# Alder Ene Functionalization of Polypropylene through Reactive Extrusion

#### MICHAEL R. THOMPSON, COSTAS TZOGANAKIS, GARRY L. REMPEL

Department of Chemical Engineering, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1

Received 9 February 1998; accepted 1 June 1998

ABSTRACT: A commercial isotactic polypropylene was degraded to increase its terminal vinylidene group concentration, and it was subsequently functionalized with maleic anhydride through the Alder Ene reaction at temperatures above 200°C in a co-rotating twin screw extruder. Characterization of the maleated product by Fourier transform infrared spectroscopy, <sup>1</sup>H NMR, differential scanning calorimetry, and gel permeation chromatography showed the anhydride group to be terminally attached, and the degree of functionalization was determined by infrared analysis. Increased temperature and maleic anhydride concentration, as well as improved mixing in the extruder, were found to improve the extent of the reaction. The catalytic contribution of Lewis acid species was evaluated, and ruthenium chloride was found to increase the extent of the reaction by 16% in comparison with stannous chloride as a catalyst in the Alder Ene reaction. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 503–516, 1999

**Key words:** maleation; polypropylene; reactive extrusion; Alder Ene reaction; Lewis acids

## **INTRODUCTION**

Comonomer grafting onto polypropylene was, as stated by Kowalski,<sup>1</sup> a logical development of the radical chemistry from controlled rheology polypropylene. Maleation of polypropylene is probably the most developed process of functionalizing polyolefins, yet the grafting site and structure of the functionality on the polymer chain is still a subject of contention.<sup>2–8</sup> In a simplistic mechanism, the maleic anhydride species or an excimer of the anhydride<sup>4,9</sup> is attached through chain addition to the polymer at a macroradical site. The strong tendency of the bound succinyl radical, as well as maleic anhydride excimers, to terminate by chain transfer leads to numerous side reactions in the presence of free radicals. The

radical grafting efficiency (ratio of grafted maleic anhydride to peroxy radicals), which can be used as a measure of the degree of chain transfer occurring in the reaction system, is characteristically high during free radical maleation, always greater than unity.<sup>7</sup> The radical grafting efficiency increases with temperature due to the activation energy of the chain transfer mechanism and decreases with increased peroxide and maleic anhydride reactant concentrations due to excimer quenching. Extensive degradation of the polypropylene chain results from the high radical grafting efficiency. From the numerous macroradicals generated, only those in proximity to a maleic anhydride species are involved in grafting.<sup>7</sup>

To reduce the occurrence of polymer degradation, several researchers have recently been examining chemistries that would produce "sitespecific" functionalization. In polypropylene, the only prevalent reactive site for reactions not involving free radical chemistry is its terminal vinylidene group. Studies to date on the terminal

Correspondence to: C. Tzoganakis (ctzogan@cape.uwaterloo. ca).

Journal of Applied Polymer Science, Vol. 71, 503-516 (1999)

<sup>© 1999</sup> John Wiley & Sons, Inc. CCC 0021-8995/99/030503-14

functionalization of polypropylene have typically been performed in solution. The majority of the example chemistries producing terminally functionalized polypropylene begin with low molecular weight polymer, either degraded or synthesized to a degree of polymerization where sufficient vinylidenes are present, typically with  $\overline{M}_N$  $< 5,000 \text{ g mol}^{-1}$ . The chemistries explored include hydroboronation, hydroalumination, epoxidation, silylation, Alder Ene addition, chlorination, and oxymercuration-demurcuration.<sup>10–14</sup> Among the chemistries listed, the Alder Ene reaction is best suited to the field of reactive extrusion.

The intermolecular Alder Ene reaction proceeds through a concerted mechanism that involves a cyclic six-member transition state.<sup>15</sup> The ene moiety of the Alder Ene mechanism is a double bond with an allylic hydrogen, which in the present case is the terminal vinylidene of polypropylene. Commercial polypropylene resins generally lack this reactive site due to the method of chain termination and even in the new metallocene-based resins where the vinylidene is more prevalent, the high molecular weight of the polymer chain translates into doublebond concentrations too low to accurately identify by modern analytical methods. Therefore, the degree of unsaturation of polypropylene must be increased by  $\beta$ -scission<sup>16,17</sup> before this reaction. The enophile of the Alder Ene reaction possesses a double bond, preferably an  $\alpha,\beta$ -disubstituted unsaturated group that is less prone to polymerization, such as maleic anhydride. Unlike the Diels-Alder mechanism, the formed adduct possesses a new double bond, generally exhibiting two isomer products that have been previously identified.<sup>13</sup> The rate of the Alder Ene reaction has been found to depend on the acidity and basicity of the ene and enophile, respectively, and the reaction conditions of the system. To improve the rate of an Ene reaction, researchers<sup>18-20</sup> have observed that a Lewis acid may be used as a catalyst.

Research work into Lewis acid-catalyzed Alder Ene reactions with polymers has received limited attention.<sup>20–22</sup> Maleation of a vinylidene-terminated polyisobutylene by the Alder Ene reaction was performed in solution at 41°C in the presence of titanium chloride and aluminum chloride,<sup>20</sup> with conversions of 67% and 14%, respectively. Roncetti and Banzi<sup>23</sup> attempted to improve the extent of maleation in ethylene-propylene-diene terpolymer (EPDM) rubber (3.5% 5-ethylidene-2norbornene (ENB) or 1.2% butadiene termonomer) via the Alder Ene reaction at 270°C in a Brabender PLE 651 plastograph. They used group VIII metal species as catalysts<sup>24,25</sup> to reduce scission and cross-linking reactions, and yet to improve anhydride incorporation without requiring excessive maleic anhydride reactant to drive the reaction. Based on titrimetric analysis, Roncetti and Banzi<sup>23</sup> obtained conversions between 67-100%, with rhodium halides yielding the highest degree of maleation. Stannous chloride dihydrate was used to functionalize a low melt flow index (MFI = 0.8) polypropylene with a dimethylol phenolic species in a Haake Rheocord mixer at 185°–190°C.<sup>21</sup> It was felt that the olefinic unsaturation in polypropylene was reacting with the dehydrated quinone methide species through the Alder Ene reaction. The presence of a reaction was confirmed by improved mechanical properties in a blend of polypropylene with nitrile butyl rubber when the modified polymer was present as a reactive compatibilizer. In a similar reaction based on reactive functionalities, a polypropylene with 1.7 wt % unsaturation was attached to a phenol formaldehyde polymer through a stannous chloride dihydrate catalyzed Alder Ene reaction.<sup>22</sup> The reaction was conducted in a co-rotating twin screw extruder with a minimum residence time of 2.5 min. From a two-dimensional contour plot, it was found that the optimal level of phenol formaldehyde attached to polypropylene was dependent on minimizing the concentrations of the catalyst and the vinylidene group and maximizing the concentration of the phenol formaldehyde polymer in the reaction. Based on the success of the latter two experiments using stannous chloride in a polymer processing system, this Lewis acid was chosen for the present work.

This article expands on previous work<sup>13,14</sup> and addresses the terminal maleation of a degraded polypropylene in a twin screw extruder by the Lewis acid-catalyzed Alder Ene reaction. This "site-specific" method of functionalization was expected to produce a polypropylene with a terminal anhydride group without significant degradation occurring.

#### **EXPERIMENTAL**

#### Materials

Polypropylene was supplied by Montell Canada  $(\overline{M}_N = 49,800 \text{ g mol}^{-1}, \overline{M}_W = 528,000 \text{ g mol}^{-1};$ MFI<sub>230°C</sub> = 3 g/10 min). The Lewis acids, stan-



**Figure 1** Two screw configurations used in the Leistritz co-rotating twin screw extruder. The kneading elements are denoted by KS, with the stagger angle of  $60^{\circ}$  unless the block was designated as neutral (N). Reversing elements are denoted with a L suffix.

nous chloride dihydrate, and ruthenium chloride hydrate, along with TEMPO (a free radical trapping agent), were supplied by Aldrich Chemical. The catalysts were stored in a desiccator under vacuum until needed. Maleic anhydride was provided by Monsanto Chemical in the form of briquettes. Dimethylformamide (EM Science) was dried by distillation over a 4A molecular sieve and stored with more molecular sieve to remove residual water. All other solvents were supplied by BDH Chemicals.

#### Equipment

The reaction was conducted in a Leistritz LSM30.34 modular twin screw extruder (screw diameter = 34 mm; length/diameter (L/D) = 30) set up in a co-rotating screw configuration. The extruder possesses 10 heating zones, not including the die. The liquid reactants were fed into the extruder at zone 4 using a syringe pump. The syringe body and the exit tubing were traced to maintain the temperature of the reactants above the solidification temperature of maleic anhydride.

The screw design must provide sufficient residence time and adequate mixing for the reaction to proceed to a desirable extent. The introduction of low viscosity liquid reactants into the polymer melt requires that the screw design provides both intensive dispersive and distributive mixing. Two screw configurations were used in this work (Fig. 1) in an attempt to provide adequate mixing and residence time for a reaction that is characteristically slow. The second screw design was intended as an improvement over the initial configuration. A pressure of 2.4 MPa was measured at the point of injection while running degraded polypropylene (designated TD370 as discussed herein) through the extruder at 210°C, demonstrating an improved fill characteristic for screw configuration 2 compared with a pressure of 0.08 MPa for screw configuration 1 under the same conditions.

# Preparation of Polypropylene with a High Vinylidene Content

Terminal vinylidene concentration increases in polypropylene from  $\beta$ -scission through termination by disproportionation of the primary macroradical.<sup>26,27</sup> Scission reactions in polypropylene may be thermally or peroxide induced. The presence of oxygen during these high temperature reactions may lead to generation of oxidative functionalities, including methyl esters, methyl ketones, aldehydes, carboxylic acids, and lactones<sup>26,27</sup> in place of the unsaturation at the chain

Degradation Method		The	Thermal		Peroxide	
Barrel temperature	Zone 1	150°C	150°C	140°C	140°C	
	2	240°C	240°C	180°C	180°C	
	3	$370^{\circ}\mathrm{C}$	380°C	$230^{\circ}\mathrm{C}$	230°C	
	4	$290^{\circ}\mathrm{C}$	$290^{\circ}\mathrm{C}$	190°C	190°C	
Sample name		TD370	TD380	PD075	PD100	

 Table I
 Barrel Temperature for Polypropylene Degradation

end. These functional groups may affect the catalyzed Alder Ene reaction by interfering with the formation of the Lewis acid-maleic anhydride adduct, as well as reducing the initial vinylidene concentration.

In this work, polypropylene materials having increased vinylidene concentrations were produced by both thermal- and peroxide-initiated degradation. Both methods of generating the vinylidene group were examined, to determine if the oxidation functional groups interfere with the reaction. Because the vinylidene group concentration affects the extent of reaction due to the bimolecular nature of the Alder Ene mechanism, it was desirable to make the degree of unsaturation similar between the products from the two methods. Polypropylene was thermally degraded in a Haake Rheomex 252 single screw extruder (L/D = 25) fitted with a 6-mm diameter rod die. Two vinylidene concentrations were produced for the Alder Ene reaction, by altering the temperature of the third barrel zone. Table I shows the barrel temperature profile used to induce thermal degradation. To increase the difference between the two double-bond concentration levels in the subsequent factorial experiments, TD370 was diluted 50/50 (w/w) with virgin polypropylene. Obviously, the molecular weight distribution (MWD) of the resins before and after dilutions, will result in different mixing performance in the twin screw extruder during the Alder Ene reaction; however,

no practical alternative was available. For the peroxide-induced degradation products, samples were produced in the single screw extruder at 30 rpm using the barrel profile detailed in Table I. Two dialkyl peroxide (Lupersol 101, Elf AtoChem) levels were used, 0.75 wt % and 1.0 wt %, producing average vinylidene concentrations similar to the thermally degraded resins. Sample PD100 was diluted 50/50 (w/w) with virgin polypropylene. Table II shows the gel permeation chromatography results of the degraded materials along with their respected vinylidene concentration measured by an infrared calibration technique described previously.<sup>17</sup> All of the results presented in Table II are given before any dilution if used.

The infrared spectra in Figure 2 indicates that several oxidation functional groups (i.e., lactones, carboxylic acid, and methyl esters at 1,780, 1,714, and 1,745 cm<sup>-1</sup>, respectively) are not favored at temperatures above 350°C, making thermolysis (cracking) the more desirable method of inducing  $\beta$ -scission when the goal is to maximize the vinylidene group concentration. Supporting evidence of the benefits of thermolysis was shown by Sawaguchi and Seno,<sup>16</sup> who thermally degraded polypropylene at 370°C in a Pyrex glass tube to produce a telechelic polymer with diisopropenyl (vinylidene) end groups. Based on nuclear magnetic resonance (NMR) analysis,<sup>16</sup> they determined the average functionality of isopropenyl

Table IIMolecular Weight Averages and Vinylidene Concentrationof Degraded Polypropylene

Sample	$\overline{M_N}$ (g mol <sup>-1</sup> )	$\overline{M_W}$ (g mol <sup>-1</sup> )	Vinylidene Concentration $(mol g^{-1})$
TD370	22,270	66,140	$4.66 imes 10^{-5}\ \pm 5.8 imes 10^{-6}$
TD380	18,600	53,200	$4.92 imes 10^{-5}\ \pm 5.2 imes 10^{-6}$
PD075	19,850	64,900	$4.84 imes 10^{-5}\ \pm 4.9 imes 10^{-6}$
PD100	17,620	53,380	$6.02  imes 10^{-5} \ \pm 4.3  imes 10^{-6}$



**Figure 2** Fourier transform infrared spectra of thermally and peroxide-degraded polypropylene.

groups per molecule to be 1.8 after an excessively long reaction time of 45 min, showing this method to be highly efficient for producing the desirable vinylidene group.

#### **Experimental Design**

Three experimental designs were examined in this work. The first experimental design was a  $2^{5-1}$  fractional factorial (Table III) at a screw speed of 20 rpm and 20 g min<sup>-1</sup> feed rate to identify the effects of several factors on the succinyl anhydride concentration due to the reaction. The factors examined were vinylidene concentration, maleic anhydride concentration, stannous chloride concentration, barrel temperature, and method of double-bond generation. The second experimental design was a 2<sup>4</sup> full factorial (Table IV) examining the effect of mixing on the reaction conversion through the factors of screw speed and feed rate, and the contributions of catalyst concentration and the method of vinylidene generation. In this design, the maleic anhydride concentration was fixed at 4 mol Eq, with respect to the vinylidene group, and the barrel temperature was 210°C. These first two experimental sets used the same screw design (configuration 1 in Fig. 1). Three additional experiments were run using screw configuration 1. The first run, denoted as

Sample No.	$\begin{array}{c} Vinylidene\\ Concentration\\ (mol \; g^{-1}) \end{array}$	Maleic Anhydride Concentration (mol Eq) <sup>a</sup>	Temperature (°C)	${{ m SnCl}_2} \ { m Concentration} \ (\% \ { m mol} \ { m Eq})^{ m b}$	Degradation Method	Conversion (%)
1G	$4.92 imes10^{-5}$	2	200	0.01	Thermal	3.45
2G	$2.33 imes10^{-5}$	4	200	0.01	Thermal	6.44
3G	$2.33 imes10^{-5}$	2	220	0.01	Thermal	6.52
4G	$4.92 imes10^{-5}$	4	220	0.01	Thermal	5.48
$5\mathrm{G}$	$2.33 imes10^{-5}$	2	200	0.05	Thermal	6.32
6G	$4.92 imes10^{-5}$	4	200	0.05	Thermal	4.35
7G	$4.92 imes10^{-5}$	2	220	0.05	Thermal	4.48
8G	$2.33 imes10^{-5}$	4	220	0.05	Thermal	6.99
9G	$3.01 imes10^{-5}$	2	200	0.01	Peroxide	5.20
10G	$4.84 imes10^{-5}$	4	200	0.01	Peroxide	3.80
11G	$4.84 imes10^{-5}$	2	220	0.01	Peroxide	3.80
12G	$3.01 imes10^{-5}$	4	220	0.01	Peroxide	6.11
13G	$4.84 imes10^{-5}$	2	200	0.05	Peroxide	3.51
14G	$3.01 imes10^{-5}$	4	200	0.05	Peroxide	5.50
15G	$3.01 imes10^{-5}$	2	220	0.05	Peroxide	5.90
16G	$4.84 imes10^{-5}$	4	220	0.05	Peroxide	4.51
17G	$2.33 imes10^{-5}$	4	200	0.01	Thermal	6.47
(2G)						
18G	$4.92 imes10^{-5}$	2	220	0.05	Thermal	4.11
(7G) 19G (13G)	$4.84 imes10^{-5}$	2	200	0.05	Peroxide	3.40

#### Table III Experimental Design 1

<sup>a</sup> Maleic anhydride mol Eq with respect to vinylidene concentration.

<sup>b</sup> Stannous chloride mol Eq with respect to maleic anhydride concentration.

Sample No.	Screw Speed (rpm)	Feed Rate $(g \min^{-1})$	Catalyst Concentration (% mol Eq) <sup>a</sup>	Degradation Method <sup>b</sup>	Conversion (%)
20G	20	20	0.01	Thermal	6.97
21G	40	20	0.01	Thermal	7.08
22G	20	40	0.01	Thermal	6.47
23G	40	40	0.01	Thermal	7.00
24G	20	20	0.05	Thermal	7.16
25G	40	20	0.05	Thermal	7.00
26G	20	40	0.05	Thermal	6.84
27G	40	40	0.05	Thermal	6.92
28G	20	20	0.01	Peroxide	7.44
29G	40	20	0.01	Peroxide	7.30
30G	20	40	0.01	Peroxide	7.43
31G	40	40	0.01	Peroxide	6.32
32G	20	20	0.05	Peroxide	7.47
33G	40	20	0.05	Peroxide	7.36
34G	20	40	0.05	Peroxide	6.19
35G	40	40	0.05	Peroxide	6.87

Table IVExperimental Design 2

<sup>a</sup> Stannous chloride mol Eq with respect to 4 mol Eq. maleic anhydride.

<sup>b</sup> Lower vinylidene concentration levels used for both methods.

36G, attempted to dramatically increase the degree of channel fill by running at a feed rate of 40 g min<sup>-1</sup> and a screw speed of 10 rpm. The temperature of the barrel was 220°C, and the reactants were PD100, 4 mol Eq maleic anhydride, and 0.05% mol Eq SnCl<sub>2</sub>. Samples 37G and 38G used the same conditions as 9G and 12G, respectively; however, Lewis acid was now ruthenium chloride dissolved in 2-octanol.

The screw design used for the third experimental set (configuration 2 in Fig. 1) was expected to increase the degree of channel fill within the intensive mixing regions. The kneading blocks in the second configuration were mostly left-handed, as opposed to the use of neutral kneading blocks in the first screw configuration. Thus, the second screw design increased the residence time as well as mixing for the reaction. The third experimental design was developed from results of the previous two experimental sets. It was a 3<sup>3-1</sup> fractional factorial design (Table V) examining the main factors of barrel temperature, catalyst concentration, and maleic anhydride concentration. The screw speed and polymer feed rate were fixed at 30 rpm and 30 g min<sup>-1</sup>, respectively. The only source of polypropylene was TD380 for the third experimental set.

#### Procedures

The Lewis acid catalyst and TEMPO were weighed into a vial and subsequently dissolved

into 140  $\mu$ L of the chosen solvent. Dimethylformamide was used to dissolve stannous chloride, whereas 2-octanol was used for ruthenium chloride. The liquid reactants, combined with molten maleic anhydride, were drawn into the syringe pump and subsequently allowed to thermally equilibrate. The system maintained maleic anhydride above its melting point at 75°C. At this temperature, the density of molten maleic anhydride had been measured to be  $\rho_{75^{\circ}C} = 1.28$  g  $mL^{-1}$  using a graduated vial, thereby ensuring that accurate reactant-polymer ratios were maintained during experimentation. In addition, the equilibrium time allowed for the slow formation of the Lewis acid-maleic anhydride adduct that has been observed in the previous work.<sup>14</sup> Three sets of experiments (presented in Tables III to V) quote barrel temperatures that correspond to zones 4 through 10 in Figure 1. The barrel temperature profile before zone 4 was set as 130°/ 170°/190°C with the die at 200°C. Thompson and colleagues<sup>14</sup> observed that reaction temperatures below 240°C ensured dominance of the Alder Ene mechanism with respect to side reactions like homopolymerization of maleic anhydride or isomerization of the reactive double bond. Measured at 210°C using a carbon black tracer, the minimum residence time for screw configuration 1 varied between 225 s (at 40 rpm, 40 g min<sup>-1</sup>) to 431 s (at 20 rpm, 20 g min<sup>-1</sup>). The minimum

Sample No.	SnCl <sub>2</sub> Concentration (% mol Eq) <sup>a</sup>	Temperature (°C)	Maleic Anhydride Concentration (mol Eq) <sup>b</sup>	Conversion (%)
40G	0	210	1	3.78
41G	0	220	2	4.69
42G	0	230	3	4.92
43G	0.005	210	3	4.25
44G	0.005	220	1	3.78
45G	0.005	230	2	4.68
46G	0.01	210	2	3.81
47G	0.01	220	3	4.28
48G	0.01	230	1	4.08
49G (41G)	0	220	2	4.43
50G (41G)	0	220	2	4.61
51G (46G)	0.01	210	2	3.64
$\rm Coefficients^{c}$	-0.21	0.31	0.30	4.26

Table V Experimental Design 3

Maleic anhydride mol Eq with respect to vinylidene concentration.

<sup>b</sup> Stannous chloride mol Eq with respect to maleic anhydride concentration. <sup>c</sup> Regression coefficients for a 3<sup>3-1</sup> fractional factorial design.

residence time for screw configuration 2 used in the third experimental set at a fixed screw speed and feed rate of 30 rpm and 30 g min<sup>-1</sup>, respectively, was measured to be 370 s.

The product samples were purified by dissolving in hot xylene, followed by precipitation through the addition of an excess of acetone and finally filtering through a fine-grade fritted glass filter. Residual maleic anhydride and poly(maleic anhydride) remained in solution with acetone due to their high solubility. The polymer collected by filtration was washed repeatedly with acetone and finally dried for 16 h at 120°C in a vacuum oven.

#### Infrared Characterization

Sample films were prepared between two Teflon sheets in a hot press at 170°C under 40 kN force for 5 min. The films were scanned 20 times with a resolution of 2  $cm^{-1}$  covering a range of 500- $4,000 \text{ cm}^{-1}$ . The absorbance wavenumbers pertinent to the modification were: 888  $cm^{-1}$  (vinylidene), 1,784 cm<sup>-1</sup> (anhydride), 1,792 cm<sup>-1</sup> (succinvl anhydride), and  $1,865 \text{ cm}^{-1}$  (succinvl anhydride). The C-C-C bending vibration at  $459 \text{ cm}^{-1}$  was used as an internal reference. Vinylidene concentration in polypropylene was determined using a calibration curve presented previously.<sup>17</sup> A correlation between the succinyl anhydride concentration in the product and its

relative infrared absorbance at  $1,792 \text{ cm}^{-1}$  was established using different concentrations of a highly maleated low molecular weight polypropylene wax (Polypol-19, Crowley Chemical) smeared onto a film of KF6100 polypropylene. The terminally functionalized Polypol-19 containing a high anhydride concentration  $(1.439 \times 10^{-4})$  $\pm$  1.020  $\times$  10<sup>-5</sup> mol anhydride per g of polymer, as measured by the titration method of Gaylord and Mehta<sup>9</sup>) was produced at 240°C for 16 h under nitrogen and in the presence of hydroquinone.<sup>13</sup> The calibration curve for succinyl anhydride concentration is given:

$$C_{SAh} = 7.22 imes 10^{-6} \cdot rac{A_{1,792 {
m cm}^{-1}}}{A_{459 {
m cm}^{-1}}} + 7.21 imes 10^{-7}$$

where  $C_{SAh}$  is the concentration of attached succinyl anhydride in moles per gram of polymer, and A is the peak height absorbance corresponding to the subscript wavenumber. The standard error for the slope and intercept coefficients was  $5.17 imes 10^{-7}$  and  $1.25 imes 10^{-6}$ , respectively, and the correlation coefficient was  $R^2 = 0.97$ .

# <sup>1</sup>H and <sup>13</sup>C NMR Analysis

<sup>13</sup>C NMR analysis was performed in a 300 MHz Bruker AC300E instrument using inverse gated decoupling to circumvent no observed effects. The maleated samples were prepared in 10 mm tubes

at 20 wt % in 0.02 wt % Irganox 1010 (Ciba-Geigy Canada Ltd.) stabilized 1,2,4-trichlorobenzene. Spectra were acquired at 120°C using a 15 s relaxation delay for a pulse width of 4.5  $\mu$ s (30° flip angle) hoping to achieve magnetization equilibrium. The acquisition time was 0.95 s, collecting 4,000 scans over a 16-h period. All chemical shifts were referenced to tetramethylsilane. Proton NMR was done in 5-mm tubes with 5 wt % sample solutions using toluene- $d_8$  for a lock signal. The signal was acquired at 100°C using a 20-s relaxation delay for a pulse width of 11.5  $\mu$ s (90° flip angle). Spectra were comprised of 32 scans, and peak assignments were drawn from Russell and Kelusky<sup>28</sup> for <sup>1</sup>H analysis and from Busfield and Hanna,<sup>29</sup> and Rengarajan and colleagues<sup>3</sup> for <sup>13</sup>C studies.

#### **Thermal Analysis**

The crystallization temperature and the heat of crystallization of the product samples ( $T_c$  and  $\Delta H_c$ , respectively) were measured in a TA Instruments 2920 DSC cell. Samples were heated using a ramp rate of 10°C min<sup>-1</sup> to 200°C. Data from the second heating/cooling cycle were collected to determine the transition temperatures. Crystal melting temperature was not used quantitatively, because the transition was very broad and difficult to integrate consistently between samples.

#### **Molecular Weight Determination**

The MWD of the polypropylene samples was measured using a Waters 150 CV+ high temperature gel permeation chromatograph fitted with three Waters Styragel HT6E linear columns. A capillary viscometer in series with a differential refractometer was used to measure the absolute molecular weight of the polymer samples. The instrument used a mobile phase of 1,2,4-trichlorobenzene (EM Science) containing 0.02 wt % Irganox 1010, which was heated to 140°C. Samples were prepared at a concentration of 0.7 mg mL<sup>-1</sup>.

### **RESULTS AND DISCUSSION**

Due to the variance in the vinylidene group concentration among the different experimental sets, quoting the extent of reaction in terms of conversion of vinylidene groups would be more meaningful. The conversion will be calculated based on the ratio of the concentration of succinyl anhydride detected to the initial concentration of vinylidene in the polymer.

The difficulties in measuring functionalities below 1 wt % in polymer complicate the analysis of the modified polypropylene. However, it was necessary to determine the structure of the functional group attached to the polymer, whether it was terminally attached via the Alder Ene reaction or bound along the backbone due to free radicals present due to oxidation. To assist structural analysis, each maleated sample of the third experimental set (i.e., 40G-48G) was reacted with 1-hexadecylamine (Aldrich Chemicals) in refluxing xylene under a nitrogen blanket for 2 h. It was hoped that, by increasing the dimension of the functionality, discerning the anhydride structure would become easier. Full conversion was confirmed by the disappearance of the succinyl anhydride vibration in the infrared spectra. However, the presence of imide, carboxylic acid, and amide groups were detected indicating that not all attached chains proceeded to the imide functionality. For comparison, a sample of TD380 (55E) was maleated for 24 h at 190°C in 1,2,4-trichlorobenzene, followed by chain extension via 1-hexadecylamine in the manner described. Characterization of the maleated form of 55E, before chain extension, was not necessary because the structure of a terminally functionalized polymer has already been performed previously.<sup>13</sup> This sample is compared with the other chain extended ones, in later sections. The question that needed structural confirmation was whether maleation was exclusively achieved through the Alder Ene reaction or if the presence of oxygen due to the partially filled channel of a twin screw extruder was sufficient to lead to backbone grafting.

#### **MWD**

Figure 3 shows the MWD of two degraded polymers (TD380 and PD075) and four maleated species for each of the two degraded polypropylenes. The distributions for the maleated polymers show no significant difference from the unmodified material. This was the case for all modified polymers, including several repeated MWD measurements. Thus, the occurrence of  $\beta$ -scission was minimized during extrusion despite the presence of oxygen. Based on these findings, it is arguable that free radical grafting of maleic anhydride did not significantly occur, because the degree of scission should have been related to the concentration of



**Figure 3** Effect of maleic anhydride (MAh) concentration on the MWD of the maleated polypropylenes.

maleic anhydride reactant due to its propensity to initiate  $\beta$ -scission through chain transfer.

The usefulness of the chain extended samples to distinguish the manner by which the maleic anhydride was attached to the polymer was based on their individual reaction mechanisms. Maleation via the Alder Ene reaction will be greatest among polymer chains of lower molecular weight where there are more reactive sites and an improved chance of polymer/comonomer interaction. However, with the polymer sufficiently degraded to assume that the average chain possesses at least one terminal vinylidene,<sup>17</sup> we expect to find anhydride groups even in the higher molecular weight fractions provided the extent of reaction was sufficiently high. Therefore, maleated polymer produced through the Alder Ene reaction should favor hexadecylamine attachment to the lower molecular weight fraction of the polymer distribution with the possibility of observing no change if chains of each molecular weight fraction reacted with the maleic anhydride. Maleation via free radical grafting, based on hydrogen abstraction from the polymer backbone, is a random process statistically favoring higher molecular weight chains of a polymer distribution, provided we accept the notion that the anhydride group reacts with a tertiary macroradical as opposed to a primary macroradical. Thus, chain extension through reaction of the maleated polymer with hexadecylamine would increase the weight fraction in the high molecular weight region of the distribution. Figure 4 compares two chain-extended polymers (41E and 47E) against their maleated counterparts (41G and 47G) and sample 55E as an example of effects of high maleation through the Alder Ene reaction. Examining the given MWDs in Figure 4, the low end fraction of both chain-extended samples is slightly increased, compared with their maleated counterparts. Also, sample 55E does show the expected change in the weight fraction of the low molecular weight chains, lower than samples 41E and 47E, because the higher molecular weight fraction would also have been increased. Unfortunately, the error attributed to the measured distributions from the GPC does not provide significant quantitative differentiation between the MWDs.

#### **Infrared Analysis**

Figure 5 shows the spectra of four maleated polypropylenes: samples 9G and 12G produced in the presence of stannous chloride, and samples 37G and 38G produced in the presence of ruthenium chloride. The anhydride absorbance at  $1,792 \text{ cm}^{-1}$  was quite small, and the corresponding  $1,865 \text{ cm}^{-1}$  vibration was not detectable. The structure of the succinyl anhydride moiety was



**Figure 4** MWDs of two maleated polypropylenes (41G and 47G) and their hexadecylamine-grafted counterparts (41E and 47E). Sample 55E was a highly maleated polypropylene sample grafted with hexadecylamine and used for comparison.



**Figure 5** Carbonyl region of the Fourier transform infrared spectra for several maleated polypropylenes produced in the presence of either stannous chloride (9G and 12G) or ruthenium chloride (37G and 38G).

best determined from the maleated polypropylene with the highest succinyl anhydride incorporation (i.e., sample 38G, where the  $1,784 \text{ cm}^{-1}$  anhydride vibration appeared as a shoulder in the  $1,792 \text{ cm}^{-1}$  peak). Both  $1,792 \text{ cm}^{-1}$  and 1,784cm<sup>-1</sup> vibrations are attributed to mechanical coupling of the carbonyl stretching modes within the anhydride.<sup>30</sup> The intensity of the lower frequency band increases in systems of increasing polarity or with increasing intermolecular hydrogen bonding.<sup>31</sup> Therefore, maleic anhydride-bound as single, isolated units-should show a stronger high-frequency band than low-frequency band unless high localized concentrations of anhydride exist. Grafts of poly(maleic anhydride), if present in the polymer chain, would favor the low-frequency band. Conversion among all experimental sets varied between 3-7%, based on the infrared calibration curve [eq. (1)]. It was due to the low concentration of succinyl anhydride in the product that classical titration methods could not be used to quantify the extent of reaction.

#### NMR Analysis

Due to the low concentration of succinyl anhydride bound to the polypropylene chain, <sup>13</sup>C NMR yielded no information concerning the structure of the anhydride moiety. Consequently, any analysis of the maleated samples had to be based on the proton analysis. Figure 6 shows the <sup>1</sup>H NMR spectra for the maleated 42G sample and its chain extended counterpart, sample 42E. Peak assignments for the polypropylene backbone lie between the region of 1-2 ppm. The terminal vinylidene was characterized by two fully resolved peaks at 4.76 ppm and 4.81 ppm corresponding to the two hydrogens at the chain end. Evidence of the alkyl segment of the hexadecylamine chain extender was seen as two small doublets at 0.8 and 1.2 ppm not seen in sample 42G. The maleated polymer (sample 42G) showed succinyl anhydride resonances at 2.6 and 2.82 ppm that fit within the succinyl anhydride region given by Russell and Kelusky<sup>28</sup> and Thompson and colleagues.<sup>13</sup> Succinyl anhydride groups reacted along the backbone, due to free radical grafting, were found to exhibit peak resonances shifted downfield to 3.3 ppm according to their tertiary site instead of the primary site corresponding to a terminal position.<sup>13</sup> No indication of free radical grafting is seen in Figure 6. The noise in the baseline made it difficult to identify the internal vinyl at 4.98 ppm,<sup>13</sup> which may have occurred in one of the isomer products. However, at least a very small peak appears to be present. There seemed to be sufficient evidence to conclude that maleic anhydride had been predominantly attached onto polypropylene as single units via the Alder Ene reaction. The proton spectrum of the chain extended sample in Figure 6 does not show the succinyl anhydride resonances previously mentioned. However, four new peaks are distinguishable from the baseline. The two peaks centered at 3.1 and 3.3 ppm were similar to those



**Figure 6** <sup>1</sup>H NMR spectra of a maleated sample (42G) and its hexadecylamine-grafted product (42E) in the region of 0-6 ppm for the upper two plots, with the alkyl region (0-3 ppm) of 42E expanded in the lower view.

Sample No.	$T_c$ (G) (°C)	$T_c (\mathrm{G^a}) \ (^{\circ}\mathrm{C})$	$T_{c}^{-}(E)$ (°C)	$\begin{array}{c} \Delta H_c \ (\mathrm{G}) \\ (\mathrm{J \ g^{-1}}) \end{array}$	$\Delta H_c (E)$ (J g <sup>-1</sup> )
40	102.09		112.81	55.25	99.78
41		110.71	112.2	98.55	99.60
42	101.85		112.17	60.99	101.30
43		110.60	112.66	77.83	101.10
44		108.98	110.71	63.27	96.98
45	101.32		113.10	66.83	87.62
46	101.47		112.18	64.85	98.35
47		109.40	111.10	86.46	100.20
48	102.14		112.49	71.10	102.30

Table VI Crystallization Transition Properties ( $T_c$  and  $\Delta H_c$ ) for Modified Polypropylenes

<sup>a</sup> Sample hydrolyzed before analysis.

observed in 1-alkylmaleimides corresponding to the N—CH<sub>2</sub>— protons. The presence of two peaks likely correspond to both amide and imide functionalities being present, as seen by infrared analysis. A broad peak observed at 9.0 ppm, which is not shown in Figure 6, confirmed the amide hypothesis, showing a carboxylic acid functionality is present in the polymer. The resonance at 5.4 ppm, obviously a double bond, cannot be explained.

#### **Thermal Transition Properties**

An attempt was made to determine the nature of the succinyl anhydride attachment through comparison of the maleated polymer (40G-48G) to the hexadecylamine grafted samples (40E-48E) with respect to changes in the crystalline structure. Unfortunately, the exact behavior of chain extension or branching on the crystallinity within our polymer is difficult to predict from other studies due to the block copolymer nature of the product and the inclusion of a polar group (carboxylic acid-amide linkage) within the chain. Therefore, maleated polymers produced by the two methods (free radical *vs.* Alder Ene) were reacted with hexadecylamine and their transition properties were measured.

A commercial grade maleated polypropylene produced by peroxide-induced grafting (FUSAB-OND<sup>®</sup> P MZ-203D, DuPont Canada) was reacted with hexadecylamine in a manner already described for the maleated product of this work. Examining the crystallization transition for a side chain-grafted product showed no significant difference in the crystallization temperature, 113.14°C and 113.97°C, with only a small change in the enthalpy, 72.38 and 77.13 J  $g^{-1}$ , of the grafted FUSABOND and the maleated sample, respectively. For comparison, sample 55E (highly maleated Alder Ene polypropylene reacted with hexadecylamine) showed an increase in the crystemperature, tallization from  $110.25^{\circ}\mathrm{C}$ to 116.05°C whereas the enthalpy of crystallization increased from 68.03 to 99.67 J g<sup>-1</sup>, from the maleated to the chain-extended sample, respectively. Clearly, the hexadecyl alkyl chain was involved in crystallization when it is located at the terminal site of the polymer chain, despite chain irregularities due to the polar linkage.

Table VI gives the crystallization transition properties of several alkyl-grafted samples, compared with their original maleated samples. The alkyl-grafted products exhibited an increase in the peak transition temperature of  $\sim 10^{\circ}$ C from 102°C for the maleated samples (G series) to 112°C for the hexadecyl-grafted polymers (E series). Some of the maleated samples of series G had hydrolyzed before analysis, resulting in an increase of its transition temperature to  $\sim 110^\circ C$ with  $T_c^E - T_c^G$ , now only 2°C (as listed in Table VI). The latter  $T_c^E - T_c^G$  fits within the extremes outlined by the Alder Ene (sample 55E) and free radical-grafted (FUSABOND) examples that also began in the hydrolyzed form. These results suggest that the hexadecyl chain was positioned at the terminal site similar to sample 55E, just at a lower concentration. No correlation was observed between  $T_c^E - T_c^G$  and the succinyl anhydride concentration. The average increase in the crystallization enthalpy between series G (anhydride form) and series E was 32 J g<sup>-1</sup>, whereas between



Figure 7 Crystal melting endotherms for several maleated and hexadecylamine-grafted product.

series G (acid form) and series E, it was considerably lower at 8 J  $g^{-1}$ .

The crystal melting transitions were shown in Figure 7, where the endotherms appear quite broad, including two transitions that correspond to  $\alpha$ - and  $\beta$ -crystallite structures in the polymer. The figure indicates that the higher temperature transition seen in both series G and series E samples increases in intensity and becomes better resolved for the chain-extended samples.

#### **Reaction Parameters**

Beginning with experimental set 1, the results in terms of conversion are listed in Table III, with a pooled estimate of variance being 0.025% conversion based on repeats. The average conversions for maleated polypropylene produced from thermally degraded polymer, compared with peroxide-degraded material, were 5.51% and 4.79%, respectively. The significant difference between the two methods of generating the vinylidene group showed that the peroxide method with its higher concentration of oxidation groups in the polymer yielded lower conversion. The result could be due to the Lewis acid-forming adducts. with these oxidation groups interfering with the generation of the anhydride-Lewis acid enophile, or the result could arise from the polymer forming a polar phase domain, thus isolating the maleic anhydride from the vinylidene group of the hydrophobic hydrocarbon domain. Analysis of the results of the fractional factorial for experimental set 1 showed that the vinylidene concentration was the most important factor in the reaction with a decrease of nearly 2% conversion for the higher vinylidene concentration level, compared with the lower level. Because the Alder Ene reaction exhibits bimolecular kinetics,<sup>13,14,32</sup> the contradiction the result offers must be attributed to mixing effects related to the high molecular weight virgin polypropylene being used to dilute the vinylidene group. The high molecular weight peak of the bimodal distribution in the diluted polymer will improve channel fill in the mixing regions of the extruder where the shear was sufficiently high to breakup the maleic anhydride domain, thus increasing the interfacial area between the two reactants. Both temperature and maleic anhydride reactant concentration showed a positive effect on the conversion of the vinylidene group. Catalyst concentration was the only factor without significance to conversion, with an average increase in conversion of 0.1% for the higher catalyst level. Categorizing the catalyst effect further, for the thermally degraded polymer with high vinylidene concentration (and low viscosity), conversion did not change; yet, for the thermally degraded polymer with the low vinylidene concentration (and high viscosity), conversion increased by 0.17% for the higher Lewis acid level. For the peroxide-degraded polymer, the trend was exactly opposite. Clearly, the effect of mixing and the method of vinylidene generation were both important parameters.

Experimental set 2 examined the effects of screw speed and feed rate on the degree of mixing during extrusion, along with catalyst concentration (because it was the principal parameter under study) and the method of polymer degradation. Analysis of the complete factorial design (results included in Table IV) showed the feed rate as the only significant factor in the experiment, increasing the extent of reaction with decreasing feed rate. By looking at the experimental set according to the method of degradation, a screw speed-catalyst concentration interaction was also observed, and it appears that the effect of feed rate on conversion was greater among those samples produced using peroxide-induced chain scission. The increased contribution of feed rate to conversion in the case of the peroxide-degraded polymer was probably due to the molecular weight of the polymer, with PD100 being higher

Sample No.	Average Conversion (%)	Batch Variance $\sigma_B^2$	Sample Variance $\sigma_S^2$	Testing (IR) Variance $\sigma_T^2$
40G	3.781	$2.873 imes10^{-1}$	$2.357 imes10^{-3}$	$1.886 imes 10^{-3}$
41G	4.699	$1.523 imes10^{-2}$	$5.361 imes10^{-2}$	$9.926 imes10^{-4}$
42G	4.932	$3.392 imes10^{-1}$	$4.560 imes10^{-2}$	$1.582 imes10^{-3}$
43G	3.571	$2.262 imes10^{-1}$	$2.619 imes10^{ m o}$	$2.181 imes10^{-3}$
44G	3.783	$4.132 imes10^{-2}$	$9.046 imes10^{-3}$	$1.108 imes10^{-3}$
45G	4.680	$5.184 imes10^{-3}$	$4.559 imes10^{-2}$	$6.866 imes10^{-4}$
46G	3.817	$1.666 imes 10^{-3}$	$7.967 imes10^{-3}$	$1.061 imes10^{-3}$
47G	4.287	$4.179 imes10^{-2}$	$2.432 imes10^{-3}$	$2.166 imes10^{-3}$
48G	4.044	$8.043 imes10^{-3}$	$3.688 imes10^{-2}$	$3.211 imes10^{-2}$

Table VII Results of the Hierarchical Analysis

IR = infrared.

than TD380 (before dilution with virgin KF6100). The difference in the MWD between the two degraded materials was small, particularly in comparison with the final diluted material of either degradation method, but that was probably why the method of vinylidene generation did not have a significant effect.

The final experimental set attempted to examine several reaction factors in the absence of mixing effects to ensure that the Lewis acid effect was not being obscured. Before analyzing the experimental design for significant effects, the product samples were used in a hierarchical (nested) design<sup>33</sup> to elucidate significant sources of variance in the measurement of the succinvl anhydride group. Three sources of variance were analyzed in the hierarchical design according to the letter designations of Box and colleagues<sup>33</sup>: batch (B), sample homogeneity (S), and infrared measurement (T). Table VII presents the conversion and pooled estimates of variance. Variance in the infrared measurements proved to be the lowest one, testifying to the good reproducibility of the spectroscopic technique. The higher batch-to-batch and sample homogeneity variances are indicators of the homogeneity of the extrusion process. It appears that a greater effort in dispersive mixing will be necessary to provide a more uniform product with respect to succinyl anhydride incorporation.

The  $3^{3-1}$  fractional factorial in Table V provided a means of determining the main effects without confounding interactions. Based on repeats, the pooled estimate of variance was determined to be 0.017% conversion. Through analysis of the conversion data for experimental set 3, regression coefficients (given in Table V) for the model showed that all three factors were significant, with positive effects observed for temperature and maleic anhydride concentration, with respect to the succinyl anhydride incorporation. The Lewis acid concentration had a negative effect on the Alder Ene reaction, increasing the succinyl anhydride concentration with decreasing catalyst concentration. The trend confirmed the observations made within experimental set 1 for the same material (TD380).

#### Ruthenium Chloride Vs. Stannous Chloride

Two maleation runs (9G and 12G) were reproduced using ruthenium chloride in place of stannous chloride. The Fourier transform infrared spectra of the samples have already been shown in Figure 5. Conversion of the vinylidene in samples 37G and 38G was 6.26% and 7.15%, respectively, showing a 16% improvement over those materials produced in the presence of stannous chloride. The improved catalytic nature of ruthenium chloride, compared with stannous chloride, was also observed in previous work using a low molecular weight polypropylene.<sup>14</sup> Ruthenium chloride does not form an adduct with the anhydride oxygen similar to stannous chloride, rather it coordinates with the vinyl group,<sup>24,25</sup> evidently producing a superior enophile for the Alder Ene reaction with respect to vinylidene group of polypropylene. Unlike stannous chloride, the robustness of ruthenium chloride toward moisture, is a useful property for a catalyst being used for reactive extrusion, and the improved rate of reaction resulting from its presence demonstrates its advantage to our system.

#### CONCLUDING REMARKS

Maleation of polypropylene through reactive extrusion *via* the Alder Ene reaction has been shown to produce a terminal functionality without significant chain scission. Increased temperature and maleic anhydride reactant concentration were found to improve the extent of the reaction. With improved mixing in the extruder, due to increase melt viscosity or increase feed rate, the degree of conversion was increased. Ruthenium chloride was found to increase the extent of the reaction by 16%, in comparison with stannous chloride as a catalyst in the Alder Ene reaction.

Financial support from the Ontario Centre for Materials Research (OCMR) and the Natural Sciences and Engineering Research Council of Canada (NSERC) is gratefully acknowledged. Also, the authors greatly appreciate the donation of polypropylene by Montell Canada and peroxide by Elf AtoChem.

#### REFERENCES

- R. C. Kowalski, in Reactive Extusion: Principles and Practice, M. Xanthos, Ed., Hanser Publishers, Munich, 1992, Chap. 1.
- B. De Roover, M. Sclavons, V. Carlier, J. Devaux, R. Legras, and A. Momtax, J Polym Sci Part A: Polym Chem 1995, 33, 829.
- R. Rengarajan, V. R. Parameswaran, S. Lee, M. Vicic, and P. L. Rinaldi, Polymer 1990, 31, 1703.
- 4. N. G. Gaylord and M. K. Mishra, J Polym Sci Polym Lett 1983, 21, 23.
- 5. J. J. Flat and M. Lambla, Annual Meeting of the Polymer Processing Society: Book of Abstracts, Seoul, Korea, 1995, p. 4.
- W. Gabara and S. Porejko, J Polym Sci: Part A-1 1967, 5, 1539; W. Gabara and S. Porejko, J Polym Sci: Part A-1 1967, 5, 1547.
- E. Borsig, A. Fiedlerova, and L. Hrckova, J. M. S.-Pure Appl Chem 1995, A32, 2017.
- R. M. Ho, A. C. Su, and C. H. Wu, Polymer 1993, 34, 3264.

- 9. N. G. Gaylord and M. Mehta, J Polym Sci Polym Lett 1982, 20, 481.
- R. Mülhaupt, T. Duschek, and B. Rieger, Makromol Chem Macromol Symp 1991, 48/49, 317.
- S. Nemes, J. Borvbely, J. Borda, G. Deak, and T. Kelen, Polym Bull 1992, 29, 135.
- T. Shiono, H. Kurosawa, O. Ishida, and K. Sogo, Macromolecules 1993, 26, 2085.
- M. R. Thompson, C. Tzoganakis, and G. L. Rempel, Polymer 1998, 39, 327.
- M. R. Thompson, C. Tzoganakis, and G. L. Rempel, Polym Sci Part A: Polym Chem 1998, 36, 2371.
- 15. H. M. R. Hoffmann, Angew Chem Int Ed Engl 1969, 8, 556.
- T. Sawaguchi and M. Seno, Polym J 1996, 28, 817;
   T. Sawaguchi, T. Ikemura, and M. Seno, Macromolecules 1995, 28, 7973.
- M. R. Thompson, C. Tzoganakis, and G. L. Rempel, J Polym Sci A: Polym Chem 1997, 35, 3083.
- B. B. Snider, J Org Chem 1974, 39, 255; B. B. Snider, D. J. Rodini, R. S. E. Conn, and S. Sealfon, J Am Chem Soc 1979, 101, 5283.
- W. Oppolzer, Angew Chem Int Ed Engl 1984, 23, 876.
- E. Walch and R. J. Gaymans, Polymer 1994, 35, 1774.
- 21. A. Y. Coran and R. Patel, Rubber Chem Technol 1983, 56, 1045.
- H. K. Kotlar and K. Borve, Proceedings of the Annual Technical Conference of the Society of Plastics Engineers, Vol. 53, Boston, 1995, p. 1843.
- L. Roncetti and V. Banzi, U.S. Pat. 5,153,270 (1992).
- 24. T. Alderson, E. L. Jenner, and R. V. Lindsay, Jr., J Am Chem Soc 1965, 87, 5638.
- 25. R. Cramer, Accts Chem Res 1965, 1, 186.
- J. H. Adams and J. E. Goodrich, J Polym Sci Part A-1, 1970, 8, 1269.
- H. Hinsken, S. Moss, J. R. Pauquet, and H. Zweifel, Polym Deg Stab 1991, 34, 279.
- K. E. Russell and E. C. Kelusky, J Polym Sci: Part A: Polym Chem 1988, 26, 2273.
- 29. W. K. Busfield and J. V. Hanna, Polym J 1991, 23, 1253.
- 30. F. H. Marquardt, J Chem Soc B 1966, 1242.
- 31. R. A. Nyquist, Appl Spectrosc 1990, 44, 438.
- F. R. Benn, J. Dwyer, and I. Chappell, J Chem Soc Perkin II, 1977, 533.
- 33. G. E. P. Box, W. G. Hunter, and J. S. Hunter, Statistics for Experimenters: An Introduction to Design, Data Analysis and Model Building, John Wiley & Sons, New York, 1978, Chap. 17.