Synthesis and Microbial Degradation of Poly(2-methyl phenylene oxide)

LI-XIA LI,[1] ERIC A. GRULKE,[2,*] and PATRICK J. ORIEL[1]

Departments of Microbiology[1] and Chemical Engineering,[2] Michigan State University, East Lansing, Michigan 48824

SYNOPSIS

The synthesis and biodegradation of poly(2-methyl phenylene oxide) was studied as an example of a synthetic polymer containing a biodegradable aromatic backbone. Polymer prepared with cuprous 2,2-isopropoxy ethyl pyridine catalyst demonstrated good blending properties with polystyrene. In soil experiments, the homopolymer degraded readily with over 50% reduction in 40 days. No oligomeric intermediates were observed by gel permeation chromatography, suggesting degradation by cell-associated enzymes. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Because landfill approaches to solid-waste disposal are both inefficient and increasingly expensive, traditional approaches to plastic utilization need to be replaced with better strategies. Although increased plastics recycling will occur in the future, it is likely that logistics and economics will limit the kinds and amount of plastics to be recycled and that disposal of plastics, particularly those used for packaging of food and household wastes, will continue at high volumes. Current plastic packaging materials are sophisticated blends, laminates, or mixtures that have specific mechanical, barrier, and processing properties for their applications.

There currently are three mechanisms of polymer degradation by environmental causes: photodegradable, chemically degradable, and biodegradable. There are three categories of biodegradable polymers: immiscible blends of a biodegradable polymer such as starch in a thermoplastic, single-phase systems of hydrolyzable homopolymers and copolymers, and soluble polymers that can dissolve in water and presumably might be attacked by microorganisms. To date, most single-phase biodegradable polymers have hydrolyzable linkages, including ester and amide types.[1] Because of their polarity, these polymers do not blend well with the more hydrophobic polymers such as polystyrene and polypropylene typically used in packaging applications.

Development of hydrophobic polymers that can be biodegraded could lead to alternative systems and strategies for packaging materials. The polyphenylene ether family of polymers are miscible with other polymers containing aromatic rings. The aromatic component of these polymers may lead to their wetting of other synthetic polymers in laminate applications or miscible blends in other applications.

Our selection of poly(2-methyl phenylene oxide) (PMPO) as a model biodegradable synthetic polymer is based on the known microbial degradation of many simple aromatic compounds by oxidative ring cleavage following hydroxylation.[2] We reasoned that this polymer might provide the attractive engineering properties of poly(2,6-dimethyl phenylene oxide) (PDMPO) but with increased biodegradability due to the decreased methyl substitution on the ring, which should facilitate biodegradation. In addition, its monomer, *o*-cresol, is known to be biodegradable.[3] This work describes the synthesis, physical properties, and biodegradation characteristics of PMPO.

EXPERIMENTAL

Materials

o-Cresol was obtained from Sigma Chemical and used without purification. 2,6-Dimethyl phenol was

* To whom correspondence should be addressed.

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obtained from Aldrich Chemical and used without purification. Polymerization solvents (pyridine, toluene, chloroform, and methanol) were obtained as reagent grade. The catalyst system was cuprous chloride complexed to 2,2-isopropoxyethyl pyridine.

Polymer Synthesis

PDMPO was prepared by the method of Hay.[4] The synthesis of low molecular weight PMPO has been reported previously, but attempts to obtain higher molecular weight polymers were thwarted by formation of low molecular weight products and carbon–carbon linked side products.[5] High molecular weight polymer was prepared with a new catalyst system of CuCl with 2,2-isopropoxy ethyl pyridine. This system reduced carbon–carbon coupling at the 6 position on the aromatic ring by using bulky coordination groups on the copper catalyst. The reaction mixture of the catalyst system (3 g CuCl in 50 mL 2,2-isopropoxy ethyl pyridine) diluted in 150 mL toluene was purged with pure oxygen at room temperature. Powdered $MgSO_4$ was added to scavenge for residual water. A solution of *o*-cresol in toluene (32.4 g *o*-cresol in 200 mL toluene) was added dropwise over several minutes to prevent a rise in reaction temperature above 50°C. Several hours after the complete addition of monomer, the temperature dropped and the polymer product was precipitated by pouring the reaction mixture into 2 L of methanol. The polymer product was separated by filtration and dried at room temperature.

Molecular Weight Distribution

Molecular weight distributions for PDMPO and PMPO were determined by gel permeation chromatography using a Waters Chromatographic System. An Ultrastyragel column (10^4 Å pores) was calibrated with a series of polystyrene standards (MW = 580, 1820, 2450, 5050, 11,600, and 21,900) and one commercial sample having a molecular weight typical of commercial products (MW = 244,000; Scientific Polymer Products). Sample concentrations of 0.25 wt % in chloroform were injected and a flow rate of 1.5 mL/min was used. The column calibration curve showed the expected linear relationship between the natural logarithm of molecular weight and elution time (or volume). GPC response curves for both poly(phenylene oxides) were converted directly to molecular weight distributions using the calibration curve.

Thermal Transitions

The thermal transitions of powder and film samples were determined with a DuPont 9900 thermal analyzer using differential scanning calorimetry (DSC 910 attachment). Reported values of thermal transitions are those of the second heats due to the residual stresses in the materials made by rapid precipitation and cast film techniques.

Microscopy

Optical microscopy of film samples was done using an Olympus BH-2 microscope at magnifications of 200× and 500×. Etched scales were used to establish length dimensions. A Jeol T-330 scanning electron microscope was used to determine the particle size of precipitated polymer samples. Powders were placed on mounting stubs, coated with gold, and examined in the instrument.

Polymer Biodegradation

Polymer biodegradation studies utilized 350 g of loamy soil sampled from a tilled field at Michigan State University. The soil was sieved through a 2 mm screen and added to a 1 L Erlenmeyer flask. The polymer was ground finely with a mortar and pestle and mixed into the soil. The soil mixture was adjusted to 5 wt % water saturation and incubated at room temperature. Samples (50 g) were taken and soil moisture was adjusted at 10 day intervals. The samples were extracted three times with chloroform (50 mL each), and the solvent samples were pooled to analyze for residual polymer.

RESULTS AND DISCUSSION

Material Properties of PMPO

A typical molecular weight distribution for PMPO is shown by the solid points in Figure 1. The molecular weight averages for this sample were $\overline{M_n}$ = 5400 and $\overline{M_w}$ = 23,100 and the polydispersity was 4.27. Several common molecular weight distributions were fit to the data to determine an empirical model for this polymer. The best fit was given by the Wesslau distribution,[6] one of several log normal distributions:

$$w(M) = \frac{1}{\sqrt{2\pi\sigma^2}}\frac{1}{M}\exp\left[\frac{-(\ln M - \ln \overline{M_m})^2}{2\sigma^2}\right]$$

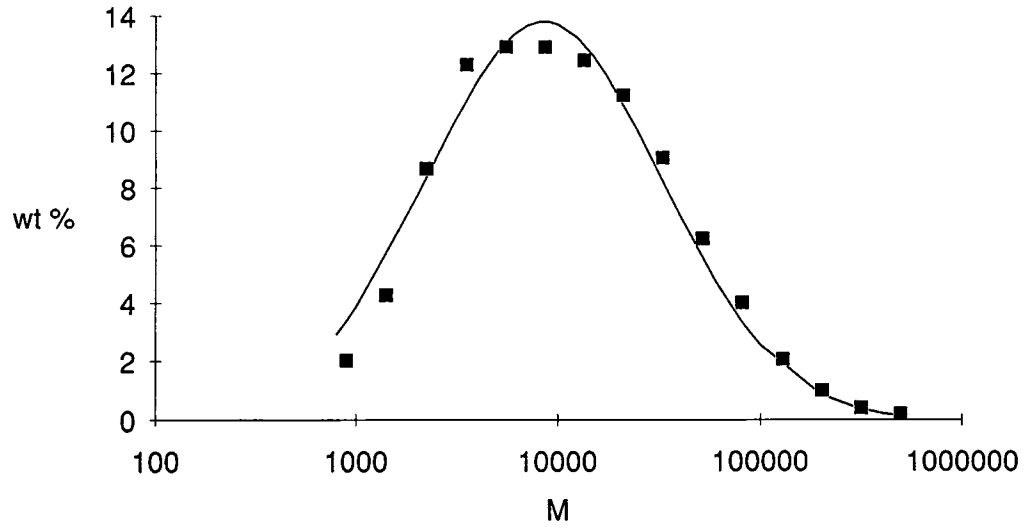

Figure 1 Molecular weight distribution for PMPO as polymerized using the 2,2-isopropoxy ethyl pyridine cocatalyst. Solid squares: data. Solid curve: eq. (1) with $\sigma = 1.34$ and $\overline{M_m} = 8500$.

where $w(m)$ is the weight frequency of the distribution; M, the molecular weight; σ, a measure of the breadth of the distribution; and $\overline{M_m}$, the mean of the sample. The Wesslau model coefficients were $\sigma = 1.34$ and $\overline{M_m} = 8500$.

The Wesslau model parameters were estimated by minimizing the least squares error between the data and the model. The differential distributions presented here have not been normalized. The continuous curve in Figure 1 corresponds to the model predictions. The Wesslau model describes the data well, but slightly overpredicts the weight frequency near the sample mean and shifts the maximum of the differential distribution curve to higher molecular weight. The model fit was considered sufficient to identify samples that might have significantly different distributions.

Figure 2 shows the molecular weight distribution for PDMPO made in this study. It also is well described by a Wesslau distribution with $\sigma = 1.14$ and $\overline{M_m} = 15{,}000$.

The PMPO made by this procedure consisted of agglomerated particles of low bulk density. The agglomerates are roughly spherical with diameters be-

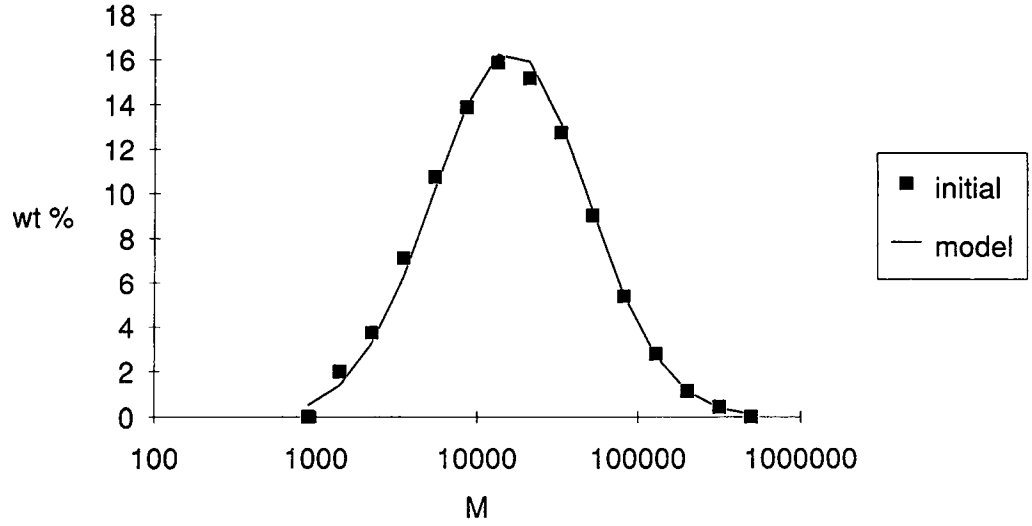

Figure 2 Molecular weight distribution for PDMPO as polymerized using the pyridine cocatalyst. Solid squares: data. Solid curve: eq. (1) with $\sigma = 1.14$ and $\overline{M_m} = 15{,}000$.

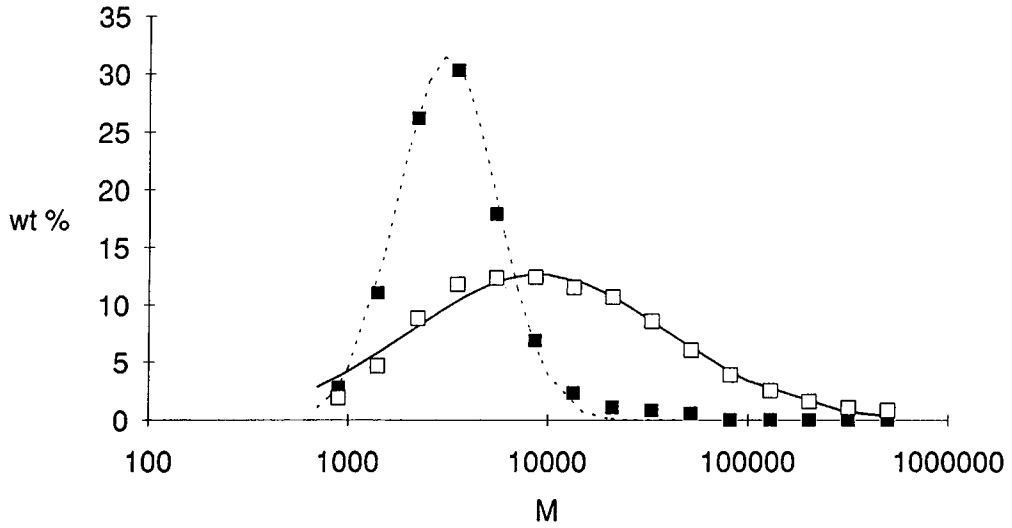

Figure 3 Comparison of PMPO molecular weight distributions for the two cocatalysts. Pyridine cocatalyst: solid squares and dashed curve. 2,2-Isopropoxy ethyl pyridine: open squares and solid curve. Distribution coefficients given in Table I.

tween 5 to 10 microns. SEM analysis showed that primary particles about 0.25 microns in diameter formed porous particles. The morphology of the particles probably can be controlled by the temperature and solvent choice of the precipitation process.

The improvement in molecular weight obtained by using 2,2-isopropoxy ethyl pyridine is shown in Figure 3. With pyridine as the cocatalyst, the weight-average molecular weight of the product was about 4500. This represents an average degree of polymerization of 45, suggesting that long chains are not formed as quickly as with the preferred cocatalyst. The product made in pyridine was fit by a Wesslau distribution as well. The difference in the distribution coefficients suggest that the two materials shown in Figure 3 are quite different. Molecular weight distribution parameters for these materials are shown in Table I.

Table I Comparison of Molecular Weight Distribution Parameters for PMPO Samples Prepared with Different Cocatalysts

Distribution Parameter	Cocatalyst: Pyridine	Cocatalyst: 2,2-Isopropoxy Ethyl Pyridine
$\overline{M_m}$	3100	9000
σ	0.57	1.48
$\overline{M_n}$	2800	3800
$\overline{M_w}$	4500	25,400
$\overline{M_w}/\overline{M_n}$	1.61	6.67

The thermal properties of PMPO should be similar to those of PDMPO, which has a T_g of 225°C and a T_m of 267°C.[7] Differential scanning calorimetry of PMPO suggests a T_g near 180°C, although further work needs to be done to verify that solvents and the fine structure of the solids are not affecting the interpretation of the data.[8]

PDMPO is known to be soluble in polystyrene and is dissolved in a polystyrene–polybutadiene blend as Noryl®, a General Electric product. The miscibility of PMPO and polystyrene was investigated with film blends cast from chloroform. Mixtures of these polymers in chloroform showed phase separations at some polymer ratios, but gave clear cast films that were uniform in color. The cast films are flexible for compositions up to 50 wt % PMPO and seem mechanically similar to polystyrene, although no tensile or burst test data have been obtained. Examination of the films by optical microscopy shows no obvious phase separation at the detection limit of the equipment (about 1–2 microns). In addition, the films appeared to have a single glass transition temperature by DSC. Figure 4 shows the blend T_g as a function of PMPO weight fraction. The data are shown as points and the curve represents a Redlich–Kister type model. The thermal and optical properties of cast films seem to be consistent with a miscible polymer blend.

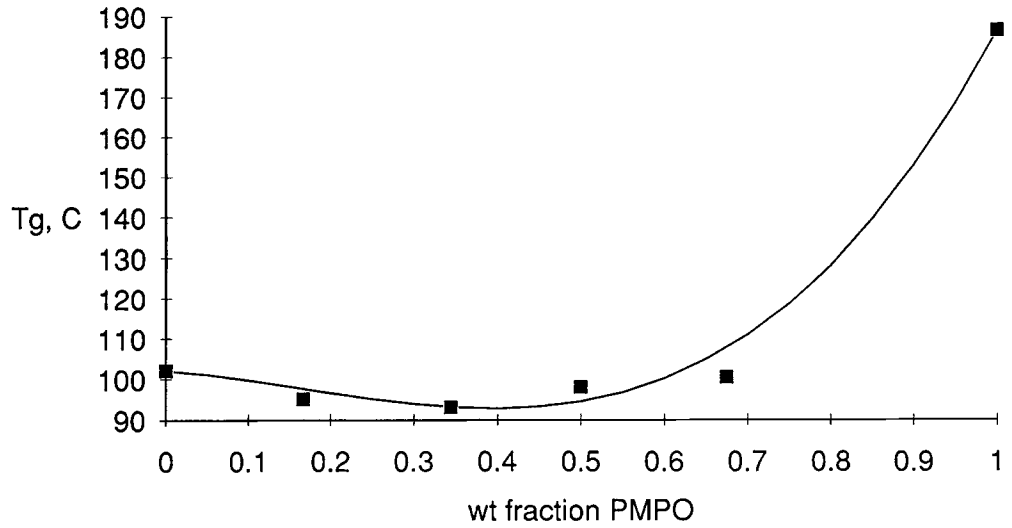

Figure 4 Glass transition temperatures of cast film blends of polystyrene and PMPO. T_g determined by the second heat of differential scanning calorimetry.

Soil Biodegradation Experiments

Figure 5 compares the amounts of PDMPO and PMPO recovered from the soil as a function of degradation time. Complete recovery was not achieved for either polymer. The percent recovered initially (day 0) represents typical recoveries of the chloroform extraction procedure. The PDMPO does not show large losses, suggesting that its biodegradation rate is low. By contrast, the PMPO recovered from the soil dropped to 50% of its initial value after 40 days, suggesting that the material biodegraded. This finding was reproduced in independent experiments.

Figure 6 shows the molecular weight distribution of a sample of PMPO that was degraded in soil for 40 days. It has $\overline{M_n}$ = 6200 and $\overline{M_w}$ = 24,100 and a polydispersity of 3.84. Its Wesslau parameters were σ = 1.30 and $\overline{M_m}$ = 10,500. The solid curve shown in Figure 6 is based on the Wesslau parameters fit to the PMPO sample before degradation. There seems to be a slight shift of the degraded sample distribution to higher molecular weights. However,

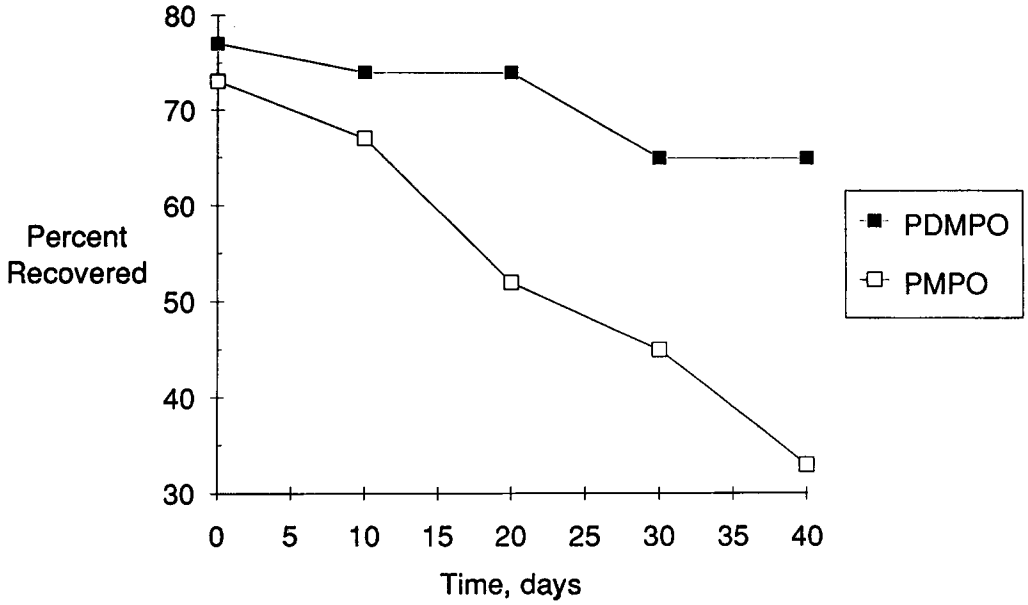

Figure 5 Polymer recovered by solvent extraction from soil after degradation at 20°C.

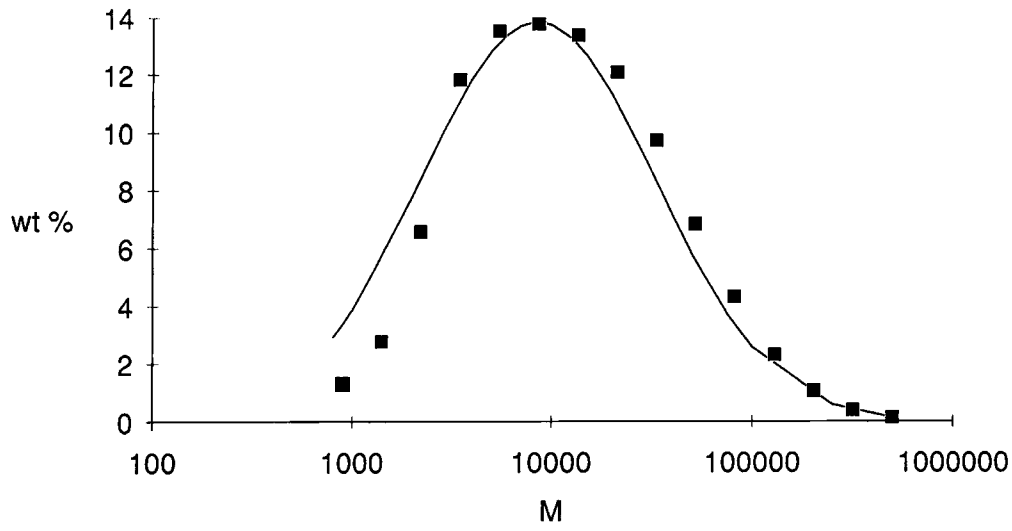

Figure 6 Molecular weight distribution of PMPO recovered from soil after 40 days of degradation. Solid squares: data. Solid curve: eq. (1) with the distribution parameters of the original material. Best fit values are given in Table II.

the differences in the curve parameters is modest (see Table II) and probably is within the error of the method. The similarity of the Wesslau parameters and the curves themselves suggest that the polymer recovered from the soil has the same molecular weight distribution as that of the initial sample. Figure 7 shows the distributions for the PDMPO samples. There are no significant differences between these molecular weight distributions.

Since the total amount of polymer recovered from the soil under degradation conditions was less than that of the control, it is likely that degradation of PMPO occurs independently of its molecular weight. The strategies used by bacteria for biodegrading synthetic polymers have not been carefully explored. There are, however, studies of bacteria attacking natural polymeric materials, such as cellulose, which are too large for introduction into the cell. Two strategies appear to be utilized by cellulolytic microbes.[9] The first (Type I), exemplified by fungi and certain bacteria, consists of secretion of a battery of extracellular enzymes into the surrounding medium, resulting in cellulose degradation to oligo- or monosaccharides that can be introduced into the cell for further degradation and utilization as carbon and energy sources. The second (Type II) has been elucidated more recently for certain cellulolytic bacteria, in which localized areas on the cell exterior called "cellulosomes" participate in binding the bacterium to the cellulose surface with degradation of the proximal cellulose with associated enzymes. Binding of the bacterium to the substrate is a strat-

Table II Comparison of Molecular Weight Distribution Parameters for PMPO and PDMPO Samples before and after Degradation

Distribution Parameter	PMPO		PDMPO	
	Initial	40 Day	Initial	40 Day
$\overline{M_m}$	8,500	10,500	15,000	20,500
σ	1.34	1.30	1.14	1.14
$\overline{M_n}$	5,400	6,200	8,900	7,500
$\overline{M_w}$	23,100	24,100	28,000	30,300
$\overline{M_w}/\overline{M_n}$	4.27	3.84	3.15	4.02

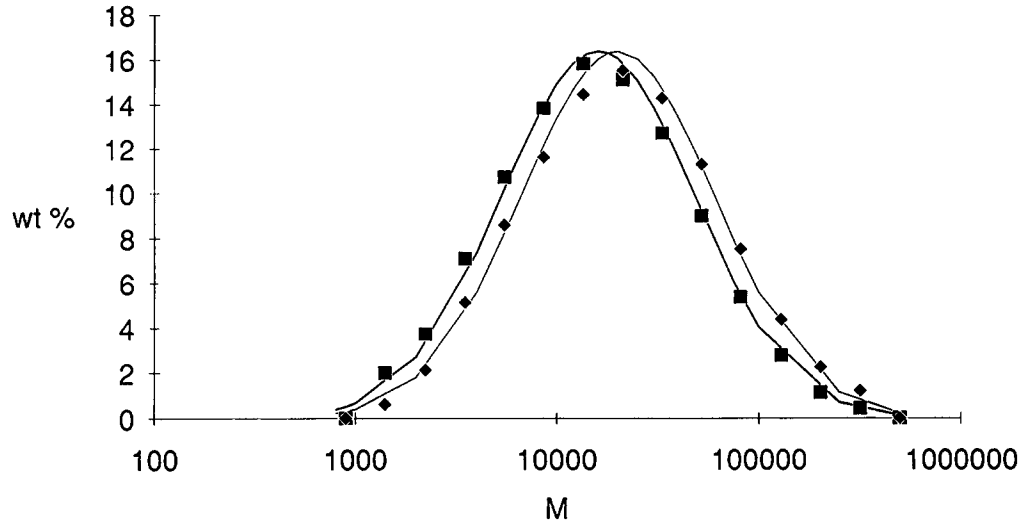

Figure 7 Comparison of molecular weight distributions of PDMPO as polymerized and after soil incubation. Solid squares: initial PDMPO. Solid diamonds: incubated PDMPO. Distribution parameters are given in Table II.

egy that conserves enzyme and prevents loss of enzyme products to competing organisms in the immediate environment. The data of Figures 5 and 6 are consistent with a Type II mechanism involving cell binding with local biodegradation in the region of contact.

CONCLUSIONS

PMPO readily degrades in soil. PMPO degrades at higher rates than does PDMPO, which is consistent with the hypothesis that methyl groups in both the 2 and 6 ring positions hinder biodegradation. The lack of change in the molecular weight distribution of PMPO after biodegradation suggests a cell-associated degradation mechanism.

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