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End Capping of Polynorbornene Produced by Titanacyclobutanes[†]

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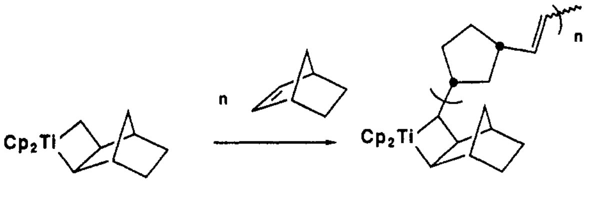
ABSTRACT: By use of 1 as a ring-opening olefin metathesis catalyst, norbornene was polymerized and the resulting living polymer allowed to react with benzophenone to give diphenylethylene-capped polymer 3. The percentage of polymer chains end capped was 70–100% as determined independently by ^{1}H NMR and UV absorbance. Additionally, there was minimal change in the molecular weights and polydispersities of the polymers during the end-capping reaction.

The ring-opening olefin metathesis polymerization (ROMP) of cyclic olefins has been extensively studied,[1] and several ring-opened polymers are currently produced on an industrial scale.[2] A recent study[3] demonstrated that titanacyclobutanes polymerize norbornene to give the first well-defined living polymerization system reported for a ROMP catalyst (eq 1). This versatile system has been extended to the synthesis of block copolymers[4] and several novel conducting polymers.[4,5]



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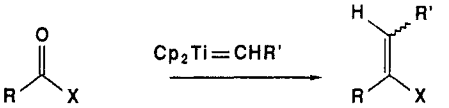
(1)

Previous work[6] has shown that titanium carbenes, generated from titanacyclobutanes and other sources, react with aldehydes, ketones, esters, amides, and imides to give Wittig-type products in excellent yields (eq 2). The novel combination of the organic and polymer chemistry of titanium carbenes would make possible the synthesis of polymers with a variety of end groups. Among the potential uses are efficient removal of the catalyst, modification of the bulk properties of the original ROMP-derived polyalkenamer, and introduction of moieties for further chemical transformations and/or polymerization.



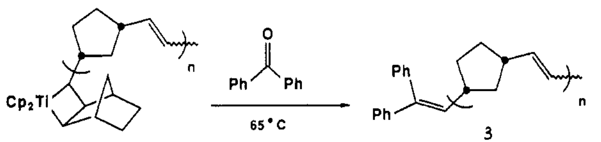
(2)

X= H, R'', OR'', NR''R''', N(R'')C(O)R'''

In our initial efforts in this area we report herein the end capping of polynorbornene with benzophenone, utilizing the Wittig-type chemistry of titanium carbenes. The efficiency of the end-capping reaction as well as the effect on polymer molecular weights and polydispersities is examined.

Results and Discussion

By use of 1 as a catalyst, norbornene was polymerized, and the resulting living polymer was allowed to react with benzophenone to give diphenylethylene-capped polymer 3 (eq 3). This capping group was chosen for its favorable ^{1}H NMR and UV properties to facilitate end group analysis. On the basis of model studies, benzophenone is also a good test of a sterically demanding ketone.



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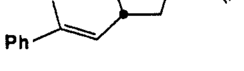
(3)

To establish the efficiency of the reaction, both ^{1}H NMR and UV analyses were used to determine the quantity of diphenylethylene end cap present in the isolated samples of end-capped polymer. Comparison of these values with the expected theoretical values (based on the molecular weights of the polymers derived from GPC and assuming 100% active catalyst) gave the percentage of chains containing the end cap.

A typical ^{1}H NMR spectrum of the capped polymer (in CD_2Cl_2) is given in Figure 1. Both the aromatic protons (δ 7.10–7.40, m, 10 H) and the olefinic proton (δ 5.95, d, J = 11 Hz, 1 H) of the end cap ($Ph_2C{=}CH$) are observable. The olefinic protons of the polymer (δ 5.10–5.40, m) overlap the residual solvent signal of the NMR solvent and could not be used for integration purposes. However, the allylic protons of the polymer (δ 2.40, 2.78) are well-resolved and were integrated and compared to the integration of the aromatic protons of the end cap. In this manner the ratio of monomer units of polymer to endcap was determined (Table I).

During GPC analysis (see Experimental Section) of the polymers, the UV trace (λ = 254 nm) was also recorded. Because of the much higher extinction coefficient of the end group compared to the polymer, the absorbance due to the polymer was minimal and could be easily subtracted from the trace by comparison to the UV trace of uncapped polymer samples of identical concentrations. The capped monomer 2 was synthesized as previously described[3] and the UV trace of a standard solution (1.02×10^{-4} M in



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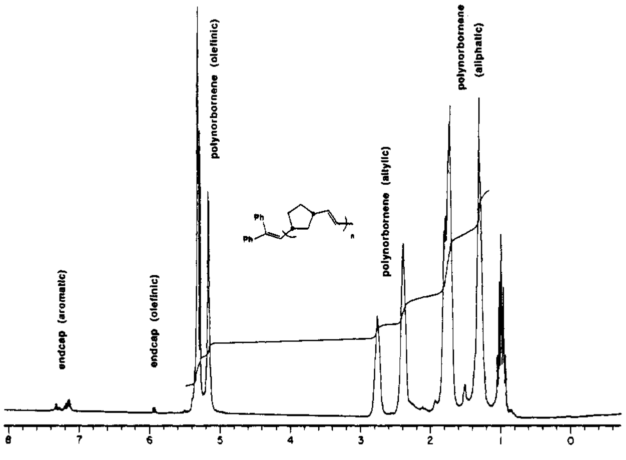

Figure 1. ^{1}H NMR 400-MHz spectrum in CD_2Cl_2 of diphenylethylene-capped polymer **3** (n = 47).

Table I
Percentage of Chains End Capped

	monomers/ end cap^a			mono-mers/	% end capped^d	
run	NMR^e	UV^f	M_n^{b}	chain^c	NMR^g	UV
1	51	65	8 500	45	88	69
2	47	63	9 000	48	102	76
3	79	83	12 400	66	84	80

[a] See text. [b] Determined by gel permeation chromatography (vs. polystyrene standards). [c] M_n/2 (MW of norbornene). [d] ((monomers/chain)/(monomers/end cap)) 100%. [e] (allylic protons of polymer/2)/(aromatic protons of end cap/10). [f] (wt of polymer in sample/MW of monomer)/(wt of end cap in sample/MW of end cap). [g] Values have an error of ±5% from ^{1}H NMR integration.

CH_2Cl_2) used to calibrate the response factor of the UV detector. Integration of the UV trace of the capped polymer after the above analysis was used to determine the quantity of end group in the polymer sample and therefore give the ratio of monomers to end cap (Table I).

Previous work has shown that GPC (using polystyrene standards) gives approximately twice the correct value of molecular weight for polynorbornene.[3,7] If the M_n values from GPC (divided by 2) are used as the correct values of average molecular weight of the polymer samples prepared, the average number of monomers per polymer chain can be calculated (Table I). Comparison of the number of monomers per end cap (determined by ^{1}H NMR and UV) to the average number of monomers per chain gives the percentage of chains that contain the end cap (Table I). Both sets of values are in good agreement (70–100%), indicating the end-capping reaction to be highly efficient.[8]

Another important aspect of the end-capping reaction is the potential degradation of the polymer under the conditions of the reaction.[9] Generation of titanium hydrides and/or radical species during end capping would lead to rapid cross-linking of the olefin-rich polymer. To examine this question, samples of uncapped and capped polynorbornene were prepared under identical conditions (see Experimental Section) and analyzed by GPC (Table II). The molecular weights and polydispersities remained relatively unchanged, indicative of minimal degradation of polynorbornene upon end capping.[10]

The successful combination of polymer and Wittig chemistry of titanium carbenes demonstrated herein will make it possible to synthesize polymers with a variety of end groups, and further research is in progress.

Experimental Section

General Procedures. All work involving air- and/or moisture-sensitive compounds was performed by using standard high-vacuum or Schlenk techniques under argon purified by passage through columns of BASF RS-11 (Chemalog) and Linde 4-Å molecular sieves and a Vacuum Atmospheres drybox under nitrogen. ^{1}H NMR spectra were recorded on a JEOL GX-400 (399.65 MHz). Analytical gas chromatographic analyses (VPC) were performed on a Shimadzu GC-Mini 2 flame ionization instrument modified for capillary use and equipped with a Hewlett-Packard Model 339A integrator (column: 0.24-mm × 15-m DBI). Thin-layer chromatography (TLC) was performed on precoated TLC plates (silica gel 60 F-254, EM Reagents). Flash chromatography was performed by the procedure of Still et al.[11] using silica gel 60 (230–400-mesh ATM, EM Reagents).

Table II
Molecular Weight Analysis of Capped and Uncapped Polynorbornene^a

run		M_n^{b}	M_w^{b}	n^{c}
1	uncapped	10 400	12 600	1.21
	capped	11 100	13 600	1.23
2	uncapped	9 000	12 400	1.38
	capped	9 100	13 100	1.44

[a] See Experimental Section for synthesis. [b] Determined by gel permeation chromatography (polystyrene standards). [c] Polydispersity.

Gel permeation chromatographic (GPC) analyses utilized Shodex KF-803 and KF-804 columns, a Spectroflow 757 absorbance detector (λ = 254 nm), and a Knauer differential refractometer. All GPC analyses were performed on 0.20% w/v solutions of polymer in CH_2Cl_2. An injection volume of 0.100 mL and a flow rate of 1.0 mL/min were used. Calibration was based on narrow dispersity polystyrene standards (Polysciences) ranging from MW = 3550 to 600 000. The molecular weight averages and distribution were calculated by standard procedures[12] from the refractive index trace and were not corrected for peak broadening. UV integration was performed by weighing photocopies of the traces recorded on an Omniscribe recorder (Houston Instruments) and averaging five copies per trace.

Materials. Metallacycle **1** and capped monomer **2** were prepared as previously described.[3] Norbornene was purchased from Aldrich, refluxed over sodium, and distilled prior to use. Benzophenone was purchased from MCB Reagents and used as received. Benzene was distilled from sodium benzophenone ketyl by vacuum transfer into a dry vessel equipped with a Teflon valve closure and stored under argon. Methanol was reagent grade and used without further purification. Octane was distilled from CaH_2 before use.

Polymerization of Norbornene. A standard solution of norbornene was prepared under argon as follows: To 8.10 g (86.1 mmol) of freeze–pump–thaw degassed norbornene was added by syringe 0.5 mL of octane and finally benzene to give a total volume of 50.0 mL (1.72 M norbornene).

In the original set of experiments only end-capped polynorbornene was synthesized. In later experiments, both uncapped and capped polymers were made by the following procedure.

In a Schlenk tube, **1** (20 mg, 0.07 mmol) was dissolved in 2.0 mL of the standard norbornene solution (3.5 mmol, 50 equiv of norbornene). The resulting mixture was transferred by syringe into two separate tubes (1.0 mL in each) equipped with Teflon valve closures. The solutions were stirred in the same oil bath at 65 °C and both polymerizations followed by capillary VPC. In each case the concentration of norbornene remained the same in each tube (VPC). At 95% completion the contents of one tube were allowed to cool to 23 °C. The resulting red solution was added to 50 mL of rapidly stirred MeOH, and the precipitated red amorphous polymer dried under vacuum (10^{-3} Torr) and stored under inert atmosphere. To the other tube was added by syringe a solution of 0.065 g (0.36 mmol, 10 equiv per Ti) of benzophenone in 1.0 mL of benzene and stirring continued at 65 °C. The initial dark-red solution became pale orange after 0.5 h, and capillary VPC indicated no further polymerization of norbornene. After cooling to 23 °C, the solution was flash chromatographed (benzene) and the polymer isolated by precipitation into MeOH and dried under vacuum (10^{-3} Torr) at 115 °C overnight. The resulting white amorphous solid (60–70% yield) was stored under inert atmosphere. The capped polymer samples were free of benzophenone and organotitanium species (TLC).

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(8) Initial studies with low molecular weight polynorbornene (M_n = 5000) indicates successful end capping with acetone-d_6 (102 ± 5%, ^{2}H NMR) and benzaldehyde (78 ± 5%, ^{1}H NMR). The latter end-capped polymer has different bulk properties compared to the uncapped polymer.

(9) It has been observed that the living polymer quickly decomposes after complete consumption of norbornene at 65 °C (see ref 3). Therefore, end capping was performed at 95% completion of the polymerization (see Experimental Section).

(10) This work was performed prior to optimization of reaction conditions which now give polydispersities as low as 1.08 (see ref 3). Current studies with acetone as an end-capping reagent routinely provide samples with polydispersities less than 1.10 (see ref 4).

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Polymerization of Polyurethane–Polyester Interpenetrating Polymer Network (IPN)

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ABSTRACT: Reaction mechanisms involved in synthesizing a polyurethane–polyester interpenetrating polymer network were studied by Fourier transform infrared spectroscopy. Results show that the reaction kinetics of urethane polymerization is not the same in bulk as in the solution state. Polyurethane reaction in the IPN resembles a solution polymerization before gelation and a bulk polymerization after gelation. Copolymerization in typical unsaturated polyester resins tends to follow the azeotropic condition. On the other hand, the polyester reaction in IPN deviates substantially from that in a pure polyester resin in the presence of a polyurethane network.

Introduction

Multiphase polymers have been used extensively in the polymer industry to provide products with superior chemical and physical properties.[1,2] Mechanically blended polymers and graft and block copolymers are used most often. Blended polymers often experience phase stability problems due to the lack of permanent chemical bonding between the two polymer phases. Graft and block copolymers are generally applied to thermoplastic polymers. An interpenetrating polymer network (IPN) is different from those mentioned above. An IPN is a composite of two polymers cross-linked or reacted in the presence of each other.[1] It is generally thought that the interpenetrated and entangled chains of the two polymer networks can increase the phase stability and, therefore, enhance mechanical properties of the final product. Additionally, this seems to be the only way to blend two cross-linking polymers. There are two reactive phases in an IPN. If phase A reacts earlier than phase B, the product is called a sequential IPN. If both reactions take place at the same time, it is called a simultaneous IPN. If both phases are cross-linked, it is called a full IPN, while if one is cross-linked and the other is linear, it is called a semi-IPN.[3]

Recently, there has been increasing interest in using IPNs in reactive processes such as reaction injection molding (RIM).[4,5] It is believed that adding the second reactive phase may make up deficiencies of conventional RIM materials like polyurethanes (PU). Such a process is obviously more complicated than conventional polymerizations since one has to deal with two reactive phases at the same time and the two phases may interfere with each other during polymerization.

There are few studies concerning polyurethane-based IPNs. Most of them have focused on the morphology and physical properties of finished products.[3,6] For example, Kim et al.[7] studied a simultaneous IPN system composed of a PU and a polystyrene or poly(methyl methacrylate). Yoon et al.[8] studied a series of PU and polyacrylate IPNs. Djomo et al.[9] and Morin et al.[10] also studied PU–PMMA systems. Hutchinson et al.[11] developed a series of PU–polyester IPNs.

The processing aspects of IPNs have not been investigated until recently. Nguyen and Suh[12,13] studied the mixing and reaction of a PU–polyester IPN in the RIM process. They found that a much higher mixing energy, indicated by a high Reynolds number in their study, was required for an IPN to reach the same extent of reaction reached in polyurethanes. Hsu and Lee[14] studied the kinetics of a similar PU–polyester IPN by using thermal

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