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Synthesis of Diblock Polyolefin and Polyester Copolymers Using Zirconium and Aluminum Catalysts

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Introduction

Block copolymers are in an interesting class of macromolecules as they provide an excellent way of chemically combining the characteristics of two or more homopolymers. The synthesis of diblock polymers typically relies on a "living" polymerization reaction since these reactions result in stable but reactive chain ends.[1] However, any polymer with a reactive chain end can function as a macroinitiator for the synthesis of a block copolymer. For a chain-growth polymerization reaction, the critical issue is to control the chain-transfer step to yield a polymer selectively terminated with a reactive chain end functionality.

Recent advances in the development of well-defined homogeneous Ziegler–Natta catalysts have facilitated mechanistic studies of the processes involved in initiation,[2] propagation,[3] and chain transfer.[4] We have previously reported the formation of hydroxy-terminated poly(methylene-1,3-cyclopentane) (PMCP-OH) via selective chain transfer to aluminum in the cyclopolymerization of 1,5-hexadiene.[5] Herein we describe the synthesis of diblock polyolefin and polyester copolymers from the aluminum alkoxide of PMCP-OH which acts as a macroinitiator for the ring-opening polymerization of ϵ-caprolactone (ECL).

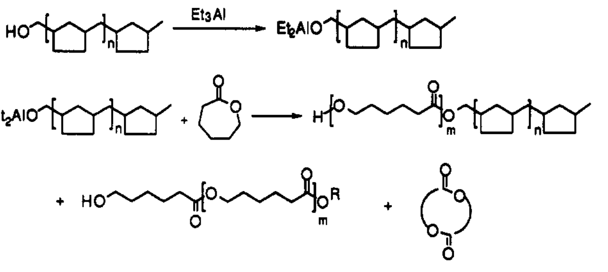
Experimental Section

All experiments were carried out under a dry nitrogen atmosphere, using standard Schlenk-tube techniques. Toluene was distilled from sodium/benzophenone. 1,5-Hexadiene (Wiley) and methanol (Aldrich) were both dried over CaH_2; ϵ-caprolactone (ECL; Aldrich) was dried over CaH_2 for 48 h and vacuum distilled prior to use. D_2O, $AlEt_3$, Et_2NH (Aldrich), $Cp^*_2ZrCl_2$ (Strem), and $C_2D_2Cl_4$ (Cambridge Isotopes) were used as received; methylaluminoxane (MAO; Schering, 30% toluene solution) was used after removing all volatiles and drying the resulting white powder in vacuo (4 h, 21 °C, 0.1 mmHg).

Molecular weights (M_n) were calculated from ^{1}H NMR spectra. ^{1}H NMR spectra were run on a Varian XL-400 instrument at 80 °C in $C_2D_2Cl_4$ and referenced to the central line of the $C_2D_2Cl_4$ triplet at 74.120 ppm or at 21 °C in $CDCl_3$ and referenced to the central line of the $CDCl_3$ triplet at 77.000 ppm. Polymer melting points (T_m's) were determined on a Perkin-Elmer differential scanning calorimeter (DSC-7). The samples were first heated to 220 °C at 10 °C/min, followed by crash-cooling to 30 °C. The values reported were obtained from the second heating from 30 to 220 °C at 10 °C/min.

Hydroxy-Terminated Poly(methylene-1,3-cyclopentane) (PMCP-OH). $Cp^*_2ZrCl_2$ [(5–10) $\times 10^{-4}$ M], MAO (Al/Zr = 1000), and toluene were placed in a Schlenk tube at −25 °C, and 1,5-hexadiene (2 M) was added dropwise over 3 min. After 5.5 h the polymerization was terminated by bubbling a dry air/nitrogen mixture into the solution for 30 min going from −25 °C to room temperature followed by hydrolysis (*Careful! Exothermic!*). After removing the volatiles, the remaining white solid was dried in vacuo. Residues from the hydrolyzed MAO were removed by extraction of the polymer into refluxing toluene for 24 h. ^{13}C NMR ($CDCl_3$, 21 °C): δ 21.1, 28.0, 31.8, 33.4, 36.9, 39.2, 39.6, 41.2, 43.7, 67.8 (referenced to the central line of the $CDCl_3$ triplet at 77.000 ppm). ^{1}H NMR ($CDCl_3$, 21 °C): δ 0.5–0.7 (broad range, 6H), 0.9–1.0 (broad range, 4H), 1.0–1.2 (broad range, 12H), 1.2–1.4 (broad range, 16H), 1.6–2.0 (broad range, 36H), 3.5 (PMCP-CH_2OH, m, 2H) (referenced to the central line of the $CDCl_3$ triplet at 77.000 ppm).

Scheme 1. Synthesis of Diblock Copolymers



Poly(methylene-1,3-cyclopentane-*b*-caprolactone). Diblock polyolefin and polyester copolymers were obtained by treating PMCP-OH with a stoichiometric amount of $AlEt_3$ (∼3 $\times 10^{-3}$ M) in toluene at room temperature. The mixture was stirred for 1 h (ethane evolution) followed by dropwise addition of ϵ-caprolactone. The reactions were quenched with a 10-fold excess of 2 N HCl solution with regard to Al, the solution was washed with water until neutral, and $^2/_3$ of the initial toluene was removed via vacuum distillation. The remaining solution was dried in vacuo, yielding a white solid. Extraction of the crude diblock polymer in refluxing dry methanol with a small amount of Et_2NH led to the isolation of pure block copolymers. ^{13}C NMR ($C_2D_2Cl_4$, 80 °C): δ 21.3, 24.7, 25.7, 28.6, 32.2, 33.4, 34.3, 38.1, 39.5, 41.6, 44.0, 64.2, 67.8 (referenced to the central line of the $C_2D_2Cl_4$ triplet at 74.120 ppm). ^{1}H NMR ($C_2D_2Cl_4$, 80 °C): δ 0.6–0.8 (q, 130H), 0.9–1.5 (broad range, 700H), 1.6–2.0 (broad range, 888H), 2.3 (t, 28H), 3.6 (PCL-CH_2OH, t, 2H), 3.9 (PMCP-CH_2-O-PCL, d, 2H), 4.1 (t, 28H) (referenced to the central line of the $C_2D_2Cl_4$ triplet at 74.120 ppm).

Results and Discussion

Cyclopolymerization of 1,5-hexadiene with $Cp^*_2ZrCl_2$/MAO at −25 °C leads to low molecular weight, yet fully saturated, polymers after hydrolytic workup.[6] Under these conditions chain transfer to aluminum predominates,[7] leading to oligomers containing reactive alkyl aluminum end groups. Oxidation of these alkyl aluminum terminated oligomers with O_2 yields PMCP-OH (T_m = 133 °C, M_n = 2300 by ^{1}H NMR) (eq 1).[5] Jérôme[8] and co-workers have extensively investigated the activity of aluminum alkoxides for the ring-opening polymerization of lactones. Following their procedure,[9] we treated PMCP-OH with a stoichiometric amount of triethylaluminum in toluene at room temperature to produce an aluminum alkoxide macroinitiator for the ring-opening polymerization of ϵ-caprolactone (ECL) (Scheme 1). The polymerization of ϵ-caprolactone was carried out under a variety of conditions (Table 1) to yield the diblock copolymers (poly(methylene-1,3-cyclopentane-*b*-caprolactone) (P(MCP-*b*-CL)) of various compositions. The rate of polymerization of ϵ-caprolactone increases with temperature, but attempts to run the reactions to high conversion lead to a significant increase in transesterification reactions which result in the formation of homopolycaprolactone as well as low molecular weight cyclic lactones.[10]

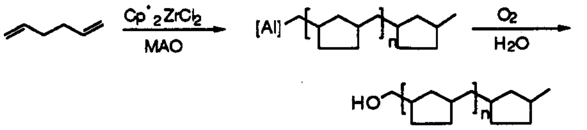


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Table 1. Diblock Copolymerizations

run no.	$[ECL]_0/Al$	$[ECL]_0$ (M)	T (°C)	t (h)	conv[a] (%)	M_n[b]	M_n[c]	M_w/M_n crude	M_w/M_n block	PCL (%)
0[d]	180	1.17	rt	49.5	40	209		3.4		
1	54	0.16	rt	43	100	2890		4.3		
2	154	0.46	rt	45.5	76	5300		5.7		
3	180	1.17	rt	49.5	64	7440	3440[e]	4.2	4.0	54
4	185	1.17	50	30	84	25110	14840	2.1	2.3	40
5	136	0.35	rt	44.5	100	8750		3.4		
6	123	0.35	98	24	83	8790	7300	3.4	4.7	17

[a] Conversion by weight. [b] M_n from ^1H NMR of the PCL part of block in the crude diblock polymer sample (add $M_n = 2300$ for PMCP-OH). [c] M_n after fractionation in dry MeOH and in the presence of Et_2NH. [d] No PMCP-OH in the reaction mixture, blank run. [e] No Et_2NH present.

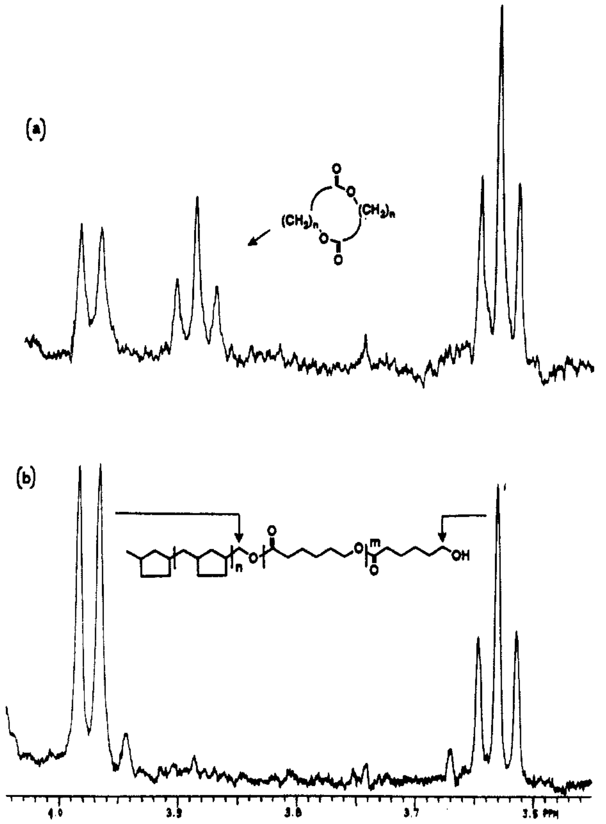

Figure 1. ^1H NMR spectra of the diblock copolymer end groups in $C_2D_2Cl_4$ at 80 °C (a) before and (b) after methanol extraction.

End-group analyses by ^1H NMR were carried out on low molecular weight diblock copolymers to evaluate the efficiency of initiation and the purity of the diblock copolymer. The ^1H NMR resonance for the hydroxymethylene of PMCP-OH appears at 3.5 ppm in $C_2D_2Cl_4$. This resonance is absent in the spectrum of the crude polymer sample but is replaced by a doublet at 3.97 ppm due to the ester linkage of the diblock copolymer. These results provide strong evidence for the diblock copolymer and indicate that the efficiency of initiation is quite high; that is, all of the PMCP-OH was incorporated into a diblock copolymer.

Shown in Figure 1 is a portion of the ^1H NMR spectrum of a representative diblock copolymer (run 3, Table 1). As shown in Figure 1a, the ^1H NMR spectrum of the crude polymer sample contains a triplet at 3.88 ppm which is due to the cyclic lactone oligomers.[11] The triplet at 3.63 ppm is due to the hydroxymethylene end group of the polycaprolactone. The fact that the triplet at 3.63 ppm is larger than the doublet at 3.97 ppm indicates that the crude polymer sample contains some homopolymer of ϵ-caprolactone as well as cyclic oligomers and diblock copolymer. Integration of the ^1H NMR spectra of the entire diblock copolymer region indicates that approximately 70% of the crude product (mol %) consists of the diblock copolymer.[12] A blank run of ϵ-caprolactone and Et_2Al with no PMCP-OH present (run 0, Table 1) resulted in the formation of some PCL. This adventitious polymerization of ϵ-caprolactone by impurities is the likely source of ϵ-caprolactone homopolymer produced in these diblock copolymerizations.

Extraction of the crude polymer mixture in refluxing dry methanol readily separates the diblock copolymer from PCL and cyclics. Addition of a small amount of Et_2NH ensures a slightly basic medium, thus preventing transesterification reactions between the polyester and methanol. After extraction, the signal at 3.88 ppm due to the low molecular weight cyclics disappears and the ratio of the integrated PMCP–ester linkage end group at 3.97 ppm to the PCL methylene alcohol end group at 3.63 ppm becomes 1:1, as expected for a pure diblock copolymer.

These block copolymers are a class of new polymers found to be quite soluble in alcohols as well as aromatic and chlorinated solvents.

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(11) Assignment based upon the model compound of polycaprolactone (cyclic dimer) given by: Pham, Q. T.; Petiaud, R.; Llauro, M.-F.; Watson, H. J. *Proton and Carbon NMR Spectra of Polymers*; Hermes Publishing Ltd.: Chichester, Great Britain, 1984; Vol. 3, pp 544, 545.

(12) Percent yield of pure diblock copolymer is based upon M_n values from ^{1}H NMR spectra taken before and after methanol extraction (run 5, Table 1, where M_n = 8790 before and M_n = 7300 after; run 6, Table 1, where M_n = 25 110 before and M_n = 14 840 after).