Macromol. Symp. ***153**, 17–25 (2000)*

Immortal Polymerization of Propylene Oxide: Application to the Synthesis of Macrocycle Precursors

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SUMMARY: Immortal polymerization of propylene oxide (PO) was conducted with aluminum porphyrin (TPPAlOAr) as catalyst in order to obtain linear polymers with well-defined functional end-groups together with molecular weight control and narrow chain length distribution. Polymerization conditions were adjusted for preparing telechelic polyoxypropylenes (PPOs) whose structure was controlled by various spectroscopic methods (NMR, MALDI-TOF MS, UV) as well as by analytical means (GPC, VPO). PPOs with α-methoxycarbonyl ω-hydroxy end groups are macromonomers well designed for undergoing condensation coupling under appropriate conditions. Macrocyclization was observed by performing end groups transesterification under high dilution.

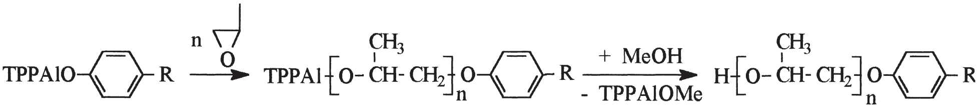
Introduction

Living polymerization methods provide the chemist with a powerful tool for preparing building blocks designed for complex macromolecular architectures.[1] The degree of control over resulting molecular weight, molecular weight distribution and end groups functionality of linear polymers is the usual criterion for measuring the merit of a given method.[2] Easy handling and extension to large scale preparation are some other important points for passing judgment on the process.

With the aim to develop synthetic methods producing in high yield macrocycles from linear precursors,[3] we have investigated some aspects of the immortal polymerization originally developed by Inoue with (5,10,15,20-tetraphenylporphynato) aluminum (TPPAl) derivatives as initiators.[4] Among the various types of monomer accepting this catalysis with the features of living polymerization,[5,6] propylene oxide (PO) was selected to afford PPOs with secondary hydroxy function at the ω position, the α terminal functionality of the polymer being determined by the nature of the axial ligand introduced on the porphinatoaluminum initiator (Scheme 1). We focused our attention on the effectiveness of functionality control without

CCC 1022-1360/00/$ 17.50+.50/0

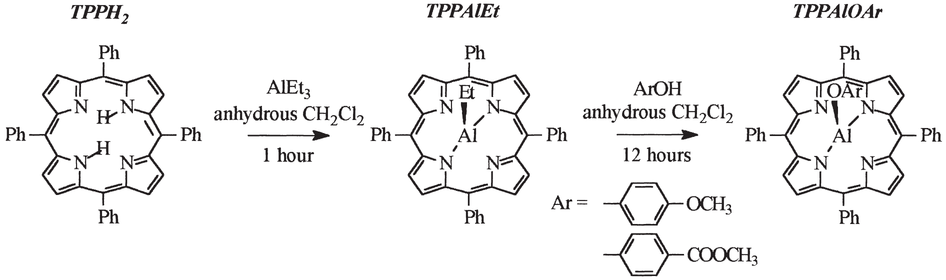
neglecting the beneficial aspects of living systems on molecular weight control.



Scheme 1. Aluminum porphyrin catalyzed polymerization of PO

Results and Discussion

Initiator preparation. Two substituted phenol derivatives of simple structure were chosen for introducing methoxy (Ar ≡ -(pC_6H_4)OMe) and methoxycarbonyl (Ar ≡ -(pC_6H_4)COOMe) functionalities in the TPPAlOAr initiator. We have investigated the efficiency of these initiating species under various conditions. The early stages consisting in the in-situ preparation of the catalyst TPPAlOAr were shown essential for obtaining well-behaved systems in terms of living character and functionality control (Scheme 2).



Scheme 2. Synthesis of porphinatoaluminum phenoxide initiators

It was checked by ^1H and ^{13}C NMR that the quantitative transformation of the reactant is possible under appropriate experimental conditions (anhydrous solvent, reactants and Schlenk tube technique under inert atmosphere) and with a slight excess of trialkylaluminum for the first step of Scheme 2 and slight excess of substituted phenol for the second one. Functionalization of the initiator can be quantitatively monitored from the observation of shifted ^1H NMR signals for substituted aluminum phenoxide compared to the corresponding free phenol. With the paramethoxy derivative (Ar ≡ -(pC_6H_4)OMe), slightly broadened singlet signal at 6.8 ppm assigned to the four aryl protons of the neutral phenol are shifted to high magnetic field upon salification and complexation to the metallated porphyrin. New doublet signals are observed at 5.45 and 2.35 ppm which are assigned respectively to the protons of the meta and ortho position of phenoxide. Similar shifts were observed with Ar ≡ -$(pC_6H_4)CO_2Me$ where doublet signals appearing at 7.9 and 6.9 ppm in the free phenol disappear to give new signals at 6.6 and 2.5 ppm. It was essential to remove the excess of triethylaluminum after step 1 to avoid dramatic contamination with species of ill-defined reactivity when polymerization is started by introduction of the purified monomer. In the case of such contamination, polymerization proceeded much faster and was sometimes completed in a timescale of few minutes, the resulting polymer exhibiting broader molecular weight distribution (MWD). Catalysis activation by Lewis acids of structure $Et_{3-x}ArO_xAl$ can be invoked as a perturbating phenomenon. The ^1H NMR spectra recorded just before PO injection show typical signals of low intensity that can be assigned to aluminum complexes not inserted in a porphyrin ring. The activation process would be similar to the methyldiaryloxyaluminum complexes reported to induce accelerated living polymerization of various epoxides and lactones$^{7)}$.

Conditions for catalyst preparation were thus optimized for ensuring complete metallation and functionalization of porphyrin together with careful elimination of the alkylaluminum between the two steps.$^{8)}$ Polymerizations reported in the following sections were conducted with the relative molar proportions $TPPH_2/AlEt_3/ArOH$ = 1/1.1/1.1.

Initiation with $TPPAlO(pC_6H_4)OMe$. PO polymerization initiated with the methoxy functional aluminum complex gave PPO samples with narrow MWD as shown by GPC analysis calibrated with polystyrene standards (see Tab. 1).

Table 1. Polymerization$^{a)}$ of PO initiated with $TPPAlO(pC_6H_4)OMe$.

run	PO/initiator	time / h	conv. in %	$\overline{M}_n$ (conv.)	PI$^{b)}$	$\overline{M}_n$ (UV)$^{c)}$
1	175	120	52	5400	1.1	5000
2	175	120	66	6700	-	6500
3	175	150	92	9600	1.4	9700
4	175	163	93	9600	1.1	-
5	175	3	17	1850	1.6	-

a) All experiments conducted with 0.815 mmol of porphyrin initiator in a total dichloromethane volume of 25 mL.
b) Polydispersity index deduced from GPC analysis with polystyrene calibration.
c) End group titration by UV spectroscopy with methoxyphenol as standard.

Spectroscopic analyses were used to determine the structure and the chemical functionality of the purified PPO. NMR spectra reveal the typical structure of polyoxypropylene with methyl, methylene and methine groups observed as main peaks at 17.4, 73-73.5, 75-75.5 ppm respectively in ^{13}C NMR and 1.1, 3.5 and 3.35 ppm in ^{1}H NMR.[9)] The presence of functional end groups is confirmed but only qualitatively from the small intensity signals located at 65.5 and 55.6 ppm in the ^{13}C NMR spectra and assigned to terminal secondary hydroxyl and methoxyaryl functions respectively. Two singlet signals of (pC_6H_4-OMe) at 6.75 (4H) and 3.7 (3H) ppm in the ^{1}H NMR spectra also show the presence of the terminal function PhOMe. The ratio of the intensity of these protons to that from the repeat units is too small to allow precise calculations from the integral values.

In order to verify the accuracy of absolute number-average molecular weights deduced from PO conversion at the end of the runs with the assumption that all and only the introduced catalyst has initiated polymerization, UV spectrophotometry was used to perform end group titration. Hydroquinone methylether was used as standard for obtaining the absorbance calibration curve. The calculated $\overline{M_n}$ value for one chromophore per chain was in total agreement with the value deduced from conversion data (see Tab. 1).

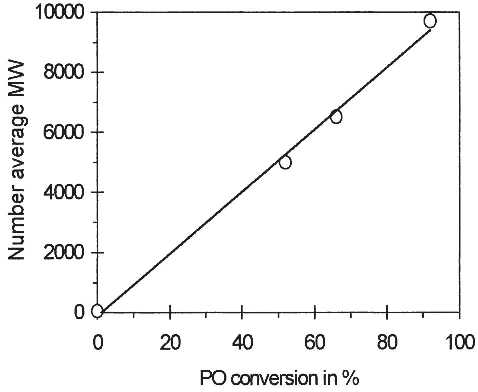


Figure 1. $\overline{M_n}$ (UV titration) dependence upon PO conversion after polymerization initiated with TPPAlO(pC_6H_4)OMe (3 runs at 30°C, same conditions for reactant concentrations).

The living character of PO polymerization is confirmed by the linearity of the number average molecular weight with monomer conversion (Fig. 1). A kinetic investigation was undertaken at 30°C to afford data for molecular weight control. Several medium scale experiments (4 g of PO involved for each run) were conducted independently and the conversion of aliquots was determined gravimetrically after monomer and solvent evaporation. The conversion plot of Fig. 2 obtained from six different experiments demonstrates fair reproducibility.

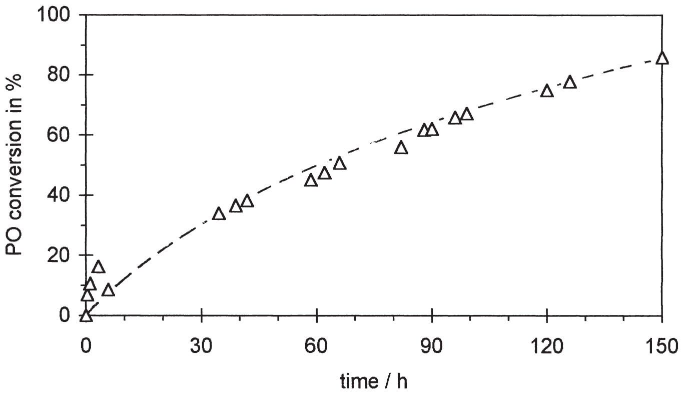


Figure 2. PO conversion as a function of polymerization time at 30°C initiated with TPPAlO(pC_6H_4)OMe (6 different runs).

The linearity of the integral function Ln($[PO]_0/[PO]_t$) = Ln(1-conversion) expressed as a function of time supports a simple kinetic scheme with fisrt order in monomer concentration over a broad range of conversion (Fig.3).

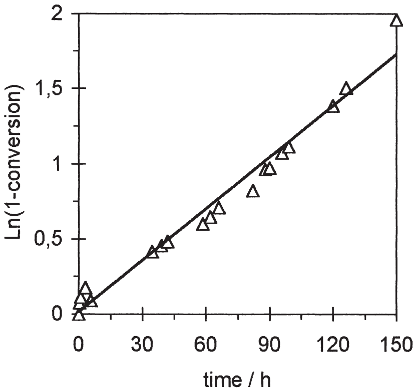


Figure 3. Plot of the integral first order function for PO polymerization kinetics initiated by TPPAlO(pC_6H_4)OMe (data from Fig. 2).

Initiation with TPPAlO(pC_6H_4)CO_2Me. The procedure determined for the methoxyphenol catalyst was succesfully applied to the hydroxybenzoate initiator, thus yielding PPOs with the Ar-CO_2Me end function. For this series we have tempted to obtain PPO samples of desired molecular weight not through reaction kinetic control but at maximum conversion by adjusting the monomer to initiator ratio (Tab. 2).

Table 2. Polymerization[a)] of PO initiated with TPPAlO(pC_6H_4)CO_2Me.

run	PO/initiator	$\overline{M}_n$ (conv.)	PI [b)]
1	175	10500	1.10
2	79	4800	1.11
3	42	2500	1.06
4	37	2300	1.12

[a)] All experiments conducted for 96- with 39 mmol.L^{-1} of porphyrin initiator in a total dichloromethane volume of 20 mL (runs 1-3) or 40 mL (run 4).

[b)] Polydispersity index deduced from GPC data with polystyrene calibration.

At comparable temperature and reactant concentration, polymerizations initiated with the methylbenzoate catalyst appeared to be faster than those initiated with the 4-methoxyphenoxide derivative. Of course the functional end group is not directly involved in the propagation step whose kinetic seems to be activated with the former type of catalyst. It is still unclear whether this difference arises from the possible presence of trace amounts of Lewis acid activators in the system exhibiting higher polymerization rate or if the end group interacts to some extent with the metal complex. Obviously, this effect of end groups on propagation kinetics, already observed with various other ligands present on the starting initiator needs further investigation to be clarified. In the present case, since end groups can exhibit only Lewis base behavior, their degree of interaction with the metallic center should be compared.

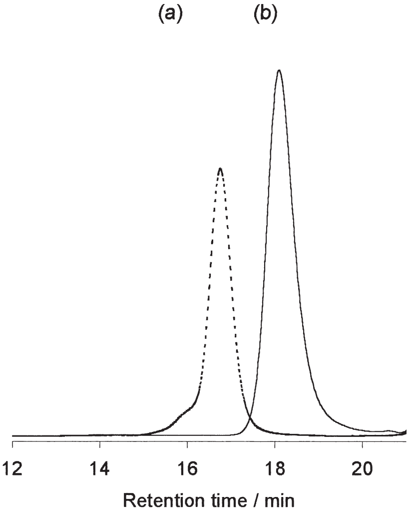


Figure 4. GPC curve of polypropylene oxide obtained with Ar ≡ PhCO_2Me ; (a) discontinuous line, $\overline{M_n}$ = 10500, PI = 1.15 ; (b) continuous line, $\overline{M_n}$ = 2500, PI = 1.1.

Depending on the reaction conditions, PPOs of various $\overline{M_n}$ were obtained and purified to a 10 gram-scale for a typical preparative run. Figure 3 shows typical GPC chromatograms of two examples with narrow MWD. The products were submitted to various analyses to prove their structure before being used for further reactions. Similarly to the previous comments made for the methoxy derivative, the methoxy and aryl groups of the terminal function are detected as weak peaks at 6.85, 7.9 and 3.85 ppm, the intensity of which does not permit quantitative determination of effective end group functionalization.

Conclusive information can be obtained from Matrix-Assisted Laser Desorption/Ionization Time of Flight (MALDI-TOF) mass spectrometry. The spectrum of Fig. 5 corresponds to the PPO sample obtained from run No 4 of Table 2. The series of peaks forming the envelope of the mass spectrum correspond to sodium cation attachment to individual PPO polymers, the shadow appearing with a lower intensity is shifted towards higher masses from the preceding distribution by a difference of 16 that corresponds to a potassium attachment instead of sodium. On the whole range of mass analyzed, the peaks of the main envelope appear at abscissa M_i given by the relation $M_i = 58i + 175$, where i is the monomer units number, 58 the molecular mass of the monomer and 175 the sum of the molecular weights of sodium and methyl 4-hydroxybenzoate. These data afford a definite proof that all the PPO macromolecules synthesized in a given run are formed with the expected ester as terminal group.

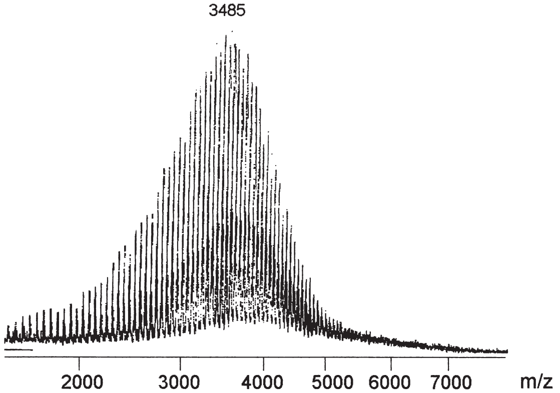


Figure 5 : MALDI-TOF MS spectrum of a typical α-methoxycarbonyl ω-hydroxy PPO.

Condensation of functionalized PPO by transesterification. Telechelic α-ester, ω-hydroxy PPO (Ar ≡ Ph-CO_2Me with $\overline{M_n}$ ranging from 2400 to 10500 and narrow MWD were submitted to transesterification under various conditions. Preliminary experiments with acid catalysis[10)] or with butyl lithium[11)] gave no satisfactory result. Encouraging results obtained in the presence of metallic sodium lead us to experiment various procedures (dilution, solvent, Na/hydroxyl ratio and temperature) in order to observe significant coupling. With PPOs of $\overline{M_n}$ = 10500 (1 mmol.L^{-1} in toluene), the reaction conducted over sodium wire at room temperature for 94 hours leads to partial polycondensation. ^{1}H NMR spectra indicate that under these conditions the extent of transesterification deduced from the decrease of methyl ester signal is slightly above 50%, in good agreement with the ratio of macromonomer area to that of oligomers measured in the GPC trace of Fig. 6. Oligomers of $\overline{M_n}$ values from 2 and up to 5 times the $\overline{M_n}$ for the macromonomer are detected in the low retention time part of the chromatogram. There is no evidence for ring formation, the peak at higher retention times overlapping well that of the starting PPO.

It is quite evident that not only the reactant concentration but also the dispersion degree of metallic sodium in refluxing toluene and the interactions at solid surface the ratio influence the competition between macrocycle / polycondensate formation.

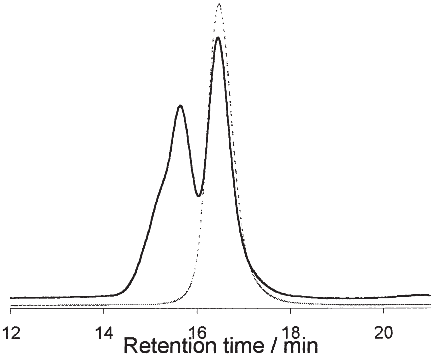


Figure 6 : GPC trace of condensation products after transesterification of α-methoxycarbonyl ω-hydroxy PPO ($\overline{M_n}$ = 10500), in toluene (1 mmol.L^{-1}) at 25°C, 94 h. over sodium wire.

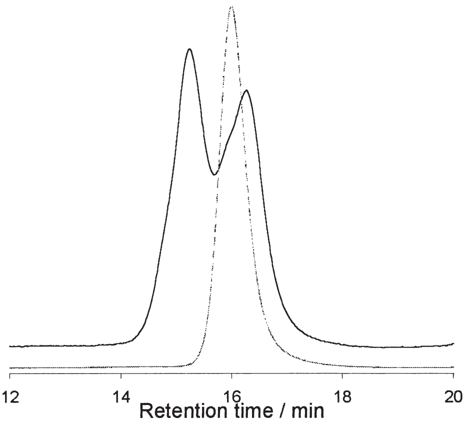


Figure 7 : GPC trace of condensation products after transesterification of α-methoxycarbonyl ω-hydroxy PPO ($\overline{M_n}$ = 10500), in refluxing toluene (0.12 mmol.L^{-1}), 90 h. over dispersed sodium.

Very fine sodium particles prepared by slowly heating of toluene yield macrocycle of retention time longer than that for the parent linear PPO. By refluxing in toluene under nitrogen during 90 hours a PPO sample of same $\overline{M_n}$, we have obtained the macrocycle approximately in the same amount than the dimer, as indicated by the GPC traces of Fig. 7. The results can be further improved by reacting under the same conditions macromonomers of smaller chain length or by using a more convenient chemistry than the base-catalyzed transesterification. Further purification, separation and spectroscopic characterization are underway to demonstrate unambiguously the cyclic nature of the major transesterification products.

Conclusion

This study demonstrates the applicability of PO immortal polymerization to the synthesis of polymers with controlled end group functionality. Various spectroscopic methods of characterization were used to ascertain the nature of the α end group introduced by the functional initiator. The complementary end groups of α-methoxycarbonyl ω-hydroxy PPOs can react inter or intramolecularly to afford polycondensates or macrocycles, depending the reaction conditions. The obtained results give an additional proof of the macromonomer structure which is simply based on chemical reactivity criteria. Further studies to increase macrocyclization yields with this chemistry and with some other using the ether linkage for introducing appropriate functions on telechelic macromonomers are underway.

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