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Carboxyl-Terminated Isotactic Polypropylene. Preparation, Characterization, Kinetics, and Reactivities

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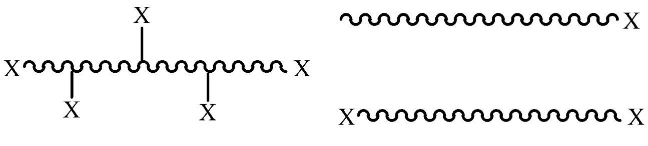
ABSTRACT: The present contribution describes an unsophisticated yet highly efficient process to make dicarboxyl telechelic isotactic polypropylene containing pendant nitro groups via the oxidative degradation of commercially available crystalline polypropylene with nitric acid. The obtained crystalline polymer has a narrow molecular weight distribution ($M_w/M_n = 2-4$) and maintains the same degree of isotacticity as the virgin polypropylene. The molecular weights of the product can be well controlled by varying the reaction temperature, reaction time, or the concentration of nitric acid. It was found that the higher reaction temperature and higher concentration of nitric acid, the faster the degradation is. Kinetic studies shown that the reaction is 4.2 orders in nitric acid, indicative of the complex nature of the reaction mechanism. Both liquid/solid and gas/solid interface interactions were found simultaneously existing in the present system. The carboxyl-capped polypropylene with low NO_2/COOH ratio can be produced at a higher reaction temperature with a higher concentration of nitric acid. Importantly, the nitric acid utilized in the reaction can be recycled and reused in the subsequent reaction. Other functional (acyl chloride, allyl, ester, amide, and hydroxyl) capped isotactic polypropylenes have been readily made through the transformation of the carboxyl group of the dicarboxyl telechelic isotactic polypropylenes in high yields.

Introduction

There has been much current interest in functional polyolefins (PO) since these polymers are expected to exhibit better chemical and physical properties than their nonfunctional counterparts in areas such as adhesion, dyeability, permeability, and compatibility with polar polymers.[1] Furthermore, they are very important precursors for making block and graft copolymers.[2] Unfortunately, because of the highly electron deficiency nature, the catalysts used for olefin polymerization normally cannot tolerate monomers containing functional groups owing to the catalysts poisoning, whereas the catalysts utilized for initiating vinyl monomer polymerization are generally incapable of polymerizing unfunctional olefins. Thus, the search for means to synthesize functional polyolefins has long been and still remains a serious challenge.

In principle, the functional polyolefin can be categorized into two main groups: (a) PO with functional group(s) on the backbone of the polymer chain, **I**; (b) PO with functional group(s) at the end of the polymer chain, **II**. The second type can be further divided into mono- and difunctional terminated polyolefins. During the past two decades, a number of methodologies have been developed to make functional polyolefins. These include using "mask" comonomer,[3] α,ω-diene,[4] boron-containing comonomer,[5] free radical grafting,[6] and ROZP processes for **I**[7] and β-H elimination,[8] chain transfer,[9] living process,[10] and chain end coupling for monofunctional terminated **II**,[11] even though the efficiency of most of these processes is quite low. On the contrary, very limited success has been achieved toward the preparation of difunctional polyolefins. In particular, only two reports have mentioned about the synthesis of difunctional terminated polypropylene. Sawaguchi et al. reported the preparation of about 80% pure α,ω-diisopropenyloligopropylene ($M_n = 3300-4800$) via the pyrolysis of isotactic polypropylene at 370 °C under vacuum, but only feasible at less than 1 g scale.[12] Soga et al. described a method for making a double-bond-capped polypropylene telechelics by using a titanium-based catalyst with a bifunctional chain transfer agent; the process, however, suffers very low catalyst activity as well as poor yield.[13] Apparently, an ideal process, which would be highly efficient and capable of directly implanting the functionality at the two termini of the polymer chain, is still lacking.



(I) **(II)**

(X = functional group)

It is well-know that cyclohexanol can be selectively oxidized with nitric acid to yield adipic acid (acid-terminated butane) in good yield,[14] a reaction involving a C−C bond cleavage and a subsequent oxidation. As a matter of fact, nitric acid has been used in the early 1970s to oxidize the surface of polyethylene single crystals to unravel the surface folding in crystalline polyethylene,[15] which led to the isolation of the low molecular weight nitrated dicarboxylic acid-terminated paraffin.[16] An intriguing question than arises as to whether this unique reactivity channel might be exploited to make high molecular weight dicarboxyl-terminated telechelic polypropylene, an important building block for making polypropylene block copolymers. In the present contribution, we present a full account of our studies on such a process, including product preparation, characterizations, kinetic studies, and reactivities.

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Experimental Section

Materials and Methods. Isotactic polypropylene (sphere particles, diameter = 0.5−1.0 mm) was obtained from Ashland Chemical. Nitric acid, ethylene glycol, ally alcohol, 1-propanol, and *p*-toluenesulfonic acid were purchased from Aldrich. Deuterated 1,1,2,2-tetrachloroethane (99.5% D) was obtained from Isotec Inc.

Physical and Analytical Measurements. NMR spectra were recorded in $C_2D_2Cl_4$ at 120 °C on a Varian Mercury-300 (FT, 300 MHz, ^{1}H; 75 MHz, ^{13}C) spectrometer. IR spectra were obtained on a Nicolet 710 FT-IR spectrometer. Gel permeation chromatography (GPC) was performed at elevated temperatures on a Waters 150 CV plus chromatograph equipped with a refractive index detector and a capillary viscometer using universal calibration with polystyrene standards. DSC was carried out on a Du Pont 910 differential scanning calorimeter.

Representative Example for Making Dicarboxyl-Capped Isotactic Polypropylene. To a 1 L three-neck flask equipped with a condenser were added 100 g of isotactic polypropylene (M_n = 95 000; M_w/M_n = 3.22; T_m = 168.5 °C) and 400 mL of concentrated nitric acid (70%). The mixture was heated to 130 °C and stirred for 16 h. During this time, a small amount of aliquot was taken out periodically, washed with water and acetone, and analyzed by IR and GPC. After cooling, the suspended polymer was filtrated and rinsed with water to remove the nitric acid. The product was then placed in a Buchner funnel and washed with acetone, whereby the high molecular weight fraction was retained in the funnel, whereas the low molecular fraction was collected in the liquid phase. The yield of the high molecular fraction (crystalline powder) was 88 g after drying under high vacuum, and that of the low molecular weight fraction (grease) obtained from the liquid phase after removing the solvent was 7 g. The total yield was 95%. The polymers for both high and low molecular weight fractions have been characterized.

Crystalline Powder: M_n = 1652; M_w/M_n = 2.33 (GPC); T_m = 139 °C (DSC). IR (KBr): 1709 cm^{-1} ($-CO_2H$); 1557 cm^{-1} ($-NO_2$). ^{1}H NMR (in $C_2D_2Cl_4$ at 120 °C, relative to TMS): δ 8.46 ($-\mathrm{COO}H$); 5.03 [$-\mathrm{C}H\ (\mathrm{NO_2})(\mathrm{COOH})$], 4.18 ($-\mathrm{C}H\mathrm{NO_2}$), 2.50 ($-\mathrm{C}H\mathrm{COOH}$) 2.10 ($-\mathrm{C}H\mathrm{COOH}$), 1.6 [$-\mathrm{CH_2C}H(\mathrm{CH_3})-$], 1.22 [$-\mathrm{C}H_2\mathrm{CH(CH_3)}-$], 0.90 [$-\mathrm{C}H_2\mathrm{CH(CH_3)}-$], 0.90 [$-\mathrm{CH_2}$-$\mathrm{CH(C}H_3)-$]. ^{13}C NMR (APT, $C_2D_2Cl_4$ at 120 °C, relative to TMS): δ 181.21, 180.86, 180.02 (Cq), 120.47 (C_q), 97.20, 95.23 (CH), 46.34 (CH_2), 41.62 (CH_2), 37.41 (CH_2), 28.70 (CH), 27.23 (CH), 22.54 (CH_3), 21.8 (CH_3), 20.81 (CH_3), 18.02 (CH_3).

Grease: M_n = 652, M_w/M_n = 3.21 (GPC). IR (KBr): 1709 cm^{-1} ($-CO_2H$); 1557 cm^{-1} ($-NO_2$).^{1}H NMR (in $C_2D_2Cl_4$ at 120 °C, relative to TMS): δ 8.46 ($-\mathrm{COO}H$); 5.03 [$-\mathrm{C}H\ (\mathrm{NO_2})$-$(\mathrm{COOH})$], 4.18 ($-\mathrm{C}H\mathrm{NO_2}$), 2.50 ($-\mathrm{C}H\mathrm{COOH}$), 2.10 ($-\mathrm{C}H\mathrm{COOH}$), 1.90−0.9 [$-\mathrm{C}H_2\mathrm{C}H\mathrm{(CH_3)}-$], 1.10−0.70 [$-\mathrm{CH_2CH(C}H_3)-$]. ^{13}C NMR (APT, $C_2D_2Cl_4$ at 120 °C, relative to TMS): δ 181.21, 180.86, 180.02 (Cq), 120.47 (C_q), 97.20, 95.23 (CH), 47.50−44.50 (CH_2), 41.90−40.05 (CH_2), 37.41 (CH_2), 37.08 (CH_2), 28.85−28.10 (CH), 27.03 (CH), 26.98 (CH), 26.73 (CH), 22.42 (CH_3), 21.72−19.10 (CH_3), 20.49 (CH_3), 18.10 (CH_3), 18.00 (CH_3).

Kinetic Studies of the Oxidative Degradation of Polypropylene with Nitric Acid. In a typical experiment, 100 g of isotactic polypropylene (M_n = 95 000; M_w/M_n = 3.22; T_m = 168.5 °C) and 400 mL of concentrated nitric acid (42%) were added into a 1 L three-neck flask equipped with a condenser. The mixture was heated to 100 °C while stirring; a small amount of aliquot was taken out every 2 h, washed with water and acetone, and analyzed by GPC. The $1/M_n$ of the product is plotted against reaction time (Figure 7). In addition, two similar runs with two different concentrations of nitric acid (55% and 70%) were carried out for the kinetic study.

Diester-Capped Isotactic Polypropylene. To a 250 mL flask equipped with a Dean & Stark head and a condenser were added dicarboxyl-capped isotactic polypropylene (5 g, 4.6 mmol, M_n = 1375 g/mol, M_w/M_n = 2.46), 1-propanol (1.1 g, 18.4 mmol), toluene (40 mL), and concentrated sulfuric acid (1 mL). The mixture was heated with an oil bath while stirring and maintains refluxing for 5 h, whereby the water was gradually collected in the Dean & Stark receiver. Next, the solution was cooled and quenched with methanol (50 mL). The product was collected by filtration, washed with methanol and acetone, and dried in a vacuum oven (80 °C). Yield: 5.1 g (94%). IR (film): 1736 cm^{-1} (ester). ^{1}H NMR (in $C_2D_2Cl_4$, 120 °C): 4.04 ppm (t, J = 6.3 Hz). ^{13}C NMR (in $C_2D_2Cl_4$, 120 °C): 176.50 ppm ($-\mathrm{O}C\mathrm{(O)}-$); 65.79 ppm ($-\mathrm{O}C\mathrm{H_2CH_2CH_3}$), 22.61 ppm ($\mathrm{OCH_2}C\mathrm{H_2}$-$\mathrm{CH_3}$), 10.47 ppm ($\mathrm{OCH_2CH_2}C\mathrm{H_3}$).

Divinyl-Capped Isotactic Polypropylene. To a 250 mL flask equipped with a Dean & Stark head and a condenser were added dicarboxyl-capped isotactic polypropylene (5.00 g, M_n = 1375 g/mol, M_w/M_n = 2.46), allyl alcohol (5 mL, excess), toluene (100 mL), and tosic acid (0.50 g). The mixture was heated at 140 °C and stirred for 60 h. After cooling, the solution was quenched with methanol. The product was collected by filtration, washed with methanol and acetone, and dried under vacuum. Yield: 4.9 g (91%). IR (film): 1736 cm^{-1} (ester). ^{1}H NMR (in $C_2D_2Cl_4$, 120 °C): 4.58 ppm (d, $-\mathrm{C}H_2-\mathrm{CH{=}CH_2}$), 5.24 ppm ($-\mathrm{CH_2-CH{=}C}H_2$), and 5.90 ppm ($-\mathrm{CH_2-C}H\mathrm{{=}CH_2}$). ^{13}C NMR (in $C_2D_2Cl_4$, 120 °C): 176.18 ppm ($-\mathrm{O}C\mathrm{(O)}-$); 133.00 ppm ($-\mathrm{OCH_2}C\mathrm{H{=}CH_2}$), 117.71 ppm ($-\mathrm{OCH_2CH{=}}C\mathrm{H_2}$), 64.73 ppm ($-\mathrm{O}C\mathrm{H_2CH{=}CH_2}$).

Dihydroxyl-Capped Isotactic Polypropylene. To a 250 mL round-bottom flask equipped with a reflux condenser and a Dean & Stark head were added 100 mL of toluene, 5 g of dicarboxyl-capped isotactic polypropylene (M_n = 1375 g/mol, M_w/M_n = 2.46), 5 mL of ethylene glycol, and 0.5 g of tosic acid. The mixture was heated under reflux for 22 h. After cooling, the mixture was quenched with methanol. The product was collected by filtration, washed with methanol and acetone, and dried under vacuum. Yield: 4.95 g (90%). IR (film): 1736 cm^{-1} (ester). ^{1}H NMR (in $C_2D_2Cl_4$, 120 °C): 4.23 ppm ($\mathrm{HO-C}H_2-$ $\mathrm{CH_2-C(O)O}-$), 3.71 ppm (t, $\mathrm{HO-CH_2-C}H_2\mathrm{-C(O)O}-$).

Diacyl Chloride-Capped Isotactic Polypropylene. Fit a 250 mL three-necked flask with a dropping funnel and a reflux condenser connected to an oil bubbler. Placed dicarboxyl-capped isotactic polypropylene (5 g, M_n = 1375 g/mol, M_w/M_n = 2.46) in 100 mL of toluene. The mixture was stirred while heated to 130 °C to dissolve the polymer. Next, the solution was cooled to 100 °C, and thionyl chloride was added dropwise. After the completion of the addition, the solution was stirred at 100 °C for 12 h. After removing the volatiles in vacuo, the title product was obtained as an off-white powder. Yield: 4.90 (96%). IR (film): 1797 cm^{-1} (ester).

Titrimetric Method for Determining the Number of Carboxylic Acid (COOH) Groups per Polymer Chain. *Solutions Preparation*. (1) Prepare a 0.1 M solution of KOH in IPA, which was titrated using a 0.1 N standard HCl solution (Aldrich) to give an actual concentration of 0.103 M KOH in IPA. (2) Prepare a solution of 100 mg of thymol blue in 100 mL of ethanol.

Titration. Titration is performed by dissolving a weighted quantity (about 2 g) of dry polymer in 75 mL of xylene on a hot plate. After the polymer has been dissolved, the temperature is brought to about 100 °C and held constant during the titration. After the addition of four drops of the indicator solution, the titration is performed by the addition of the KOH/2-propanol solution (0.103 M) to the visual end point. There is a small temperature fluctuation (±3 °C), but no polymer precipitation was observed although the solution becomes a little bit hazy during the process of titration. The indicator gives a yellow color to the solution before the end point is reached and shows a blue-purple coloration at the end point. The blue-purple coloration must be visual for a short period of time (over 10 s) and should not disappear immediately. The average number of carboxylic acid (COOH) groups per polymer chain is calculated according to eq 1, where N is the number of COOH groups per polymer chain, V is the volume of KOH solution added to the end point, C is KOH concentration in IPA, M_n is the number-average of molecular weight of the polymer, and W is the weight of the titrated sample.

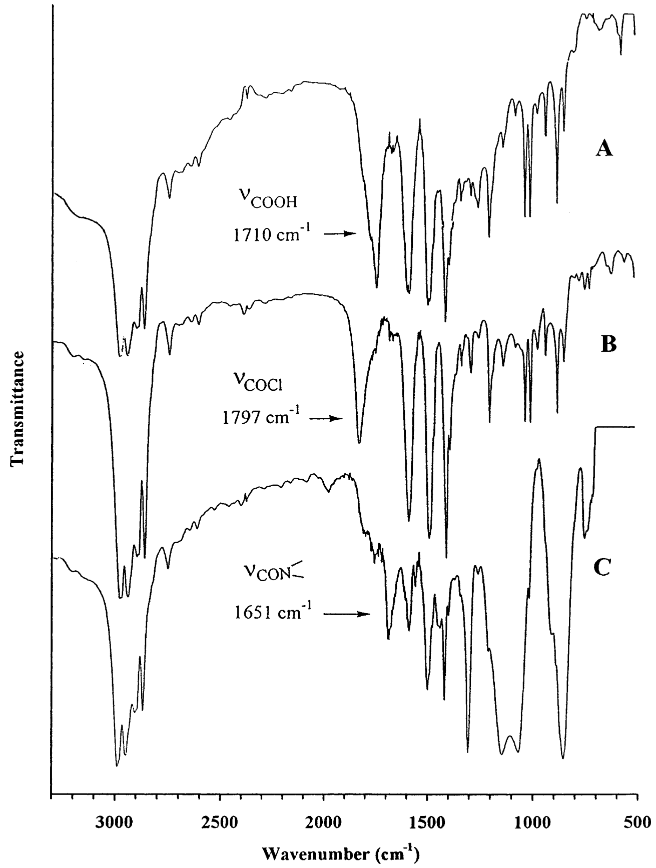


Figure 1. Infrared spectra (film): (A) carboxyl-terminated isotactic PP; (B) acyl chloride-terminated telechelic isotactic PP; (C) PDMS−PP−PDMS triblock copolymers with amide linkages.

$$N = \frac{V\,(\mathrm{mL}) \times C\,(\mathrm{mol/L}) \times M_n}{W\,(\mathrm{g}) \times 100} \qquad (1)$$

Results and Discussion

A. Process and Product Characterization. Isotactic polypropylene ($M_n = 95\,000$, $M_w/M_n = 3.22$; $T_m = 168.5$ °C) in spherical powder form was stirred as a suspension at 80−130 °C in the concentrated nitric acid. At periodic intervals, a small aliquot of the reaction mixture was removed, filtrated, washed with water and acetone, and dried under vacuum. The infrared spectra of the obtained polymer samples revealed the appearance of two new peaks at 1710 and 1558 cm^{-1}, characteristics of carboxyl and nitro group absorption, respectively (Figure 1A). The intensity of the absorptions was found to rise with the reaction time. Assuming the extinction coefficient ratio of NO_2/COOH in the degraded products is same as the extinction coefficient ratio of COOH/NO_2 (=1.2) obtained from 12-nitrododecanoic acid, the molar ratio of NO_2/COOH of the products can be readily calculated and is found to be always larger than unity (vide infra). GPC analysis of the samples obtained shows a gradual decease of the polymer molecular weight with the increase of the reaction time, indicating the occurrence of C−C bond chain scission along the polymer backbone as required to form the carboxyl (COOH) group (Table 1). Remarkably, the product obtained is almost monomodal and exhibits a narrower or comparable molecular weight distribution to the original polymer, although occasionally a small amount of low molecular weight tail was observed. This observation is in sharp contrast to the conventional polymer surface treatment, which is usually accompanied with multimodal molecular weight distribution.[15] The GPC curves (Figure 2) reveal that the product peak shifts downward cleanly with the reaction time, and the starting material peak is undetectable after even 2 h reaction. These results suggest that the reaction of the polymer with nitric acid proceeds quite uniformly, not only on the polymer surface.

Table 1. GPC, DSC, and Acid Titration Results of the Crystalline Product from the Reaction of Isotactic Polypropylene with Nitric Acid (70%)

entry	temp (°C)	reaction time (h)	M_n[a] (GPC)	M_w/M_n[a] (GPC)	T_m (°C) (DSC)	no. of COOH per chain[b]
1[c]		0	95000	3.22	169	0
2	130	1	18004	1.89	151	1.95
3	130	3	5786	1.92	139	2.01
4	130	8	2941	1.91	139	2.15
5	130	16	1652	2.33	139	1.90
6	130	29	1375	2.46	134	2.10
7	100	2	20182	2.35	162	1.92
8	100	4	12994	2.08	156	1.98
9	100	8	4545	3.07	141	2.04
10	100	24	2161	3.41	140	2.10
11	80	2	17715	3.25	165	2.13
12	80	8	14905	2.65	161	2.06
13	80	24	6025	3.05	151	2.08

[a] By GPC analysis in 1,2,4-trichlorobenzene vs polystyrene standards. [b] The average number of carboxylic acid (COOH) groups per polymer chain by base titration. [c] Starting isotactic polypropylene.

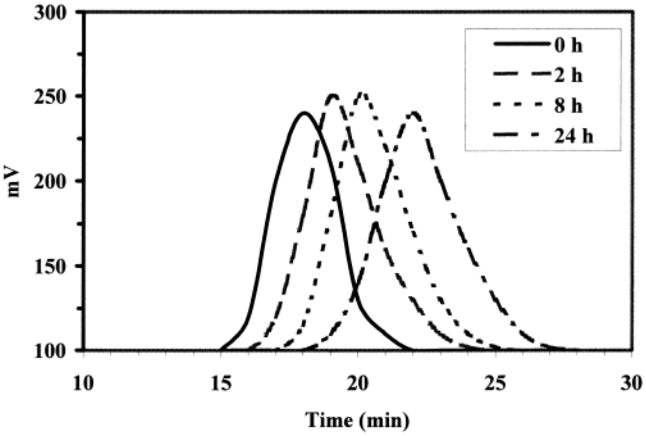


Figure 2. GPC curves of the virgin polypropylene and products as a function of reaction time (h) with nitric acid (70%) at 80 °C.

Interestingly, the average number of acid group per polymer chain, determined by the acid titration of the polypropylene degradation products using KOH, is approximately two, regardless of the molecular weight of the product (see Table 1 and Experimental Section). These results imply that the formation of the acidic functionality is mostly likely a result of the polymer C−C chain scission and subsequent oxidation. ^{1}H NMR analysis (in $C_2D_2Cl_4$, at 120 °C) of a low molecular weight product ($M_n = 1375$, $M_w/M_n = 2.46$) revealed the fine features of the polymer structure. In addition to the typical resonances derived from polypropylene in the ^{1}H NMR, a broad peak around 7−8 ppm was observed, which can be assigned to acidic protons; a singlet at 2.14 ppm is due to the methyl group connected to the β-carbon, and a multiplet at 2.54 ppm is due to the adjacent CH_2. The fact that the methyl group bonded to the β-carbon is a singlet imparts that the β-carbon is a quarternary carbon, which most likely has a nitro

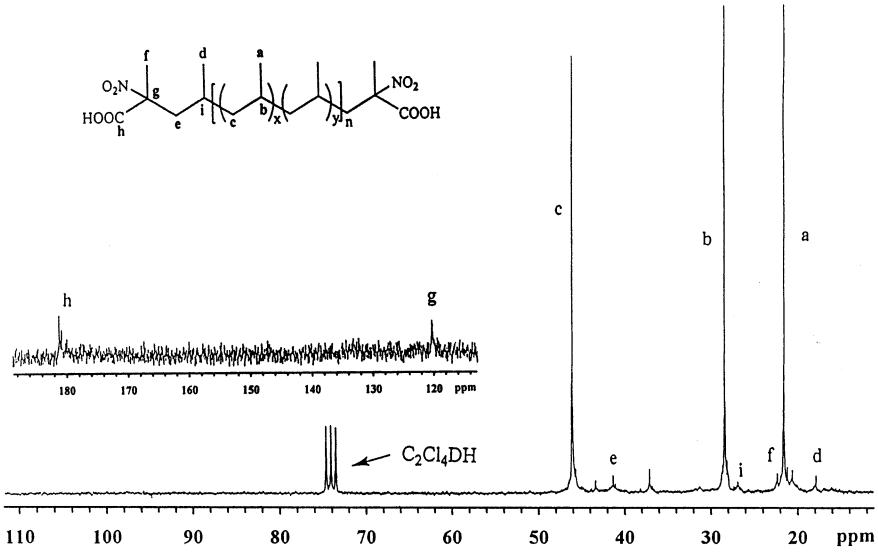
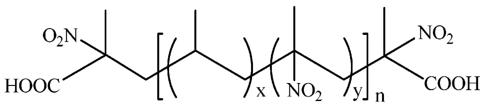


Figure 3. ^{13}C NMR spectrum of carboxyl-terminated isotactic polypropylene ($M_n = 1375$, $M_w/M_n = 2.46$, in $C_2Cl_4D_2$ at 120 °C).

substitute. This assignment was confirmed by ^{13}C decoupled NMR analysis, which shows that the β-carbon observed at 120.5 ppm is indeed a quarternary carbon (Figure 3). Likewise, all the other ^{13}C resonances were readily assigned, and the identity of each carbon was further verified by the ^{13}C attached proton test (APT).[17]

These analytical results indicate that the degradation products have a general structure **III**, where the two acid groups reside at the end of a polymer chain, and two nitro groups distribute at the end of a polymer chains and the rest of nitro group(s) along the polymer chain since the molar ratio of $NO_2/COOH$ in the products is larger than one. No significant oxidation of $-CH_3$ was observed possibly due to the lower stability of $-CH_2^{\bullet}$ (kinetic factor) and the high bond strength of $-CH_2-H$ (thermodynamic factor) than that of the corresponding $-CR_2-H$ group (R is alkyl group).[18] Importantly, the structure of the products has further been confirmed by their chemical reactivities (vide infra).



(**III**)

In addition, the product retains the same degree of isotacticity as the virgin polypropylene, as revealed by ^{13}C NMR pentand analysis. DSC measurement shows the product has a very sharp melting point (Figure 4), indicative of a high crystalline polymer. As illustrated in Table 1, the melting point is sensitive to the molecular weight of the product, especially, in the middle range, possibly attribute to the change of the end group's concentration in the product, which leads to melting point depression.[19] The higher the molecular weight of the product, the closer is the melting point to that of the original polypropylene, but when the molecular weight of the products gets lower, the melting point difference between them becomes trivial. No significant effect of the nitro groups on the T_m is observed probably because of the presence of only a few such groups on the polymer chain.

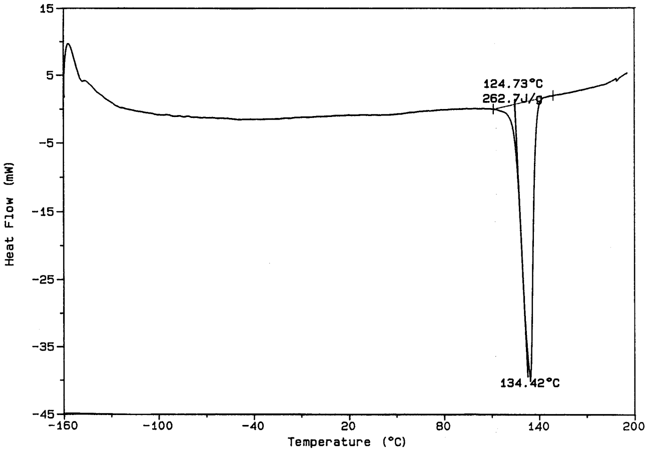


Figure 4. DSC analysis of carboxyl-terminated isotactic polypropylene ($M_n = 1375$, $M_w/M_n = 2.46$).

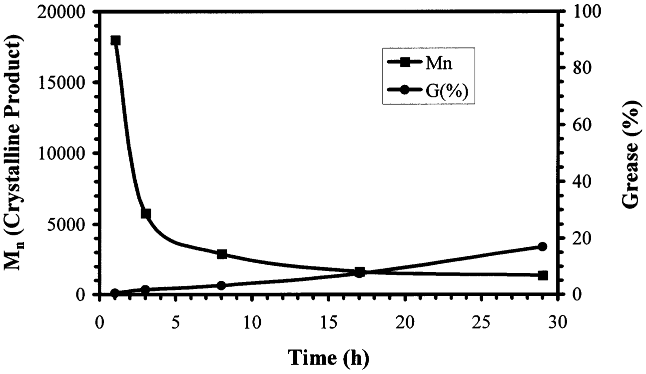


Figure 5. Formation of the grease as a function of time and molecular weight of the crystalline product.

In addition, a small portion of low molecular weight grease was obtained while washed with acetone. The ^{13}C NMR spectrum of the grease shows a similar microstructure as the crystalline product, but a much lower isotacticity. In general, the yield of the grease is very low, consisting of only about a few percent of the overall yield. However, the yield of the grease increases rapidly as the molecular weight of the product drops below 2000 g/mol (Figure 5). This is probably because with the decrease of the molecular weight of the product, the concentration of the polar group portion in the

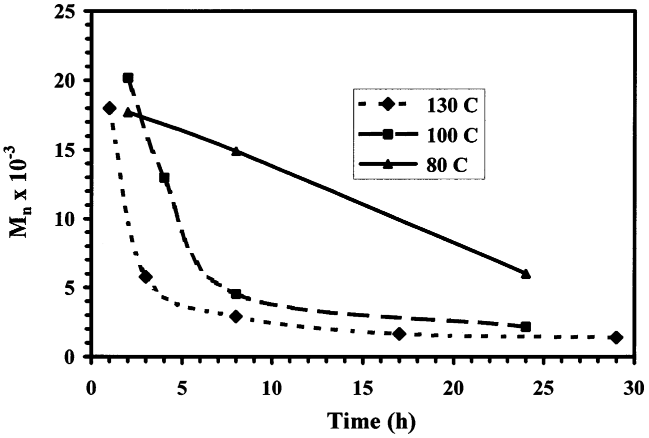
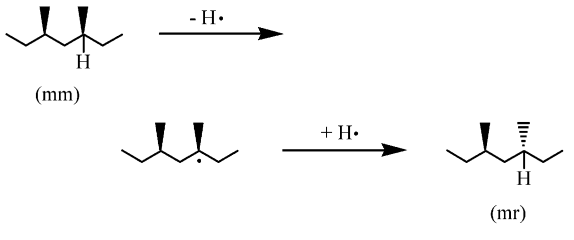


Figure 6. Effect of the reaction temperature on the molecular weight of the high molecular weight fraction (70% HNO_3).

product increases; consequently, the polymer becomes more hydrophilic and more soluble in nitric acid. Perhaps, the molecular weight of 2000 is a critical or balance point at which the hydrophilicity of the polymer begins playing a role. As matter of fact, the crystalline product with molecular weight below 1000 (g/mol) is inaccessible from this process since these polymer products become very soluble in aqueous media where they undergo the aforementioned epimerization to yield atactic grease.

The epimerization most likely proceeds through a free radical mechanism. The free radicals generated in situ preferentially attack the tertiary hydrogen atoms, not only because the tertiary carbon−hydrogen bond is more vulnerable bond than the secondary hydrogen and primary carbon−hydrogen bonds but also that is where the inversion of configuration can take place (eq 2). Of course, the attack by H_3O^+ or other cationic species on the tertiary carbon−hydrogen bond is also plausible.[20] As a matter of fact, Lewis acids are capable of inducing the same epimerization. For example, the isotacticity of the polypropylene changes from original 98% to 40.2% based on *mmmm* pendant group analysis when the polypropylene solution in dichlorobenzene is stirred in the presence of a small amount of $AlCl_3$ at 170 °C for 7 h. A similar process using metallic palladium as catalysts was reported but is roughly 2 orders of magnitude slower.[21]



(2)

B. Kinetics of the Oxidative Degradation. The rate of the polymer chain session was found to be related to the reaction temperature and the concentration of nitric acid. In general, the higher the reaction temperature, the faster the reaction is. As shown in Figure 6, the polypropylene degradation proceeds very rapidly initially at 100 or 130 °C and then levels off after a few hours. The sluggishness of the reaction toward the later stage is probably related to a lower nitric acid concentration since free brownish-red NO_2 is constantly formed as the decomposition product of nitric acid and gradually escapes from the reaction system. In addition, the evaporation of HNO_3 may be another factor. Whereas the rate of the reaction at 80 °C is much slower but more consistent, the loss or decomposition of HNO_3 is insignificant. Likewise, the higher the nitric acid concentration, the faster the degradation and functionalization under identical conditions.

Table 2. Dependence of the Molecular Weight (M_n × 10^{-3})[a] of the Product on the Concentration of Nitric Acid for the Oxidative Degradation at 100 °C

time (h)	0	2	4	6	8	9
M_n (42% HNO_3)	95.1	76.9	52.6			34.3
M_n (55% HNO_3)	95.1	40.1	19.6	10.2	8.3	
M_n (70% HNO_3)	95.1	25.0	12.9	4.8	4.5	

[a] By GPC in 1,2,4-trichlorobenzene vs polystyrene standards.

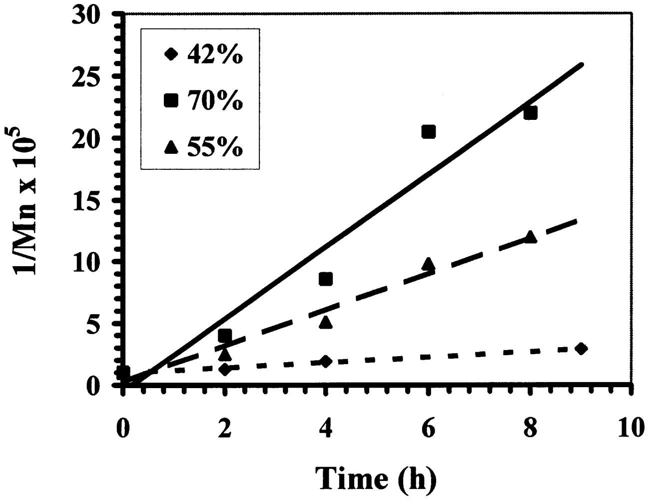


Figure 7. Kinetic plots for polypropylene degradation at different nitric acid concentration. The lines represent least-squares fits to the data points.

Since each polymer chain generally has two carboxyl end groups, the concentration of the carboxyl groups in a polymer is proportional to $1/M_n$, where M_n is the average number molecular weight of the product. Because the reactive sites of polypropylene are always in large excess and its change of the concentration during the course of the reaction is trivial, the rate dependence in polypropylene, therefore, can be set to zero order. The kinetics of the degradation can then be expressed by eq 3. Assuming that the loss of nitric acid is insignificant in the first few hours of reaction, the concentration of nitric acid would remain constant since it is used in much large of excess. Thus, the kinetics obeys a pseudo-zero-order rate law (eq 4).

$$\text{rate} = d[1/M_n]/dt = k_i[\text{polypropylene}]^0[HNO_3]^m = k[HNO_3]^m \quad (3)$$

$$d[1/M_n]/dt = k[HNO_3]^m = K_{obs} \quad (4)$$

Table 2 summarizes the molecular weight of products obtained within 10 h reaction at 100 °C with nitric acid at three different concentrations (42%, 55%, and 70%).[22] As expected, the plot of $1/M_n$ vs time yields a straight line (Figure 7) according to eq 4. A van't Hoff treatment (eq 5) gives an order of 4.2 in nitric acid (Figure 8), in which all the data could be convincingly fit ($R^2 = 0.991-0.997$) by least squares, and the unit of nitric acid concentration is in molar concentration.[23] Thus, the

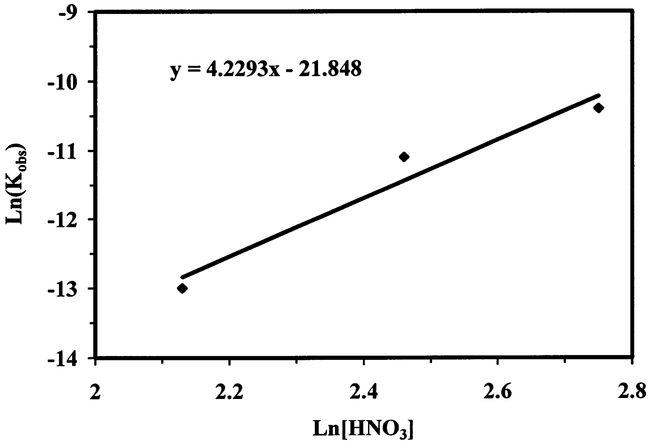


Figure 8. Dependence of the observed rate constants for the polypropylene degradation on the nitric acid concentration. The line represents a least-squares fit to the data points.

Table 3. Carboxyl Functional Polypropylenes via the Vapor-Phase Approach[a]

entry	temp (°C)	time (h)	M_n[b]	M_w/M_n[b]	T_m (°C)[c]
1	130	2	11632	2.62	161
2	130	5	10529	2.07	158
3	130	7	8203	2.51	153
4	100	24	7342	3.25	146

[a] The vapor was generated by heating the nitric acid (70%) at 130 °C. [b] By GPC in 1,2,4-trichlorobenzene vs polystyrene standards. [c] By DSC analysis.

reaction kinetics obeys the following rate law (eq 6) with $k = 2 \times 10^{-6}\ M^{-3.2}\ s^{-1}$.

$$\ln K_{obs} = \ln k + m \ln[HNO_3] \qquad (5)$$

$$\text{rate} = k[\text{polypropylene}]^0[HNO_3]^{4.2} \qquad (6)$$

Apparently, the degradation reaction is rather complicated, possibly involving multiple attacks of nitric acid onto the polymer surface. The inhomogeneous nature of the reaction system is probably a contributing factor for the complexity of the kinetic result, and it is highly possible that the vapor above the nitric acid solution is also involved in the process of polymer degradation and functionlization. This is probably why the product obtained in this cases is monomodal, rather than mutilmodal as expected from a pure polymer–surface interaction.[15] Presumably, in addition to the liquid phase reaction, the vapor also effectively permeates into the polymer particles and incites interactions interiorly. To confirm this, a flask containing a small amount of polypropylene was heated at 130 °C and exposed to the vapor from the nitric acid (70%, at 130 °C). The reaction process was monitored by taking out a small amount of sample periodically and analyzing it. As expected, the polymer after the vapor treatment yields products having a virtually identical structure as with the nitric acid. The molecular weight of the products decreases with the increase of the interaction time. The molecular weights, polydispersity, and melting temperature (T_m) of the products under various reaction conditions are summarized in Table 3. Therefore, it can be concluded that both liquid/solid and gas/solid interface reactions are simultaneously present and effective in the current system.

Table 4. NO_2/COOH Ratio and Molecular Weight of the Products from the Degradation of Isotactic Polypropylene (M_n = 95 000; M_w/M_n = 3.02) with HNO_3

entry	temp (°C)	HNO_3 (%)	reaction time (h)	NO_2/COOH (molar ratio)[a]	M_n[b]	M_w/M_n[b]
1	100	70	4	4.8	12994	2.08
2	100	70	6	5.4	4870	3.43
3	100	70	8	4.9	4545	3.07
4	100	70	24	1.5	2161	3.41
5	100	42	9	11	34315	1.79
6	100	42	20	3.6	4934	2.47
7	100	42	28	2.6	3316	2.78
8	130	70	2	3.2	12350	1.91
9	130	70	6	1.2	5367	2.55
10	130	70	8	1.2	2941	1.91
11	130	70	24	0.9	1835	1.83

[a] By FTIR analysis. [b] By GPC in 1,2,4-trichlorobenzene vs polystyrene standards.

Table 5. Evaluation of the Reusability Nitric Acid in the Oxidative Degradation of Polypropylene[a]

entry	nitric acid type	nitric acid vol (mL)	polypropylene (g)	yield (g)	M_n (g/mol)
1	fresh[b]	200	50	49 (98%)	7000
2	FRNA	160	40	38 (95%)	6000
3	SRNA	110	27.5	27 (98%)	6500

[a] Reaction time = 4 h 20 min, temperature = 115–120 °C, polypropylene/nitric acid ratio = 50 g/200 mL. [b] Concentration = 70%. [c] Estimated from IR analysis.

C. Factors Effecting Nitro Group Incorporation in the Product. The presence of the nitro group in the carboxyl-capped telechelic polypropylene is sometimes undesired, for it could affect the stability of the polymer and cause coloration. Therefore, it would be desirable if the introduction of the nitro groups can be either reduced or totally suppressed during the process of the reaction. A number of experiments were then carried out to elucidate the factors effecting the nitro group incorporation. The molar ratio of COOH/NO_2 in oxidative degaradated product was obtained on the basis of FT-IR analysis, which was used as criteria to assess the extent of nitro group incorporation. The extinction coefficient ratio of COOH/NO_2 (=1.2) was calculated from a model compound, 12-nitrododecanoic acid. The infrared absorptions of COOH at 1710 cm^{-1} and N_2O at 1558 cm^{-1} were normalized to the CH_2 band of polypropylene at 1457 cm^{-1}, and the molar ratio of COOH/NO_2 was derived from the corresponding absorption with the correction from their extinction coefficient difference. As illustrated in Table 4, the amount of nitro group incorporation is related to the reaction temperature as well as the concentration of nitric acid. Lower NO_2/COOH ratio products are favored when the reaction is carried out at a higher temperature with a higher nitric acid concentration possibly due to a higher oxidation power. One special feature worthy of note is that the nitro groups are predominantly introduced at the beginning of the reaction.

D. Evaluation of the Reusability of Nitric Acid. One of the most important issues regarding the economics of this process is whether the nitric acid can be recovered and reused. If possible, it will dramatically reduce not only the cost of raw materials but also the environmental pollution. Consequently, the reusability of nitric acid in the oxidative degradation of polypropylene was evaluated. For the simplicity of description, we name the recovered nitric acid from the first degradation reaction as first recovered nitric acid (FRNA) and the nitric acid recovered from second degradation reaction as second recovered nitric acid (SRNA). All of the

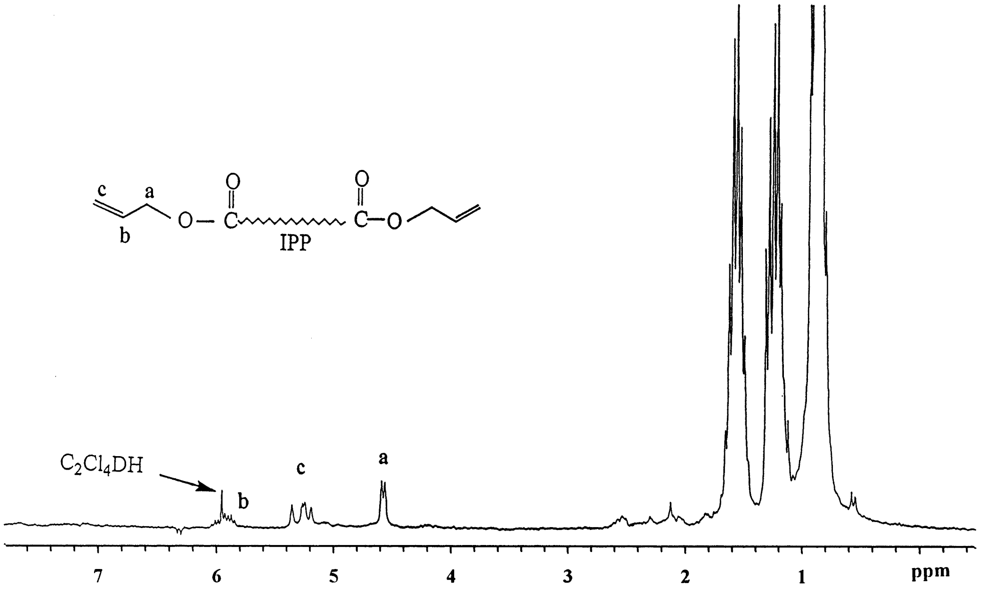
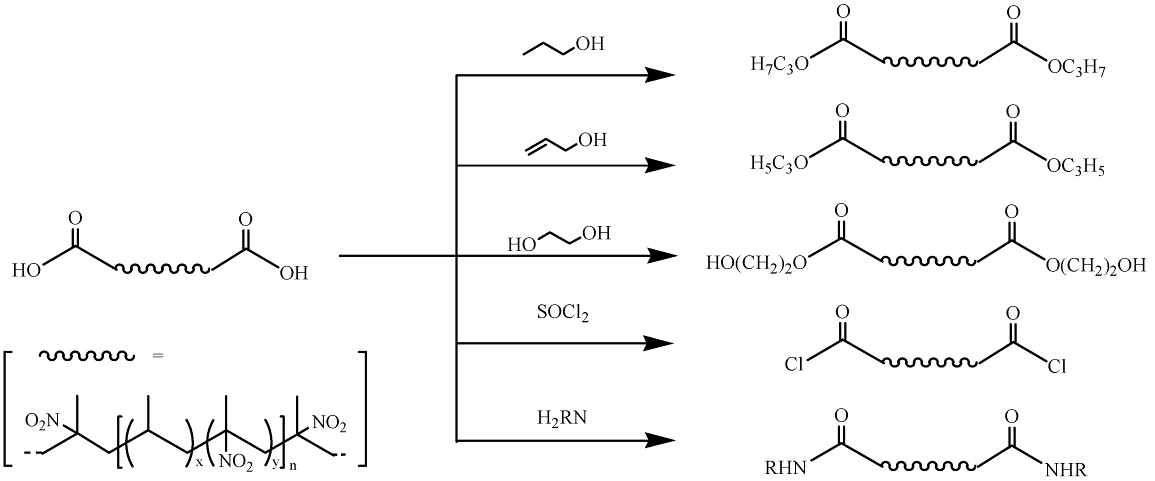


Figure 9. ^{1}H NMR spectrum of divinyl-capped isotactic polypropylene.

Scheme 1. Derivation of Carboxyl-Capped Telechelic Isotactice Polypropylene (Nitro Groups Are Omitted for Simplification)



(7)
(8)
(9)
(10)
(11)

oxidative degradation reaction of polypropylene (M_n = 95 000; M_w/M_n = 3.12) was conducted under identical reaction conditions. After the reaction, the nitric acid was recovered by filtration; the product was washed with water and acetone and dried under vacuum. The recovered nitric acid was then used in the next reaction. As shown in Table 5, the recovered nitric acid not only can be reused, but it also acts as effectively as the original nitric acid. The reduction of nitric acid volume is probably owing to (1) vapor evaporation and (2) product soaking and carrying. As a result, the concentration of the nitric acid after recovery is lower.

E. Derivation of Carboxyl-Capped Telechelic Isotactice Polypropylene via FunctionalityTransformation. In the presence of a catalytic amount of concentrated sulfuric acid, the dicarboxyl-capped polypropylene (M_n = 1375, M_w/M_n = 2.46, T_m = 134 °C) was cleanly converted into the diester-capped isotactic polypropylene (95% yield) by reacting with 1-propanol in toluene at 130 °C (eq 7, Scheme 1). The product was precipitated with methanol, filtrated, and thoroughly washed with methanol and acetone to remove the unreacted 1-propanol. The infrared spectrum of the product showed that the carbonyl absorption moved from 1709 cm^{-1} of the original polymer to 1736 cm^{-1}, pointing out the completion of the reaction and the formation of the ester linkage. ^{1}H NMR analysis revealed the presence of a triplet (J = 6.3 Hz) at 4.04 ppm, assignable to the italic protons of the $-\mathrm{OC}H_2\mathrm{CH_2CH_3}$ group; the other two proton peaks are overlapped with the polypropylene resonances. The formation of diester-capped polypropylene was further confirmed by ^{13}C NMR analysis. Thus, the chemical shift of the carbonyl carbon of the ester shifts to 176.5 ppm from 180.86 ppm of the original carboxyl carbon. The corresponding propyl resonances are found at 65.79 ppm ($-\mathrm{O}C\mathrm{H_2CH_2CH_3}$), 22.61 ppm ($\mathrm{OCH_2}C\mathrm{H_2CH_3}$), and 10.47 ppm ($\mathrm{OCH_2CH_2}C\mathrm{H_3}$).

Likewise, a divinyl-capped isotactic polypropylene can also be synthesized via an esterification reaction (eq 8). ^{1}H NMR of the product exhibits the expected ally group resonances at 4.58, 5.24, and 5.90 ppm, in addition to the typical polypropylene backbone resonance (Figure 9). In its ^{13}C NMR spectrum ($C_2D_2Cl_4$ at 120 °C), the ester carbonyl carbon is observed at 176.18 ppm. Features owing to the ally end group are also visible

(133.00 ppm, $-\mathrm{OCH_2}\mathit{C}\mathrm{H{=}CH_2}$; 117.71 ppm, $-\mathrm{OCH_2CH{=}}\mathit{C}\mathrm{H_2}$; 64.73 ppm, $-\mathrm{O}\mathit{C}\mathrm{H_2CH{=}CH_2}$). The presence of the ester linkage is further verified by a strong carbonyl absorption at 1736 $\mathrm{cm^{-1}}$. The interaction of the dicarboxyl-capped isotactic polypropylene with excess of ethylene glycol in the presence of a small amount of tosic acid (*p*-toluenesulfonic acid) resulted in the formation of hydroxyl-capped isotactic polypropylene (eq 9). The ^{1}H NMR spectrum (in $C_2D_2C_4$, at 120 °C) exhibits the expected hydroxyl proton peak around 2.18 ppm and the methylene protons at 4.23 and 3.71 ppm, in addition to the typical polypropylene resonances. The resonance at 3.71 ppm is due to the CH_2 bonded to the ester group, which splits into a triplet by coupling with the adjacent CH_2 group.

The reaction of dicarboxyl-capped polypropylene with thionyl chloride gives rise to the diacyl chloride group-capped polypropylene quantitatively at 105 °C (eq 10). As expected, the carbonyl absorption in the IR spectrum shifted from 1709 $\mathrm{cm^{-1}}$ of the original polymer to 1797 $\mathrm{cm^{-1}}$ (Figure 1B), indicating the formation of the diacyl chloride group-capped polypropylene. The condensation of the dicarboxyl-capped polypropylene with an amine-capped poly(dimethylsiloxane) macromonomer ($M_n = 1184$ g/mol, DP = 16) yields a PDMS−PP−PDMS (ABA) triblock copolymer (eq 11). The amide linkage of the block copolymer is observed at 1651 $\mathrm{cm^{-1}}$ by infrared spectroscopy, along with the typical siloxane absorptions (Figure 1C). The details regarding this block copolymer will be reported elsewhere.[24]

Conclusions

We have demonstrated that dicarboxyl telechelic isotactic polypropylene can be readily produced by the oxidative degradation of commercially available crystalline polypropylene with nitric acid. The obtained crystalline polymer has a narrow molecular weight distribution ($M_w/M_n = 2-4$) and still maintains the same degree of isotacticity as the starting polypropylene. The molecular weight of the product can be well controlled by varying the reaction temperature, reaction time, or the concentration of the nitric acid. It was found that the higher the reaction temperature and the higher the concentration of nitric acid, the faster the degradation is. Kinetic studies have shown that the reaction is 4.2 orders in nitric acid, indicative of the complex nature of the reaction mechanism. Both liquid/solid and gas/solid interface interactions simultaneously exist in the present system. The carboxyl-capped polypropylene with low NO_2/COOH ratio can be produced at a higher reaction temperature with a higher concentration of nitric acid. Importantly, the nitric acid utilized in the reaction can be recycled and reused in the subsequent reaction. The dicarboxyl telechelic polypropylene has been readily transformed into other functional group-terminated polypropylene, such as acyl chloride, allyl, ester, amide, and hydroxyl. The availability of these difunctional telechelic polypropylenes will not only greatly speed up their applications in polymer synthesis, which will ultimately lead to the development of new and useful materials, but also promote the exploitation of other related polymer systems. The combination of the difunctional telechelic polypropylene and polysiloxane polymer has produced a lot of novel and interesting block copolymers with various architectures, which have begun to show a number of very promising applications in areas such as nanoimprinting, release coating, air filtration, medical garments, and so on.[24,25]

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