of polymers. These functional groups might include hydroxyl, amine, carboxyl, urethane and any other group that can be attached via a permanent or reversible linkage to the 4-position of a TEMPO derivative.

References

[1] Dorn M. Adv Polymer Technol 1985;5:87–97.
[2] Gulmine JV, Akcelrud L. J Appl Polymer Sci 2004;94:222–30.
[3] Bremner T, Rudin A, Haridoss S. Polymer Eng Sci 1992;32:939–43.
[4] Lazar M, et al. J Polymer Sci Part A Polymer Chem 2004;42:675–88.
[5] Wu G, et al. J Polymer Sci Part A Polymer Chem 1999;37:1541–8.
[6] Abraham D, George KE, Francis DJ. Die Angewandte Makromolekulare Chemie 1992;200:15–25.
[7] Abraham D, George KE, Francis DJ. J Appl Polymer Sci 1998;67:789–97.
[8] Isac SK, George KE. J Appl Polymer Sci 2001;81:2545–9.
[9] Andersson LHU, Hjertberg T. Polymer 2006;47:200–10.
[10] Chaudhary BI, Chopin LJ, Klier J. Polymer Eng Sci 2007;47:50–61.
[11] Yang WP, Macosko CW, Wellinghoff ST. Polymer 1986;27:1235–40.
[12] Whiting LF, Labean MS, Eadie SS. Thermochim Acta 1988;136:231.
[13] Tou JC, Whiting LF. Thermochim Acta 1980;42:21.
[14] Baumgaertel M, Winter HH. Rheologica Acta 1989;28:511–9.
[15] Wasserman SH. SPE ANTEC 1997;55:1129.
[16] Lizotte JR, Anderson SG, Long TE. J Polymer Sci Part A Polymer Chem 2004;42:1547–56.
[17] Higaki Y, et al. Macromolecules 2003;36:1494.
[18] Ostsuka H, et al. Macromolecules 2007;40:1429.
[19] Higaki Y, Ostsuka H, Takahara A. Macromolecules 2006;39:2121.
[20] Skene WG, et al. Macromolecules 1998;21:9103.
[21] Marsal P, et al. J Phys Chem A 1999;103:2899.