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Terminal functionalization of polypropylene via the Alder Ene reaction

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A terminally anhydride functionalized polypropylene was synthesized via the Alder Ene reaction from a low molecular weight amorphous polypropylene. A Lewis acid, $SnCl_2{\cdot}2H_2O$, was found to catalyse the reaction, thereby improving anhydride content in the polymer for reaction conditions comparable to those in an extrusion environment, i.e. elevated temperature and short residence time. The reaction was carried out at 230°C for 5 min in the presence of TEMPO, which acted as a free radical trap, preventing maleic anhydride from being grafted onto the backbone of the polypropylene. The product was characterized by several techniques, including *FT*i.r. and n.m.r., to provide evidence of the anhydride location on the chain. Several runs of varying catalyst concentration have shown that an optimum in anhydride incorporation onto the polypropylene exists. Examination of the system kinetics has shown that the overall order of the reaction remains second-order despite the presence of a catalyst. © 1997 Elsevier Science Ltd.

(Keywords: polypropylene; terminal functionalization; Alder Ene reaction)

INTRODUCTION

Polypropylene has over the past few years shown the most rapid growth of practically any polymer on the market[1]. The entrance of this material into non-conventional engineering markets such as the automotive industry has brought with it both intense interest and difficulties. The chemical inertness of polypropylene, so often exploited in conventional commodity products such as bottles and films, restricts its use in more demanding engineering products which often require a blending of polymer characteristics to meet customer specifications. In recent years, reactive modification of polypropylene in an extruder via free radical grafting has become a vigorously pursued post-polymerization method for incorporating functionality into the material[2–9]. Collectively researched in both academia and industry, it has been found that the random covalent attachment of a comonomer onto the backbone of the polymer by a radical mechanism is often accompanied by degradation. Maleic anhydride functionalization of polypropylene has received intense interest for the improved compatibility with hydrophilic systems which the functionality imparts to the polymer. Interest in maleic anhydride has been primarily due to the difficulty in homopolymerization of this comonomer during free radical grafting. The generation of poly(maleic anhydride) chains has been theorized to proceed through a cationic mechanism which relies on the formation of an excimer[4–6]. The actual presence of poly(maleic anhydride) segments (grafted or free) under standard processing conditions has been the subject of debate in the literature for some time[4–6,8,10]. Contrary to chain backbone modification, end-group reactions are not generally applicable to polyolefins since the macromolecules lack any reactive functionality. However, researchers have studied several different chemistries to functionalize polypropylene terminally[11–16] using the only functional group present, a 1,1-disubstituted double bond (vinylidene). The functional groups produced by these reactions have included anhydride, silane, thiol, expoxide, borane and its hydroxyl derivative, and carboxylic acid species. End-group modifications have been carried out in both the melt and solution. Among the chemistries explored for end-group modification, the Alder Ene reaction[17] appears to be particularly suited for functionalization of polymers in the melt phase.

The Alder Ene reaction, sometimes referred to as a pericyclic reaction due to the 6-centre transition intermediate resulting from its concerted mechanism, involves the interaction of an *ene* (an unsaturated species with an allylic hydrogen available) and an *enophile* (an unsaturated species usually with neighbouring electron-withdrawing groups) forming a 1:1 adduct. The intermolecular reaction between the *ene* and *enophile* requires elevated temperatures in the range of 200–600°C[18] where an optimum exists, after which the retro-Ene[19] reaction dominates. A series of papers[20] on the Ene reaction between maleic anhydride and polyisobutylene (which is chemically similar to polypropylene with respect to the environment of the terminal vinylidene functionality) provided several important insights into this reaction. Two isomer products were generated from the terminal vinylidene species as shown in *Figure 1*, with the exo species (*a*) being dominant compared to the endo species (*b*). A small percentage of the original vinylidene proceeded via isomerization to an internal (endo) vinyl prior to coordinating with a maleic anhydride, thereby sterically inhibiting the Ene reaction. Finally, the pendant (exo) vinyl resulting from the reaction allowed a second maleic anhydride to attach in the case of a small model molecule, though such a reaction has been determined to be insignificant in macromolecules due to steric hindrance[21].

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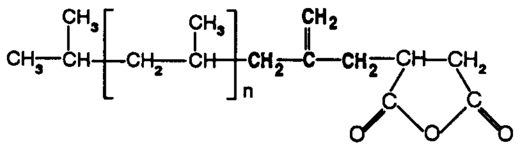

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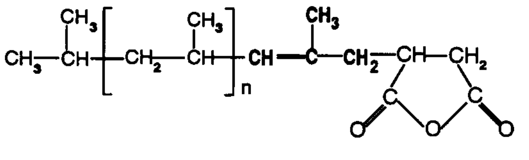

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Figure 1 Isomeric structures of succinyl terminated polypropylene: (a) exo double bond; (b) endo double bond

The reaction 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. Reaction times in the literature were in the order of hours to days for high conversion, which are adequate for bench-scale synthesis, yet scale-up to industrial processing equipment, i.e. twin-screw extruder, would require a dramatic decrease in the permissible reaction duration. To improve the rate of reaction for an Ene synthesis, researchers[21–24] have observed that a Lewis acid functions as a catalyst for the synthesis. The stoichiometric ratio of Lewis acid to *enophile* found in the literature ranged from 0.2 to 1.0[23]. The use of Lewis acids within the Ene reaction has not been very thoroughly studied, but in all reported work the reaction temperature has been lowered (typically in the range of 0–60°C), obtaining a degree of functionalization comparable to high temperature uncatalysed reactions of similar residence time. There is a sparse collection of papers on Lewis acid catalysed Alder Ene reactions with polymers[11,16,21] and no references on high temperature applications of Lewis acid catalysed systems. High temperature systems with polymer in the presence of a Lewis acid need to be pursued with caution due to the high reactivity of the acid species and the likelihood of isomerization and hydrochlorination of the (ene) species as previously observed[21,22,25]. Isomerization, as already mentioned, can inhibit the Ene reaction and hydrochlorination can degrade the polymer backbone as well as introduce safety issues and possibly damage the processing equipment. N.m.r. analysis of an Ene product has shown that vinyl isomerization was not affected[25] by the presence of a highly efficient radical acceptor. However, a radical trapping species has been shown to prevent homopolymerization of the maleic anhydride attached to alkenes during a kinetic study of the Alder Ene reaction[26]. To ensure exclusive terminal placement of a succinyl group, free radicals generated in the system must be trapped to prevent chain degradation, homopolymerization of maleic anhydride and random grafting of maleic anhydride onto the polymer. Phenothiazine, thiophenol, hydroquinone, 2,2′-di(p-hydroxyphenyl) propane and t-butylcatechol[24–27] have all been found to work effectively in uncatalysed Ene reactions, dramatically reducing the presence of poly(maleic anhydride) grafts. The kinetics of the reaction[26] have been found to be unaffected by the presence of an inhibitor.

The focus of this paper is to report on a novel study of the Lewis acid catalysed Alder Ene reaction at high temperature to shorten the reaction time for functinalization of polypropylene with an anhydride species. The goal of this research was to determine an effective reaction for controlled placemet of the functionality, which could be easily adapted to industrial processing environments for plastics and rubbers. A discussion of the reaction kinetics has been included, although a detailed kinetic study has not been the intended aim of this manuscript.

EXPERIMENTAL

Materials

The choice of a model polymer for this study was dependent on finding a material with a high vinyl content without extraneous functionalities which generally arise from polypropylene degradation (i.e. ketone, aldehydes, and γ-lactones). The material finally decided upon was a low molecular weight [$\bar{M}_n = 2010$ g/mol (GPC); 2.458×10^{-4} mol vinylidene/g. Polypropylene (n.m.r.)] amorphous polypropylene (polypol-19) supplied by Crowley Chemical. Maleic anhydride, $SnCl_4$, $TiCl_4$, $AlCl_3$ and stannous chloride dihydrate ($SnCl_2{\cdot}2H_2O$) were supplied by Aldrich Chemicals and used as received. Used as a free radical inhibitor, TEMPO (free radical 2,2,6,6-tetramethyl-1-piperidinyloxy) was also supplied by Aldrich.

Modification

A Parr 300 mL high pressure batch reactor was set up for use as a rein kettle. The lines dedicated for maleic anhydride injection and polymer sampling were traced using heating tape to prevent solidification. Approximately 75–80 g of low molecular weight polypropylene was charged into the vessel per run. The Lewis acid, $SnCl_2{\cdot}2H_2O$, was massed and added into a catalyst bucket which was attached to the inside of the reactor, in line with one of the inlet nitrogen feeds. The vessel was heated to 230°C using a Parr 4843 controller, under a nitrogen blanket and constant agitation (300 min^{-1}). Once thermal equilibrium was obtained, a 6 mole equivalence of molten maleic anhydride (70°C, $\rho = 1.30$ g/mL), with respect to the vinylidene content, was mixed with the stable free radical trapping species, TEMPO (tetramethylpiperidine nitroxide), and injected into the reactor. The system was subsequently pressurized to 0.55 MPa to prevent sublimation of the monomer and to force open the catalyst bucket. Samples were extracted from the pressurized reactor at 60 s intervals, with the nitrogen flow regulated to maintain a constant system pressure. The first fraction of each polymer sample was discarded. The individual samples were immediately dissolved in 100 mL cyclohexane and then filtered using a fritted glass filter assembly. Any residual reactants were removed during filtering due to their immiscibility in cyclohexane. The solvent was evaporated and the final product was dried in a vacuum oven for 8 h at 110°C. The samples were stored in a desiccator until spectroscopic measurements could be performed.

Titration

The colorimetric titration technique described by Gaylord and Mehta[4] was used to determine the quantity of anhydride groups bond to the polypropylene product. Due to the solubility of the amorphous polypropylene in xylene, the titrations could be carried out at room temperature compared to the elevated temperature proposed by Gaylord and Mehta[4], overcoming volatility issues with the alcohol solvents used in the acid and base solutions. Titration of each sample was repeated three times. The isopropanolic 0.05 N HCl solution was standarized using Na_2CO_3 as a primary standard.

N.m.r. analysis

Each sample was prepared as a 5–10 wt% polymer solution using benzene-d_6 or hexane-d_{14} as the solvent. The analysis was done at room temperature in a Bruker AC-300E n.m.r. spectrometer using TMS as the reference. The proton spectra spanned a field of 0–15 ppm. Typically 64 scans were accumulated. The ^{13}C n.m.r. was run using a 10 μs (79°) pulse with a pulse relaxation time of 30 s. Carbon proton decoupling was achieved by the inverse gated method. For the low concentration of anhydride in the polymer, 5000 scans were collected to maximize the signal-to-noise ratio. The spectra spanned 0–210 ppm, anticipating anhydride related peaks in the region of 150–175 ppm. Peak assignments were drawn from the published papers of Tessier and Marechal[20] for ^1H analysis and for ^{13}C studies the authors referenced were Busfield *et al.*[28], Heinen *et al.*[10], and Rengarajan *et al.*[7].

Glass transition temperature (d.s.c.)

Approximately 7–12 mg sample was used for each analysis. The differential scanning calorimeter was performed in a TA Instruments DSC Cell 2920. The temperature sweep ranged from − 40°C to 25°C using a ramp rate of 15°C min^{-1}. Solid CO_2 was used to cool the instrument sample pan. For reference, the virgin polypol-19 exhibited a glass transition with an inflection point at −25.36°C. The presence of a small peak in the thermogram centred at 17.38°C for the heat of fusion indicated that the polymer possessed some crystallinity.

FT*i.r. Analysis*

The waxy nature of the polymer allowed for simplified sample preparation by smearing the material on a NaCl disk. The sample was scanned 20 times with a resolution of 2 cm^{-1} covering a range of 500–4000 cm^{-1}. The absorbance wavenumbers pertinent to the modification were: 888 cm^{-1} (vinylidene), 1784 cm^{-1} (anhydride), 1792 cm^{-1} (succinyl anhydride), 1865 cm^{-1} (succinyl anhydride). To determine the kinetics of the reaction, the strong anhydride peak at 1792 cm^{-1} was used along with an internal reference peak at 974 cm^{-1} which pertained to the polymer backbone (mixed C-H absorbance).

Dilution viscometry

The analysis was performed at 60°C using anhydrous decahydronaphthalene (supplied by Aldrich) as the solvent. These conditions provided efflux times greater than 200 s, in accordance with ASTM D2857. The efflux times of three different concentrations between 0.001 and 0.005 g/mL were measured for each sample product. The intrinsic viscosity was determined by extrapolating the inherent viscosity to zero concentration.

RESULTS AND DISCUSSION

Several different Lewis acids, ($SnCl_4$, $TiCl_4$, $AlCl_3$), were examined in this reaction; however, the presence of HCl fumes often accompanied these catalysts upon addition to the reactor and black poly(maleic anhydride) flakes were observed in the product. A less reactive (and less toxic) Lewis acid was chosen, stannous chloride dihydrate ($SnCl_2 \cdot 2H_2O$), which had been used by other authors for reactive modifications[11,16]. Interest in this Lewis acid aside from its catalytic performance is beyond the scope of this paper, particularly regarding its structure at reaction temperature and the structure of the proposed anhydride:

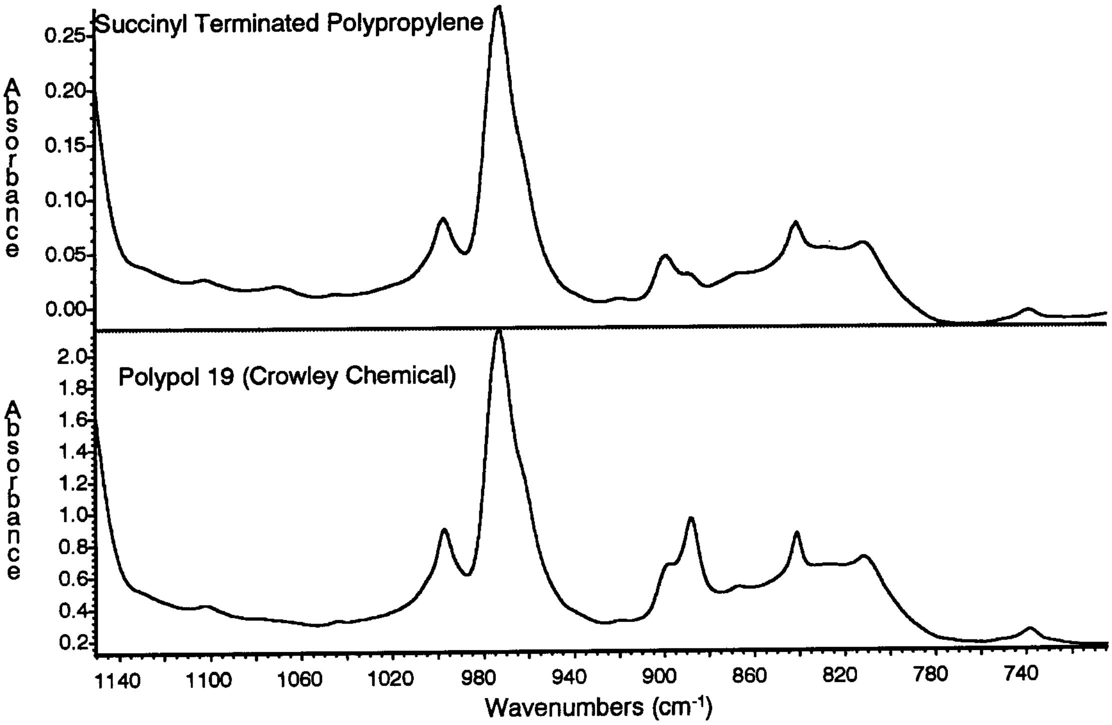

Figure 2 *FT*i.r. spectra comparing the virgin polypropylene and end product in the region of the vinylidene

acid adduct. Attempts to distinguish the consequence of forming the anhydride (enophile):acid adduct prior to injecting into the molten polymer opposed to forming the adduct *in situ* showed no significant increase in the anhydride functionality of the product. The addition of maleic anhydride and catalyst was observed to suppress the reactor temperature by 3–4°C, which the controller was not able to correct over the duration of the reaction. This observation combined with evidence presented in subsequent sections indicated that improvement in anhydride incorporation in the polymer should be attributed to the catalytic nature of the Lewis acid rather than an increase in the temperature due to the highly reactive acid being introduced. Localized heating in the molten polymer could still be present; however, no indictions of this phenomenon were observed.

Characterization of succinyl terminated polypropylene

The following analysis shows that the succinyl anhydride functionality was located terminally on the polymer chain.

FT*i.r. analysis*

Figure 2 shows the succinyl terminated polypropylene in comparison with the virgin resin in the region of the vinylidene. The strong vinylidene absorbance at 888 cm^{-1} in the virgin resin showed a significant decrease upon the conclusion of the Alder Ene reaction in the presence of a Lewis acid catalyst. Similar to the findings of Walsh and Gaymans[21], the generated vinyl at 920 cm^{-1} from the Ene reaction was not seen in the *FT*i.r. spectra, possibly due to the low intensity of the functionality in the product. *Figure 3* shows the same two polymers as in *Figure 2*; however, the region shown pertains to the carbonyl absorption. The peaks at 1745 cm^{-1} and 1780 cm^{-1} in the Polypol-19 indicate the presence of an anti-oxidant in the resin, which fortunately did not appear to interfere with the performance of the Lewis acid. The succinyl terminated polypropylene in *Figure 3* shows a succinyl absorbance at 1792 cm^{-1} with a shoulder at 1784 cm^{-1}. No chlorination of the product, due to isomerization, was observed, which would be characterized by a peak at 640 cm^{-1}. Interpreting the presence of the 1784 cm^{-1} band was complicated by conflicting views on the mechanism which maleic anhydride grafts to the polymer[8,10]. However, both 1792 cm^{-1} and 1784 cm^{-1} are attributed to mechanical coupling of the carbonyl stretching modes within the anhydride[29]. The intensity of the lower frequency band is increased in systems of increasing polarity or with increasing intermolecular hydrogen bonding[30]. Therefore, maleic anhydride bound or free in a polypropylene system should show a stronger high frequency band than low frequency band (which has been observed) unless high localized concentrations of anhydride exist. Grafts of poly(maleic anhydride), if present in the polypropylene chain, would favour the low frequency band. The presence of TEMPO maximized the intensity of the succinyl peak compared to the 1784 cm^{-1} absorbance.

Intrinsic viscosity

The intrinsic viscosity value of the virgin polymer was found to be 0.1873 dL/g, while two succinyl terminated polypropylenes with a low (0.005 mole eq.) and high (0.1 mole eq.) catalyst concentration were observed to have decreasing viscosity values, 0.1660 dL/g and 0.1046 dL/g/ respectively. The intrinsic viscosities suggest that the polymer underwent degradation in the presence of the Lewis acid.

N.m.r. analysis

Figure 4 presents a ^1H n.m.r. spectrum of a succinyl terminated polypropylene in hexane over a field range of 0–8 ppm. No peaks were observed in the region of 9–15 ppm where carboxylic acids were anticipated. Peak assignments for the polyproylene backbone lie in the region of 1–2 ppm. The terminal vinylidene was characterized by two fully

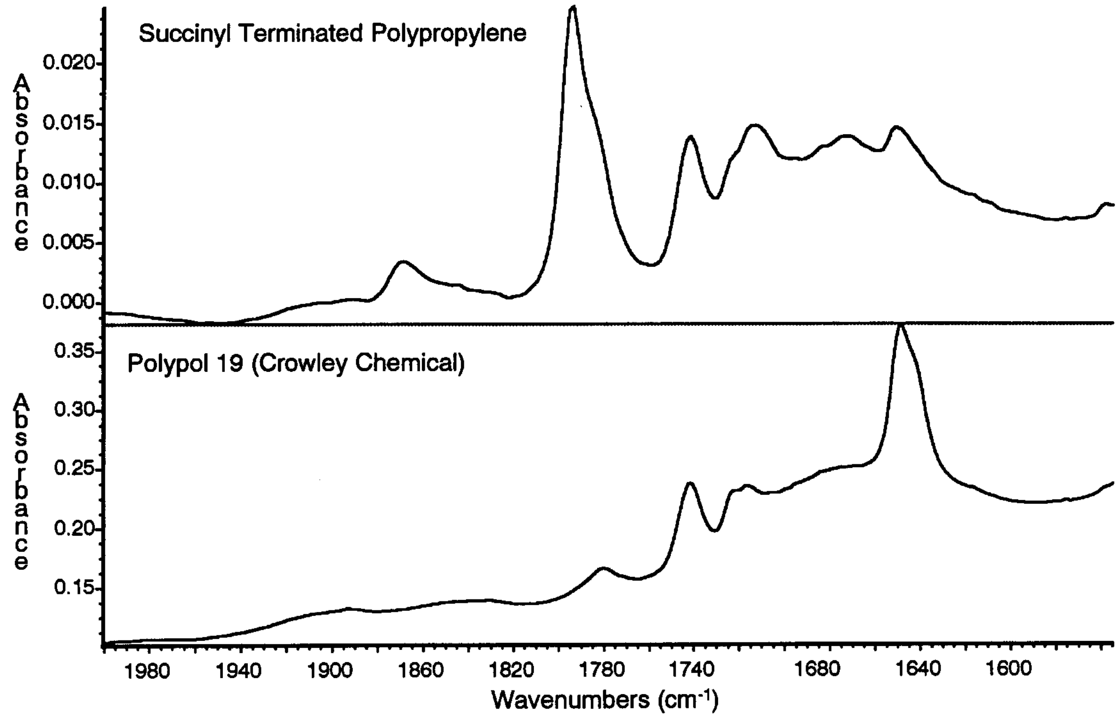

Figure 3 *FT*i.r. spectra comparing the virgin polypropylene and end product in the carbonyl region

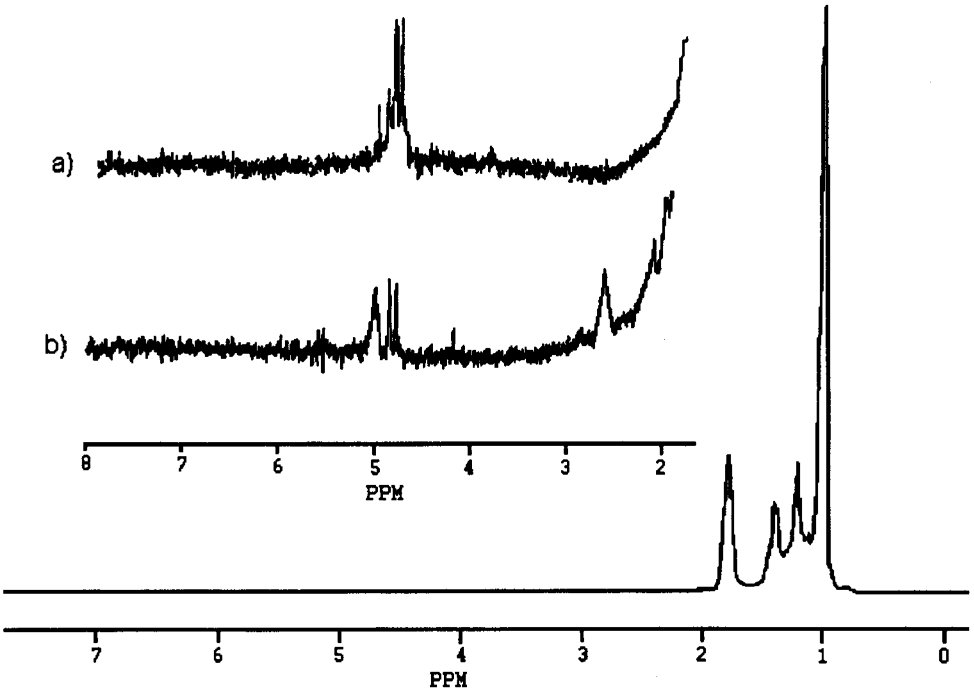

Figure 4 ^{1}H solution n.m.r. spectrum of (a) polypol-19 and (b) succinyl terminated polypropylene

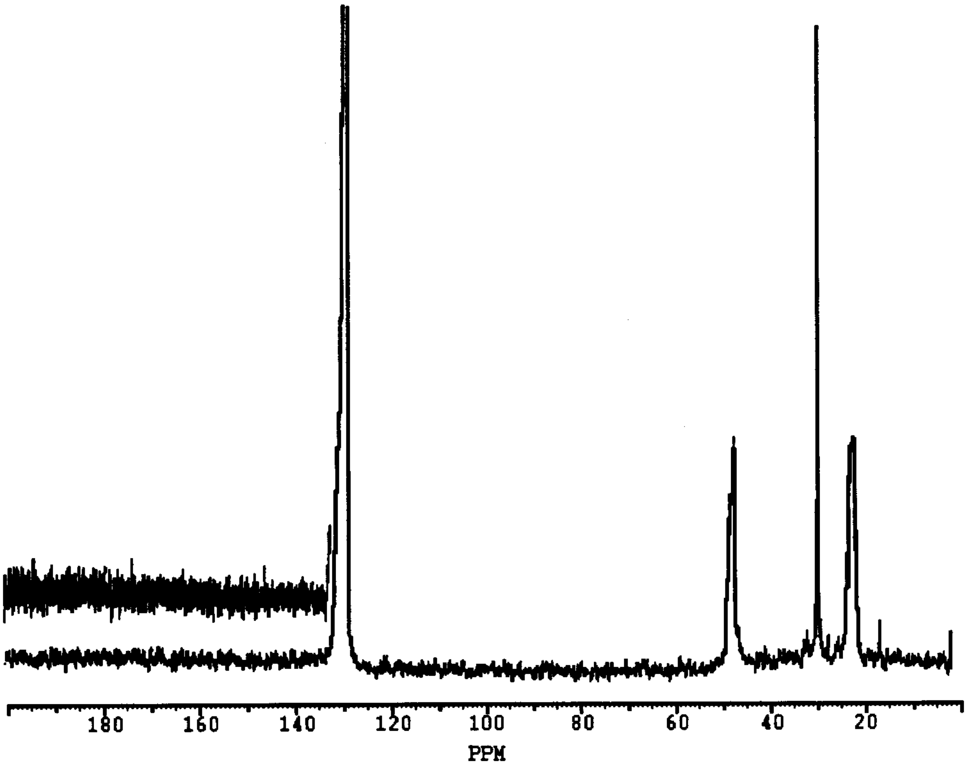

Figure 5 ^{13}C solution n.m.r. spectrum of succinyl terminated polypropylene

resolved peaks at 4.78 ppm and 4.83 ppm corresponding to the two hydrogens at the chain end. Peak integration of the vinyls relative to the polymer backbone indicated a decrease in the vinylidene content in the succinyl functionalized product compared to the virgin resin (displayed in *Figure 4a,b*). The internal vinyl assigned to 4.99 ppm was observed to increase for the same product. The isomerization of the vinylidene confirmed that the Alder Ene reaction had occurred. Terminal succinyl functional groups tend to have complex splitting patterns[20] but generally are found in the region of 2–3 ppm, which corresponds to the broad peak centred at 2.62 ppm in *Figure 4*. This assignment was compared with a maleic anhydride grafted polymer synthesized using 1.0 wt% Lupersol 101 dialkyl peroxide (Elf AtoChem) for the same time and temperature as the Ene product. The succinyl peak was observed to shift downfield to 3.3 ppm, now that the succinyl group was positioned at a tertiary site. This result seems to suggest that the product possessed terminal attachment exclusively opposed to backbone grafting. No free or polymerized maleic anhydride was seen in the spectrum of the Ene product. A ^{13}C n.m.r. spectrum of the Ene product is shown in *Figure 5*. The terminal succinyl CH and CH_2 groups of the cyclic anhydride should be observed in the region of 40 ppm and 34 ppm, respectively[20], whereas a tertiary grafted succinyl group should show chemical shifts at 63 and 53 ppm, respectively[31]. Carbonyl carbons for the succinyl group irregardless of position should produce chemical shifts of 169 and 174 ppm[20,31]. *Figure 5* showed that the natural abundance of ^{13}C was insufficient to observe the low concentration (approximately 2 mol%) of succinyl groups attached to the polypropylene chain. According to the peak assignments of Shiono *et al.*[14] for polyprpylene, the peak at 15.08 ppm corresponded to a propyl end group and the complex splitting patterns centred at 21, 28 and 46 ppm corresponded to the methyl, methine and methylene groups, respectively. Vinyl groups could not be detected above the noise of the baseline.

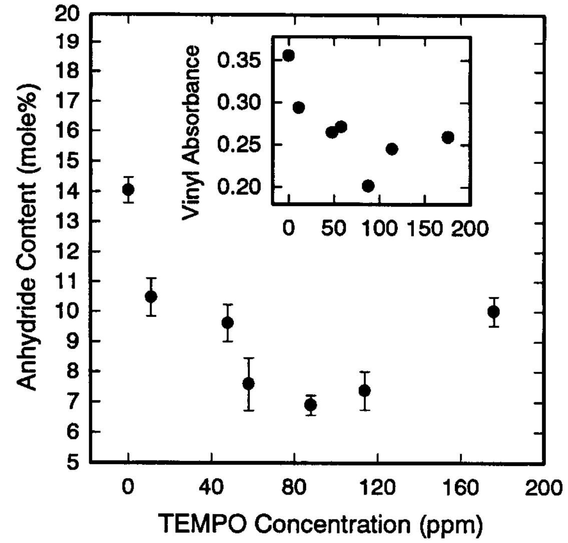

Figure 6 Effect of TEMPO concentration in the Alder Ene reaction on the anhydride and vinylidene content in polypropylene product

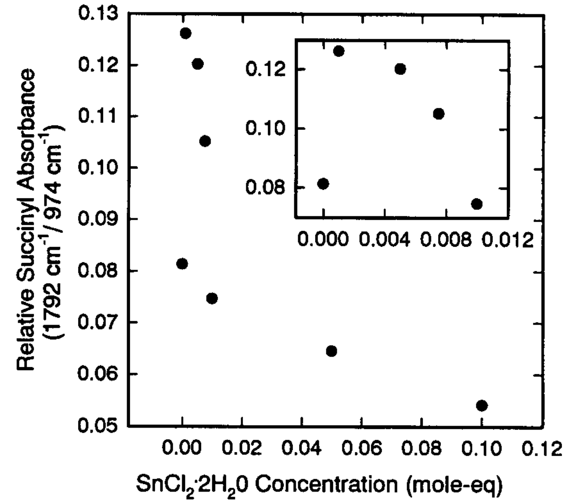

Figure 7 Effect of Lewis acid concentration on the anhydride content in the Alder Ene product (region of optimal anhydride incorportion has been expanded)

Effect of free radical inhibitor

The possible presence of free radicals generated during the reaction due to the presence of oxygen in the system and polymer degradation can lead to backbone grafting and/or homopolymerization of maleic anhydride. ^{1}H n.m.r. analysis of a catalysed reaction product with no inhibitor added showed a strong broad peak in the region of 2.6 ppm and a weak peak at 3.3 ppm. The spectrum indicated that the presence of both free radical grafting and Alder Ene mechanisms were involved in the attachment of maleic anhydride onto the polypropylene chain. Hydroquinone, a common free radical inhibitor, was initially tested in an attempt to prevent maleic anhydride from being grafted onto the chain backbone. However, *FT*i.r. analysis of samples ran with hydroquinone showed a phenyl group at 1610 cm^{-1} which was attached to the polymer. It was therefore concluded that no free radical inhibitors which possessed a phenyl group could be used in the work, which dismissed all common inhibitor candidates. Dimethyl formamide (DMF) was tested to inhibit the maleic anhydride excimer which abstracts the backbone hydrogens of the polymer[4]. The use of DMF decreased the vinylidenes consumed, as well as the anhydride content in the product. However, concerns for the possible reduction in the effective catalyst concentration due to the Lewis acid forming an adduct with the carbonyl group in DMF led to the investigation of another inhibitor. TEMPO, a stable free radical trapping species, common in living free radical research, was considered. A series of seven runs were performed in the reactor using a 0.1 mole equivalence of $SnCl_2 \cdot 2H_2O$ with respect to the maleic anhydride reactant, with the TEMPO concentration ranging from 0 to 175 ppm. *Figure 6* shows the relative *FT*i.r. absorbances for each sample at 888 cm^{-1} (vinylidene) along with the titration data, which determined maleic anhydride content in the polymer. *Figure 6* shows that vinylidene concentration reached a minimum at 75–80 ppm TEMPO, while the anhydride content decreased to a plateau at the same concentration range. During radical addition of maleic anhydride, the vinylidene has been found[10] to not participate, which explains the high vinylidene content at low TEMPO concentrations. The i.r. absorbance ratio, 1792 cm^{-1}/1784 cm^{-1}, showed a corresponding maximum at approximately 75 ppm. However, on either side of the maximum the ratio rapidly dropped below unity. It was apparent that an excess of TEMPO had a detrimental effect on the reaction similar to reactions run without sufficient inhibitor. The stable free radical, in excess, may participate in the backbone grafted or homopolymerization (or both) of maleic anhydride. It is also possible that a high concentration of TEMPO could interfere with the catalyst. No evidence of bound TEMPO was observed in any n.m.r. or *FT*i.r. spectra.

Catalytic effect of Lewis acid

The presence of Lewis acid was anticipated to increase the rate of reaction, though increasing the concentration of the acid was also expected to increase the rate at which the vinylidenes undergo isomerization prior to participating in the Alder Ene reaction. To determine if this theory was true, the reaction was ran excluding maleic anhydride. Infrared analysis of the product showed the vinylidene content to decrease over the space of 5 min. It should be noted that the concerted mechanism of the Alder Ene reaction is prohibitively slow with internal vinyls due to steric hindrance. Subsequently, a maximum in the Lewis acid concentration was anticipated as the effect of the catalyst

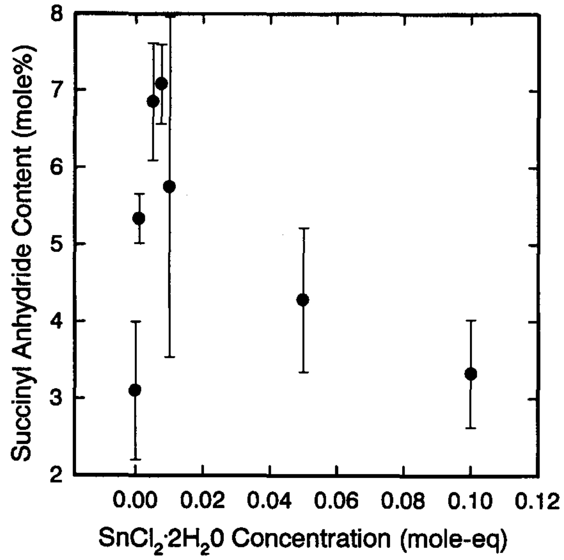

Figure 8 Titrated succinyl anhydride group in the Alder Ene product with respect to the Lewis acid concentration (standard deviation error bars)

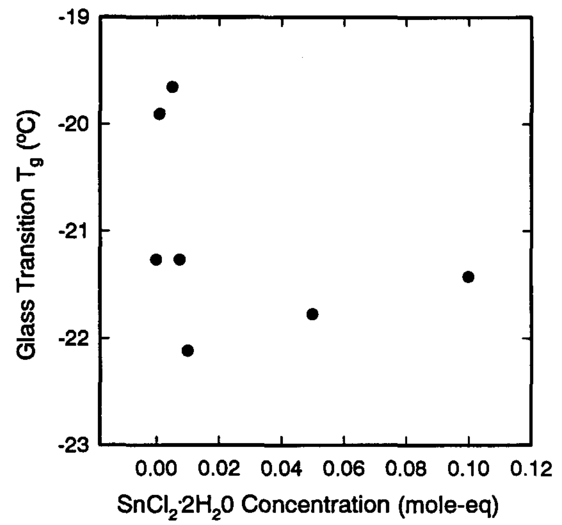

Figure 9 Effect of Lewis acid concentration on the glass transition temperature of the Alder Ene product

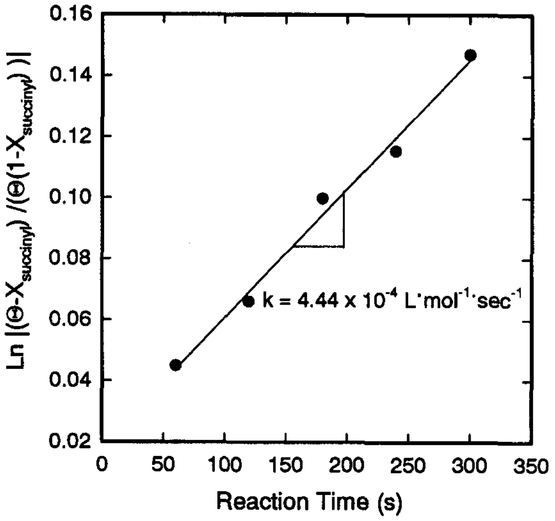

Figure 10 Best linear fit to *FT*i.r. measurements assuming second-order reaction kinetics

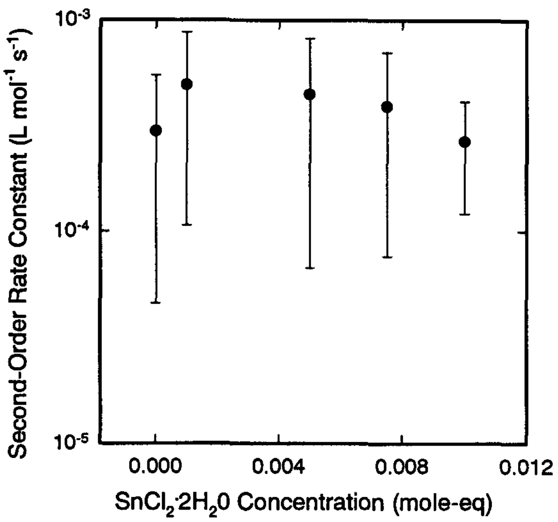

Figure 11 Pseudo first-order rate constants for the catalysed Alder Ene reaction (95% confidence interval error bars)

was investigated. *Figure 7* shows the succinyl *FT*i.r. absorbance for Lewis acid concentrations ranging from 0 to a 0.10 mol equivalence with respect to the maleic anhydride reactant. The experimental series used 75 ppm TEMPO in each run. The expanded section of *Figure 7* shows that a maximum exists at 0.001 mole equivalence of $SnCl_2{\cdot}2H_2O$. The plot shown in *Figure 8* gives the mole percentage of anhydride in the polymer based on titration analysis. The maleic anhydride content titrated was comparable to values found in free radical grafted polypropylene. A substantial increase in the anhydride functionality bound to the polymer was observed relative to the sample produced without the Lewis acid present in the reaction. The anhydride concentration within the polypropylene appeared to be greatest in the region of 0.005–0.0075 mole equivalence of $SnCl_2{\cdot}2H_2O$ with respect to the maleic anhydride reactant. The titration data represent the total anhydride content including those groups which had undergone hydrolysis despite precautions taken. The difference in the maximum value of succinyl anhydride attached to the polypropylene between *Figures 7 and 8* was due to the infrared results in which the dicarboxylic acid formed by hydrolysis was neglected. *Figure 9* shows the glass transition temperature for each sample in the Lewis acid run series. Increasing anhydride functionality with respect to the alkyl nature of the polymer increases intermolecular interaction in the species, reducing mobility in the chains and therefore increasing the transition temperature. Based on this theory and assuming that no unbound comonomer was present within the polymer sample, the increase in the material T_g is indicative of an increase of succinyl groups in the polypropylene. *Figure 9* established the region where the Lewis acid had maximum effect on the Alder Ene reaction and it generally showed the same trend observed in *Figures 7 and 8*.

For all analysis techniques, the presence of a catalyst appears to be valuable in this type of reactive modification of polypropylene.

Kinetics of the Alder Ene reaction

The kinetics of the Alder Ene reaction for maleic anhydride with various alkenes has been reported[26] to be second-order overall, first-order with respect to the individual reactants. A second-order rate constant could be obtained for the succinyl group by plotting $\ln|(\Theta - X_{\mathrm{succinyl}})\ (\Theta(1 - X_{\mathrm{succinyl}})|$ *versus* time, where X_{succinyl} is the mole fraction of anhydride in the product and Θ is the mole ratio of maleic anhydride with respect to vinylidene. *Figure 10* shows the *FT*i.r. data for the sample run with a 0.001 mole equivalence $SnCl_2{\cdot}2H_2O$ with respect to maleic anhydride. The correlation constant, R^2, for a linear fit to the data was 0.99. Only two samples, 0.05 and 0.10 mole equivalence Lewis acid, out of the entire series gave a correlation constant dramatically less than 0.98 (0.45–0.5). This observation indicates that Lewis acid concentrations significantly larger than the optimum deviate from second-order kinetics denoting reactions aside from the Alder Ene reaction are occurring. *Figure 11* presents the rate constants calculated for the series, including their 95% confidence interval, excluding the higher acid concentration rate constants which strongly deviated from a second-order system.

CONCLUDING REMARKS

An anhydride terminated polypropylene was produced using a Lewis acid catalysed Alder Ene reaction. It has been shown that the maleic anhydride incorporation onto the polymer was terminally positioned provided free radical reactions were inhibited. A stable free radical trapping species, TEMPO, has been found to be a useful inhibitor at concentrations in the region of 75–80 ppm, preventing the radical grafting of the maleic anhydride onto the polymer backbone. The presence of a Lewis acid catalyst ($SnCl_2{\cdot}2H_2O$) was observed to have a catalytic effect on the reaction, providing maximum anhydride incorporation at a concentration of 0.005 mole equivalence with respect to the maleic anhydride reactant. The overall order for the rate equation governing the kinetics of the Alder Ene reaction was not shown to change due to the addition of a catalyst.

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