ELSEVIER

Available online at www.sciencedirect.com

SCIENCE DIRECT®

Polymer 47 (2006) 4085–4093

polymer

www.elsevier.com/locate/polymer

Synthesis and characterization of telechelic phosphine oxide polyesters and cobalt(II) chloride complexes

Qin Lin [a,1], Serkan Unal [a], Ann R. Fornof [a], R. Scott Armentrout [b], Timothy E. Long [a,*]

[a] *Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061-0212, USA*
[b] *Eastman Chemical Company, Kingsport, TN 37662, USA*

Abstract

A monofunctional phosphine oxide containing endcapping reagent, 4-carboxyphenyl biphenyl phosphine oxide, was synthesized for the preparation of telechelic polyester oligomers. The chemical structure of the endcapping reagent was verified using NMR spectroscopy, mass spectroscopy, and elemental analysis. Phosphine oxide telechelic polyesters were prepared for the first time via copolymerization of a low molar mass polyester oligomer precursor and the phosphine oxide endcapping reagent in the melt state. The quantitative incorporation of telechelic phosphine oxide functionality was confirmed using ^{1}H NMR spectroscopy and elemental analysis. The corresponding complexes of phosphine oxide terminated polyesters and cobalt(II) chloride were prepared via charging the cobalt salt at the onset of melt polymerization. ^{31}P {^{1}H} NMR spectroscopy, FT-IR spectroscopy, and UV–vis spectroscopy indicated that the cobalt(II) ion preferentially coordinated with the phosphine oxide end groups. The complexes exhibited higher melt viscosity than their salt-free analogues due to the formation of coordinated polymers. The presence of the telechelic phosphine oxide end groups also aided in the homogeneous dispersion of the cobalt salt in a poly(ethylene terephthalate) (PET) matrix.

Keywords: Phosphine oxide; Polyesters; Macroligands

1. Introduction

Polymer-metal salt nanocomposites enable a wide variety of high performance applications, such as conductive adhesives, supported catalysts, sensors, luminescent films, and electro-optical devices [1–8]. The presence of metal salts in a continuous polymer matrix also influences the morphology and rheology of the resulting multiphase product. For example, improved mechanical properties, controlled gas permeability, flame resistance, and thermal stability are obtained when inorganic salts, metal oxides, or clay particles are dispersed at a nanoscale into polymer matrices [1–8]. However, metal salts tend to macrophase separate at micron dimensions in polymer matrices, which results in poor mechanical properties and limited performance [1–10]. The random incorporation of ligands into polymers in order to form coordination bonds with the metal ions prevents the formation of large aggregates [1–10]. However, significantly less attention has been devoted to telechelic polymeric ligands, and earlier efforts have primarily focused on pyridines, ethers, and Schiff-bases [1–10].

Phosphine oxide is a particularly interesting ligand in order to manipulate the functional performance of polymer-metal salt composites for different applications [11]. Moreover, the phosphine oxide ligand exhibits a stronger coordination ability than ligands such as DMSO, methanol, acetone, and water, which serves to limit complexation with functional groups other than phosphine oxide in the polymer matrix [11f]. Phosphine oxide compounds also exhibit excellent thermal stability, which results in melt processable macroligands and metal salt complexes at high temperatures [8]. For example, low molar mass phosphine oxide ligands have been used as stabilizers in the preparation of quantum dots via high temperature processes [12]. Several families of phosphine oxide containing random copolymers have been synthesized, including poly(arylene ether phosphine oxide) and metal salt complexes [8,13]. Phosphine oxide containing poly(arylene ether)s and polyimides effectively disperse metal salts into polymer matrices via coordination of the metal salts with phosphine oxide groups along the polymer backbone.

Poly(ethylene terephthalate) (PET) is an important semi-crystalline polyester used to produce textile fibers, packaging

---

* Corresponding author. Tel.: +1 540 231 2480; fax: +1 540 231 8517.
E-mail address: telong@vt.edu (T.E. Long).

[1] Present address: Department of Material Science and Engineering, Cornell University, Ithaca, NY 14853, USA.

0032-3861/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2006.02.028

materials, films, and container products [14]. PET, which is commercially prepared via melt polymerization, contains parts per million (ppm) levels of residual metal catalysts [14]. Titanium and cobalt compounds are often used as catalysts for transesterification, and antimony oxide is commercially used as a catalyst to facilitate subsequent polycondensation. Although these residual metal salts may promote thermal degradation during melt processing, phosphoric acid is commonly added prior to the polycondensation stage to deactivate reactive residual catalysts [14].

Although some metal salts promote thermal degradation, efforts to develop PET composites containing metal salts has continued in an effort to obtain mechanical property enhancement at relatively low cost [15,16]. Many earlier efforts have focused on the random incorporation of strong ligands into the PET backbone to form macroligands, and it was demonstrated earlier that metal salts preferentially coordinated with the ligands without interaction with the PET carbonyl groups. As noted above, phosphine oxide is considered a strong ligand, and McGrath and coworkers demonstrated that polyimides containing phosphine oxide coordinate with metal salts through the phosphine oxide groups, despite an excess of adjacent imide carbonyl groups [8]. Fraser and coworkers also demonstrated that metal salts preferentially coordinate with bipyridine ligands without interacting with adjacent carbonyl groups [2]. This selective coordination via phosphine oxide interaction offers promise in the preparation of polyester-metal salt complexes for mechanical property enhancement without the deleterious effects of degradation. McGrath and coworkers reported the random incorporation of phosphine oxide units into PET via the comonomer, 4,4′-bis(carboxyphenyl) phenyl phosphine oxide [13a]. Unfortunately for packaging applications, the asymmetrical structure of the phosphine oxide units disrupted chain regularity, which resulted in amorphous polymers [13]. Our previous research demonstrated that the incorporation of functional and interactive sites at PET chain ends does not significantly reduce crystallinity [17–19]. Moreover, the incorporation of ligands in a telechelic fashion results in well defined structures with predictable distances between coordination sites. McGrath and coworkers demonstrated that intermolecular coordination resulted in crosslinking when the ligands were randomly incorporated along the polymer backbone [8]. Our current research involves a novel family of polyester–metal salt composites with a predictable distance between coordination sites prepared via the complexation of metal ions with phosphine oxide endcapped polyester oligomers. The synthesis, rheological performance, and morphology of these polyester–cobalt(II) chloride composites are described.

2. Experimental

2.1. Reagents and purification

Magnesium powder (99%), biphenyl phosphinic chloride (99%), 1-bromo-4-toluene (99%), triphenyl phosphine oxide (99%), iodine (99%), potassium permanganate (97%), cobalt chloride (99%), and pyridine were purchased from Aldrich and used as received. PET oligomer ($\eta_{inh}=0.08$ dL/g) was kindly donated from Eastman Chemical Company and used as received. Dimethyl terephthalate (DMT, 99%), and dimethyl isophthalate (DMI, 98%) were purchased from Aldrich and used as received. Ethylene glycol (EG) was purchased from Baker and used as received. Titanium tetra(isopropoxide) (99%) and antimony oxide (99%) were purchased from Aldrich, and the preparation of the catalyst solutions was described in a previous report [18].

2.2. Synthesis of endcapping reagents and telechelic polyesters

2.2.1. para-Toluene magnesium bromide, (**1**)

Magnesium powder (6.0 g, 0.25 mol) was added to a three-necked flask equipped with a magnetic stir bar, reflux condenser, and addition funnel. The flask was subsequently flushed with ultra pure argon, and approximately 200 mL of THF and iodine (10.0 mg) were added [16]. The heterogeneous mixture was stirred at 25 °C until the iodine color faded to colorless, and a solution of 1-bromo-4-toluene (35 g, 0.2 mol) in THF (50 mL) was added dropwise over a 1 h period. The temperature was then raised to 65 °C and maintained at reflux for 6 h. The product was used without isolation or characterization.

2.2.2. 4-Methylphenyl biphenyl phosphine oxide, (**2**)

A solution of biphenyl phosphinic chloride (0.20 mol) in 50 mL THF was added to the compound **1** solution via an addition funnel at room temperature over 30 min. The temperature was raised to 65 °C and maintained at reflux for 6 h. THF was removed via distillation under nitrogen purge, and vacuum was applied to ensure complete removal. The resulting product was isolated by adding 300 mL of toluene and 300 mL of a 10% H_2SO_4 solution and stirring at 60 °C for 30 min. The organic layer was separated and rinsed repeatedly with 200 mL 1 N NaOH solution followed by a final rinse with 300 mL of deionized water. The toluene was removed in a distillation apparatus to yield a white crystalline solid that was subsequently dried in vacuo at 80 °C for 24 h. Typical isolated yields ranged from 80 to 85%. ^{1}H NMR (DMSO-d_6, ppm): δ 2.10 (s, 3H,–CH_3); 7.25–7.38 (m, 2H); 7.45–7.62 (m, 12H). ^{13}C NMR (DMSO-d_6): δ 76.9; 127.8–128.8; 128.6–128.6; 128.9; 131.6–131.0; 132.6; 140.8. ^{31}P NMR (DMSO-d_6): δ 25.6. Mass spectra (FAB): $(M+H)^+=293$ Da.

2.2.3. 4-Carboxyphenyl biphenyl phosphine oxide (**3**)

Compound **2** (56.96 g, 0.16 mol), 300 mL pyridine, and 200 mL water were added to a 1000 mL three-necked flask equipped with a magnetic stir bar and condenser, and the temperature was raised to 70 °C. Excess $KMnO_4$ was added in 6–8 aliquots at 30 min intervals. After the last addition, the temperature was raised to 80–90 °C for 12 h. At the end of the reaction, the mixture was allowed to cool to room temperature and the excess $KMnO_4$ was filtered off. The red solution was then acidified with concentrated HCl, and a white powder was collected using a filter funnel. ^{1}H NMR spectroscopy revealed a small amount of residual methyl due to incomplete oxidation.

A second oxidation was performed in a stoichiometric amount of aqueous sodium hydroxide solution to obtain pure product. A slight stoichiometric excess (based on ^{1}H NMR analysis) of $KMnO_4$ was added to the reaction mixture, and the reaction was allowed to proceed at 80 °C for 6–8 h. The solution was filtered and acidified, and the white powder was collected using a filter funnel. Typical isolated yields after two oxidations were 90–95%. ^{1}H NMR (DMSO-d_6): δ 7.55–7.61 (m, 4H); 7.61–7.69 (m, 4H); 7.31–7.45 (m, 6H, ArH$_4$); 7.74–7.81 (m, 2H); 8.08–8.13 (m, 2H). ^{13}C NMR (DMSO-d_6): δ 120.8; 129.4; 131.6; 132.4, 132.8, 134.0; 136.8; 138.0; 166.8. ^{31}P NMR (DMSO-d_6): δ 26.1. Mass spectra (FAB): $(M+H)^+$: 323 Da. Anal. Calcd for $C_{19}H_{15}O_3P$: C, 70.80; H, 4.60; P, 9.61. Found: C, 70.45; H, 4.49; P, 9.50.

2.2.4. Phosphine oxide endcapped PET macroligand (L) via one step melt polymerization

PET macroligand containing 5 mol% phosphine oxide endcapper was prepared via a one step melt condensation of DMT, EG, and phosphine oxide endcapper. Both titanium tetraisopropoxide (20 ppm) and antimony oxide (200 ppm) were added to facilitate ester exchange and subsequent polycondensation. The reactor consisted of a 100 mL round-bottomed flask equipped with an overhead mechanical stirrer, nitrogen inlet, and condenser. The flask containing the monomers and catalysts was degassed under vacuum and nitrogen three times and subsequently heated to 190 °C. The reactor was maintained at 190 °C for 2 h, and the temperature was increased to 220 °C over 2 h. The reaction was allowed to proceed for 30 min at 275 °C. Vacuum was gradually applied to 0.5 mmHg and polycondensation continued for 2 h at 275 °C (Table 1).

2.2.5. Telechelic phosphine oxide PET macroligands (PET-L-x) and complexes of telechelic phosphine oxide PET and cobalt(II) chloride (PET-C-x) via melt polymerization of PET oligomer and phosphine oxide endcapper

Polymers were prepared via the melt condensation of PET oligomer ($\eta_{inh}=0.08$ dL/g) and phosphine oxide endcapper both with (PET-C-*x*) and without (PET-L-*x*) cobalt(II) chloride (50 mol% of phosphine oxide endcapper), where *x* denotes the molar ratio of the phosphine oxide endcapper to the polyester repeat units, L denotes ligand, and C denotes complexes of polymer and cobalt(II) chloride salt. Antimony oxide (200 ppm) was added to facilitate polycondensation. The reaction was allowed to proceed for 30 min at 275 °C. Vacuum was gradually applied to 0.30 mmHg and polycondensation continued for 2 h at 275 °C. Elemental analysis demonstrated that the phosphine oxide endcapper was quantitatively incorporated into the complexes (Table 2). The residual antimony catalyst was close to the charged level, and the influence of this low level of antimony ion (200 ppm) on the coordination of phosphine oxide groups can be neglected relative to the effect of the high concentration of cobalt salt.

Table 1
Molecular weights of macroligands and complexes

Sample	Endcapper (mol%)	$\eta_{inherent}$[a] (dL/g)	M_n[b] (g/mol)	M_n[c] (g/mol)
PET-L-3	3.3	0.33	11,700	11,000
PET-C-3	3.3	0.32	11,700	10,500
PET-L-5	5.2	0.25	7400	6600
PET-C-5	5.2	0.25	7400	6600
PETI-L-5	5.2	0.21	–	–
PETI-C-5	5.2	0.62	–	–

[a] Measured at 25 °C in a capillary viscometer using 0.5 g/dL solution in a 60/40 w/w mixture of phenol and tetrachloroethane.

[b] Estimated based on Eq. (1) and ^{1}H NMR spectrum.

[c] Estimated using Mark–Houwink equation.

Table 2
Results of elemental analysis

Sample	Endcapper (mol%)	*P*[a] (wt%)	Co[a] (wt%)	*P*[b] (wt%)	Co[b] (wt%)
PET-C-3	3.3	0.48	0	0.47	0
PET-L-3	3.3	0.48	0.46	0.48	0.39
PET-C-5	5.2	0.81	0	0.80	0
PET-L-5	5.2	0.81	0.77	0.82	0.76
PETI-C-5	5.2	0.81	0	0.81	0
PETI-L-5	5.2	0.81	0.77	0.80	0.76

[a] Theoretical values.

[b] Measured value.

2.2.6. Amorphous poly(ethylene terephthalate-co-isophthalate) (PETI) oligomer

Amorphous PETI oligomer was prepared via the melt condensation of dimethyl terephthalate (DMT) (50 mol%), dimethyl isophthalate (DMI) (50 mol%), and ethylene glycol (EG) (200 mol% of repeat units). Both titanium tetraisopropoxide (20 ppm) and antimony oxide (200 ppm) were added to facilitate ester exchange and subsequent polycondensation. The reactor consisted of a 100 mL round-bottomed flask equipped with an overhead mechanical stirrer, nitrogen inlet, and condenser. The reactor containing the monomers and catalysts was degassed using vacuum and nitrogen three times and subsequently heated to 190 °C. The reactor was maintained at 190 °C for 2 h, and the temperature was increased to 275 °C over 2 h. The reaction was allowed to proceed for 30 min at 275 °C. Vacuum was gradually applied to 0.30 mmHg and polycondensation continued for 10 min at 275 °C.

2.2.7. Amorphous PETI macroligand (PETI-L-5) and cobalt(II) chloride complexes (PETI-C-5)

The procedure used to prepare the PETI complexes was identical to that used to prepare the PET-L-5 and PET-C-5 complexes with the exception that amorphous PETI oligomer was used in place of the PET oligomer. The concentration of residual titanium catalyst (20 ppm) was much lower than that of cobalt(II) chloride, and the influence of the residual titanium catalyst on the coordination of phosphine oxide end groups and cobalt(II) ions was considered negligible. The amorphous PETI cobalt salt complexes (PETI-C-5) were soluble in chloroform and very stable.

2.2.8. Model blends

M-1: PET (7.0 g) and 3.0 g triphenyl phosphine oxide were blended in a 25 mL flask under nitrogen at 275 °C for 5 min.

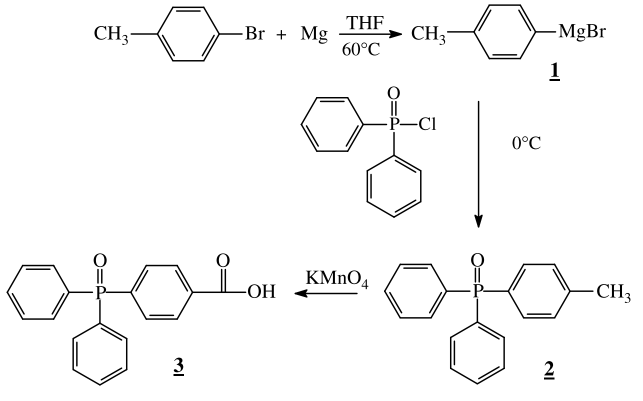
M-2: PET (7.0 g), 3.0 g triphenyl phosphine oxide (10.8 mmol), and 0.70 g (5.4 mmol) cobalt(II) chloride salt were blended in a 25 mL flask under nitrogen at 275 °C for 5 min.

2.3. Polymer and composite characterization

The inherent viscosities of the samples were measured at 25 °C in a capillary viscometer using a 0.5 g/dL solution in either a 60/40 w/w mixture of phenol and tetrachloroethane or chloroform. Solution ^{1}H, ^{13}C and ^{31}P {^{1}H} NMR spectra were recorded on a Varian 400 MHz spectrometer, and solid state NMR was performed on a MSL-300. Thermal transitions were determined on a Perkin–Elmer DSC Pyris 1 at a heating rate of 10 °C/min under N_2 purge, and reported data were obtained from the second heating cycle. The samples were heated to 290 °C and held for 10 min to eliminate any thermal history. The samples were then quenched to room temperature using nitrogen gas and heated to 290 °C at a rate of 10 °C/min. Melt rheological analysis was performed using a TA Instruments AR 1000 melt rheometer. Reflective UV–vis spectra were obtained on a Perkin–Elmer-300 spectrometer. Elemental analysis was performed at Eastman Chemical Company. GPC measurements were performed on a Waters 717 Autosampler SEC with Waters 515 Pump and external Waters 2410 Refractive Index Detector. Multi-angle laser light scattering (MALLS) was performed using an in-line Wyatt Technology miniDAWN. A Polymer Laboratories PLgel 5 micron MIXED-C column with a length of 300 mm and inner diameter of 7.5 mm was used. The flow rate was 1.00 mL/min and the temperature was 40 °C. FT-IR spectra were obtained using a MIDAC spectrophotometer equipped with a ZnSe reflection element.

3. Results and discussion

The synthetic methodology for the preparation of a novel monofunctional phosphine oxide endcapper is shown in Scheme 1. A double oxidation of 4-methylphenyl biphenyl phosphine oxide was used to ensure a highly pure product. The ^{1}H NMR spectrum verified that the oxidation reaction was quantitative (Fig. 1), and the presence of a single sharp peak in the ^{31}P {^{1}H} NMR spectrum confirmed that phosphorous-containing impurities were not present. Moreover, mass spectroscopy and elemental analysis verified the intended chemical structure.



Scheme 1. Synthesis of the phosphine oxide endcapping reagent, 4-carboxyphenyl biphenyl phosphine oxide.

The synthesis of PET via conventional melt polymerization consists of two steps, transesterification and subsequent polycondensation under reduced pressure [14]. The synthesis of high molecular weight PET macroligands was attempted using a one-step and a two-step synthetic methodology. The first method, which was a one-step reaction using DMT, a large excess of EG, phosphine oxide endcapper, and various catalysts to facilitate transesterification and polycondensation, failed due phosphine oxide deactivation of the metal catalysts as described earlier. When the temperature was raised to 220 °C after reaction at 190 °C for 2 h, a significant amount of DMT sublimed due to the low efficiency of ester exchange without active catalysts. ^{1}H NMR spectra revealed a high level of hydroxyl end groups, and inherent viscosity measurements (0.08 dL/g) confirmed that only low molar mass products were obtained. The second method involved a two-step reaction sequence in which PET macroligands were successfully prepared via the copolymerization of a precursor PET oligomer and phosphine oxide endcapper. First, terephthalic acid was reacted with a slight excess of EG in the absence of catalysts under moderately high (60 psi) pressure to prepare a low molar mass PET oligomer. The PET oligomer was subsequently copolymerized with phosphine oxide endcapper in the presence of an antimony based catalyst to facilitate polycondensation under reduced pressure. ^{1}H NMR spectroscopy and elemental analysis demonstrated that the phosphine oxide endcapper was quantitatively incorporated into the macroligand (Fig. 2 and Table 2) in a telechelic fashion, and well defined macroligands were obtained. Previous investigations in our laboratories also demonstrated that well defined polyesters with tailored functional groups at both chain ends (telechelic functional polyesters) may be prepared via melt polymerization using a monofunctional aromatic carboxylic acid endcapper in a similar fashion [18,19]. The endcapping reaction was quantitative, and the trace amount of polymer with undesired end groups did not significantly influence the thermomechanical properties.

Since excess ethylene glycol was used during the polymerization and subsequently removed via distillation during polycondensation, the conventional equation, $X_n=(1+r)/(1-r)$, was not applicable to estimate molar mass [18,19]. Based on the assumption that the endcapping reaction was quantitative and restricted to the polymer chain end, a modified equation (Eq. (1)) was utilized to estimate a theoretical number average molecular weight [18]

$$\langle M_n \rangle = \frac{\text{total mass of product}}{\text{moles of product}} = \frac{\sum(m_e + x m_{ru})}{N(A)/2} \qquad (1)$$

where, m_e, molar mass of the combined end groups; m_{ru}, molar mass of an internal repeat unit; $N(A)$, moles of monofunctional end capping reagent; x, number of internal repeat units.

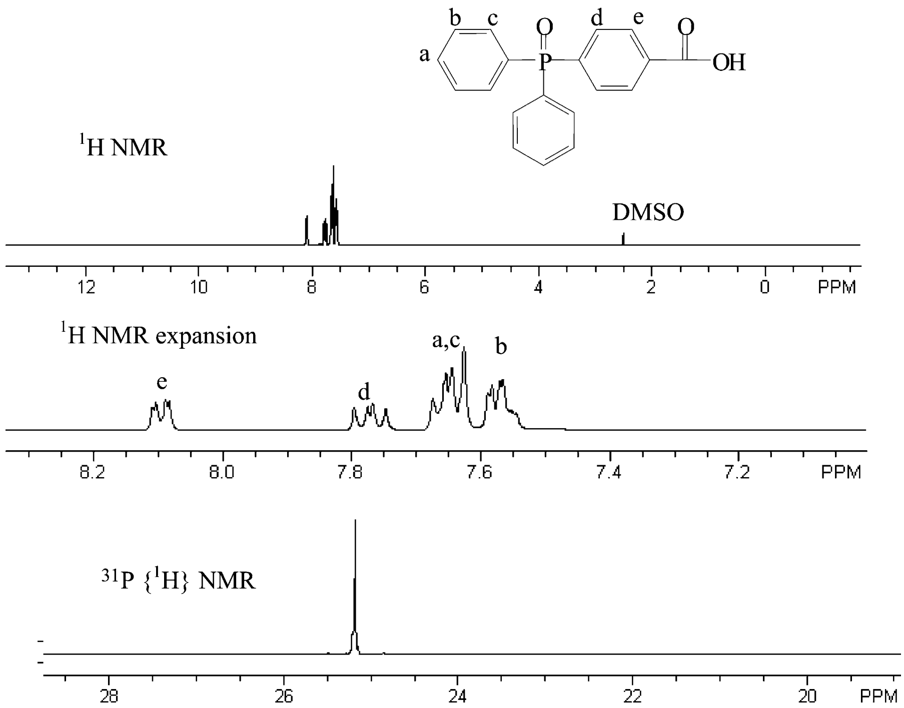


Fig. 1. ^{1}H and ^{31}P {^{1}H} NMR spectroscopy of 4-carboxyphenyl biphenyl phosphine oxide.

Table 1 lists the calculated $\langle M_n \rangle$ of the phosphine oxide endcapped PET macroligands as well as the approximate $\langle M_n \rangle$ based on inherent viscosity measurements and application of the Mark–Houwink relationship [20]. A 60/40 w/w mixture of phenol and tetrachlorethane was used as solvent for solution viscosity measurements of the semicrystalline PET samples. The PET samples dissolved in the phenol/tetrachloroethane mixture when heated at 100 °C for 10 min. Under these extreme conditions, the coordination between the phosphine oxide and the cobalt chloride was dissociated on the presumption that excess phenol forms a stable complex with phosphine oxide via hydrogen bonding [27]. The cobalt salt precipitated from solution and was filtered prior to the solution viscosity measurement. The solution viscosity of the dissociated oligomers (PET-C-*x*) was similar to the corresponding telechelic oligomers that were prepared in the absence of the cobalt salt (PET-L-*x*), which suggested that the melt polymerization led to well defined telechelic macroligands (Table 1). The theoretical $\langle M_n \rangle$ of the PET macroligands determined using Eq. (1) agreed well with the values estimated via the Mark–Houwink equation (Table 1 and Scheme 2). Amorphous PETI polymers were synthesized in order to characterize the macroligands using SEC and NMR spectroscopy in organic solvents as the semicrystalline PET telechelic oligomers were insoluble in common organic solvents. The molar mass of the 5.2 mol% phosphine oxide

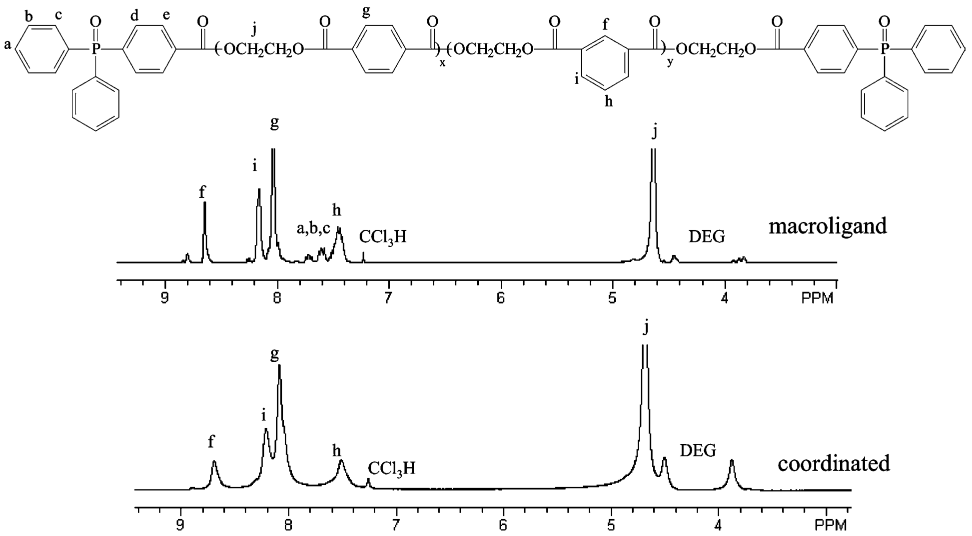
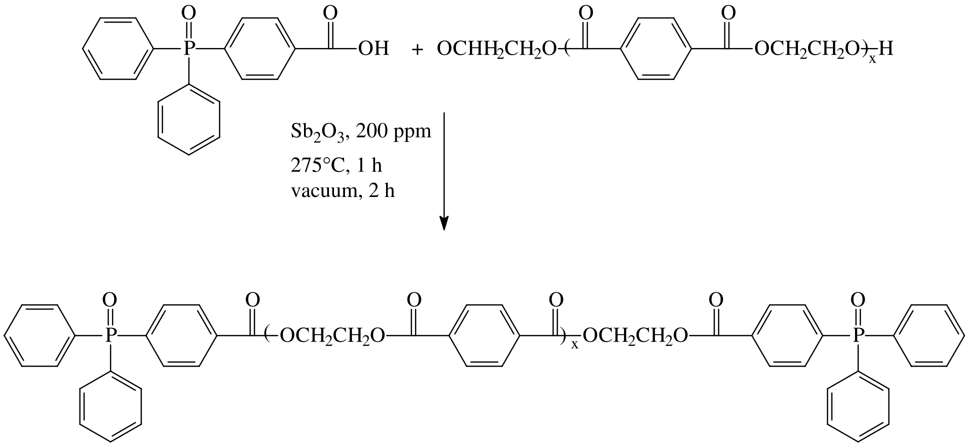


Fig. 2. ^{1}H spectra (chloroform, 400 MHz): PETI macroligand, PETI-L-5 (top); complex of phosphine oxide endcapped PETI with cobalt(II) chloride, PETI-C-5 (bottom).



Scheme 2. Synthesis of phosphine oxide endcapped PET macroligand, PET-L-*x*.

endcapped PETI (PETI-L-5) measured using SEC (M_n = 6300 g/mol, M_w = 14,200 g/mol) was within experimental error of the value (M_n = 7400 g/mol) predicted using ^1H NMR spectroscopy and the calculated value from Eq. (1). These results suggested that the endcapping reaction was quantitative and that the structure of the macroligands was well defined.

The PET macroligand-cobalt(II) chloride complexes (PET-C-*x*) were prepared via charging the cobalt(II) chloride, phosphine oxide endcapper, and PET oligomer into the flask simultaneously. Both the polymer melt and the final products exhibited a deep blue color. The proposed pseudo-tetrahedral structure of the complexes (Fig. 3) was based on prior research involving triphenyl phosphine oxide ligands [21]. Violet products were obtained when cobalt(II) chloride (2.5 mol%) and PET oligomer were reacted in the absence of phosphine oxide endcapper. A high molar mass product ($M_n > 20{,}000$ g/mol) was obtained in a short time after vacuum was applied to the system due to the presence of a high level of cobalt salt. In this high molecular weight polyester ($M_n > 20{,}000$ g/mol), it was presumed that the metal salt complexed with carbonyl sites in the repeating units as opposed to the relatively lower concentration of the hydroxyl end groups. The difference in color and UV–vis spectra between the samples with or without phosphine oxide endcapper indicated that the cobalt ions coordinated with different ligands depending on the presence of phosphine oxide end groups. Solid PET-C-*x* films containing phosphine oxide end groups and cobalt salt exhibited a broad peak at approximately 600 nm, which was similar to the $^4A_2 \rightarrow {}^4T_1(P)$ transition reported earlier for tetrahedral complexes of cobalt salts with triphenyl phosphine oxide [22]. The similarity between the obtained products and previous well defined triphenyl phosphine oxide complexes suggested that the cobalt(II) chloride coordinated with the phosphine oxide end groups preferentially to the carbonyl groups in the polyester backbone. The absorbance maximum was significantly shifted to 400 nm when cobalt(II) chloride (2.5 mol%) and PET oligomer were reacted in the absence of phosphine oxide endcapper. Solutions of amorphous PETI macroligands and cobalt(II) chloride complexes in chloroform exhibited spectra similar to those of the solid films, which suggested that the complexes were stable in relatively non-polar chloroform (Fig. 5).

The NMR resonances associated with the phosphine oxide endcapper were not present in the ^1H and ^{31}P {^1H} NMR spectra of the PET-C-*x* complexes, which suggested, based on limited molecular mobility, that a majority of the phosphine oxide groups coordinated with the cobalt(II) chloride (Fig. 2). McGrath and coworkers have demonstrated that when the phosphine oxide group coordinated with metal salts (up to 20 mol%) both a marked downfield shift and a broadening of the NMR signal were observed as the phosphine oxide group coordinated with the paramagnetic high spin Co(II) ion (d^9 with three unpaired electrons) [8]. However, if a majority of the phosphine oxide end groups are coordinated with paramagnetic Co(II) ions, then NMR resonances associated with the phosphine oxide ligands are expected to be too broad for detection. The coordinated phosphine oxide end groups were detected using solid state ^{31}P NMR spectroscopy (Fig. 4) at higher field strengths, and the resonance of the PET-C-5 complex shifted slightly downfield in the solid state ^{31}P NMR spectrum compared to the resonance of the PET-L-5 macroligand, which was consistent with previous reports [8].

FT-IR spectroscopy was used as a complementary tool to investigate the coordination of metal salts and phosphine oxide groups. Cotton and coworkers have demonstrated that the phosphoryl stretching frequency decreases upon complexation of phosphine oxide with metal salts [26]. McGrath and coworkers also demonstrated that the characteristic phosphine

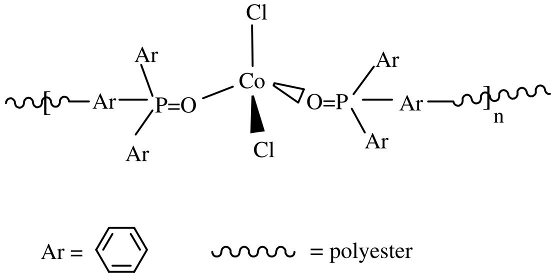


Fig. 3. The formation of linear polyester via coordination between the phosphine oxide end groups and cobalt chloride.

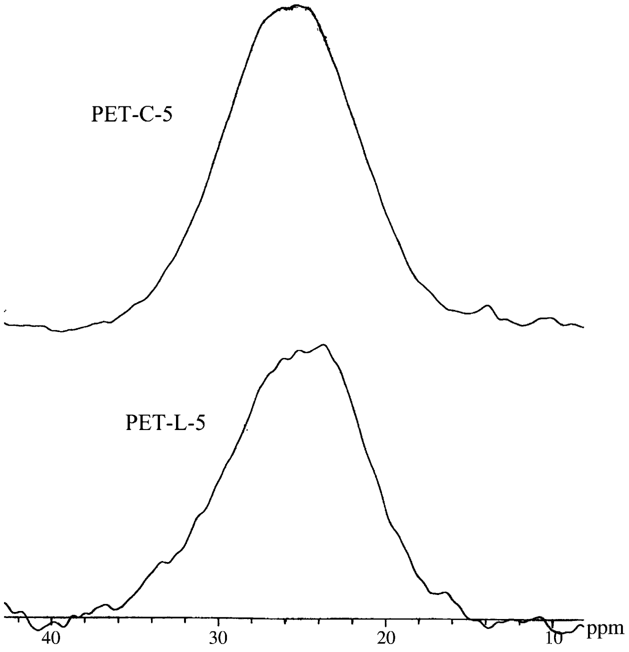


Fig. 4. Solid state ^{31}P NMR spectroscopy: complex of phosphine oxide endcapped PET and cobalt(II) chloride, PET-C-5, (top); macroligand, PET-L-5, (bottom).

oxide peak at 1190 cm^{-1} weakened or disappeared and a new band at 1145 cm^{-1} appeared upon coordination of the phosphine oxide groups with metal salts [8]. In this study, the characteristic absorbance of phosphine oxide at 1190 cm^{-1} was only a small shoulder on the carbonyl absorbance due to a relatively low chain end concentration (Fig. 6). This shoulder disappeared when cobalt(II) ions were introduced (PET-C-5). Model blends were also prepared by blending PET and triphenyl phosphine oxide with (M-2) and without (M-1) cobalt(II) chloride. The characteristic phosphine oxide absorbance at 1190 cm^{-1} was not present in the spectrum of the M-2 sample (Fig. 7), which indicated that the cobalt(II) ions preferentially coordinated with the phosphine oxide groups. Another absorbance should appear at a lower wavelength; however, this new absorbance was not resolved from strong absorbances associated with the polymer repeating unit.

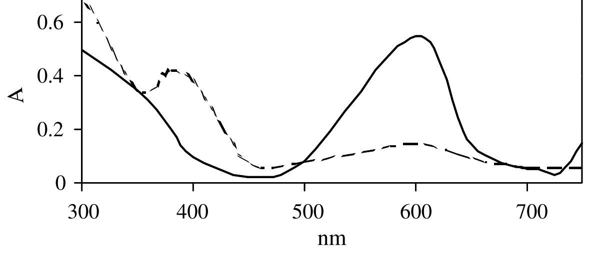


Fig. 5. UV–vis spectra of a chloroform solution (0.5 g/dL) of PETI complexes with cobalt(II) chloride: solid line: PETI-C-5, 5 mol% phosphine oxide endcapped PETI macroligand with 2.5 mol% cobalt(II) chloride; dashed line: PETI with 2.5 mol% cobalt(II) chloride.

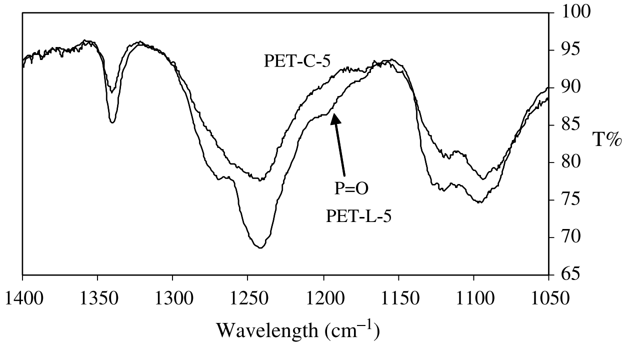


Fig. 6. ATR FT-IR spectra of macroligand, PET-L-5, (bottom); complex of phosphine oxide endcapped PET and cobalt(II) chloride, PET-C-5, (top).

DSC was used to investigate the thermal transitions of the telechelic oligomers and corresponding Co(II) salt complexes. For the moderate molar mass PET-L-5 macroligand ($\eta_{\text{inherent}}=0.25$ dL/g), only a melt transition was observed at 240 °C due to rapid crystallization during quenching. However, the cobalt salt complex (PET-C-5) of equivalent inherent viscosity behaved similarly to high molar mass PET. In particular, an obvious glass transition onset (72 °C), crystallization transition (149 °C, $\Delta H=35.0$ J/g), and melt transition (240 °C, $\Delta H=42.7$ J/g) were all clearly observed. These results were consistent with the explanation that Co(II) ions coordinated with the phosphine oxide end groups to form higher apparent molar mass polymers [8]. Gelation was not observed, and in all cases, the metal coordinated telechelic oligomers formed homogeneous solutions, which was consistent with the absence of appreciable crosslinking.

The melt viscosity versus temperature curves of the macroligand (PET-L-5, $\eta_{\text{inherent}}=0.25$ dL/g) and cobalt salt complex (PET-C-5, $\eta_{\text{inherent}}=0.25$ dL/g) are depicted in Fig. 8, which shows that the cobalt salt complex exhibited higher melt viscosity than the salt-free telechelic analogue. Moreover, a high concentration of Co(II) salt did not result in degradation of the polymer during the high temperature polymerization process (~0.5 h >240 °C). The flow activation energies of the cobalt salt complex (PET-C-5) and the salt-free telechelic analogue (PET-L-5) were estimated using Eq. (2) (Fig. 9) [28]:

$$\ln(\eta^*) = A + \left(\frac{E_a}{R}\right)^* \left(\frac{1}{T}\right) \tag{2}$$

The data fit Eq. (2) significantly well ($R^2>0.99$), and the flow activation energies (PET-C-5 complex: 43.1 KJ/mol;

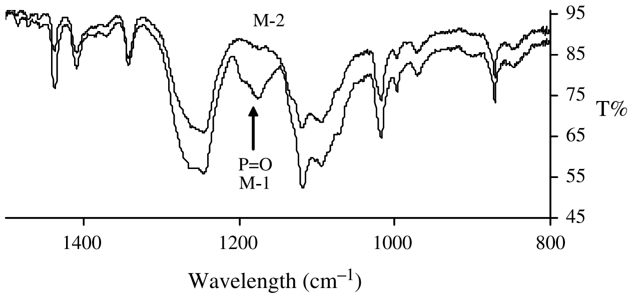


Fig. 7. ATR FT-IR spectra of model blends: M-1, blend of PET and triphenyl phosphine oxide (bottom); M-2, blend of PET, triphenyl phosphine oxide and cobalt(II) chloride, (top).

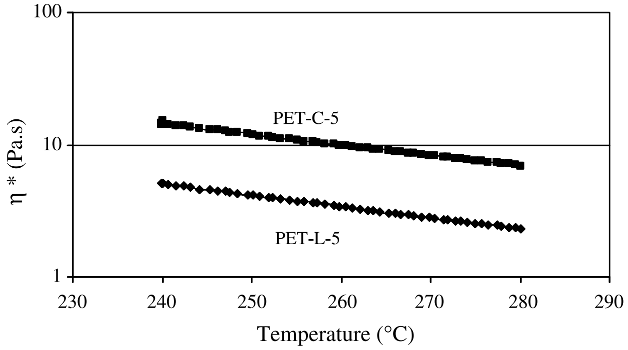


Fig. 8. Rheological analysis (temperature ramp) of PET-L-5 macroligand (bottom) and PET-C-5 complex (top).

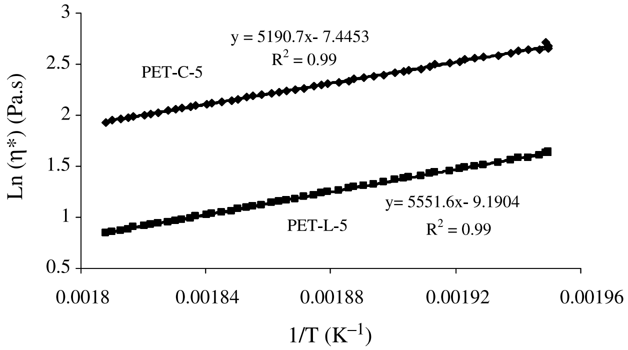


Fig. 9. Calculation of flow activation energy of PET-L-5 macroligand (bottom) and PET-C-5 complex (top).

PET-L-5 macroligand: 46.1 kJ/mol) were similar, which was consistent with the absence of strong intermolecular interaction in the PET-C-5 cobalt salt complex [20,29]. The presumption of coordination of a single Co(II) ion with two phosphine oxide ligands was consistent with previous reports [8].

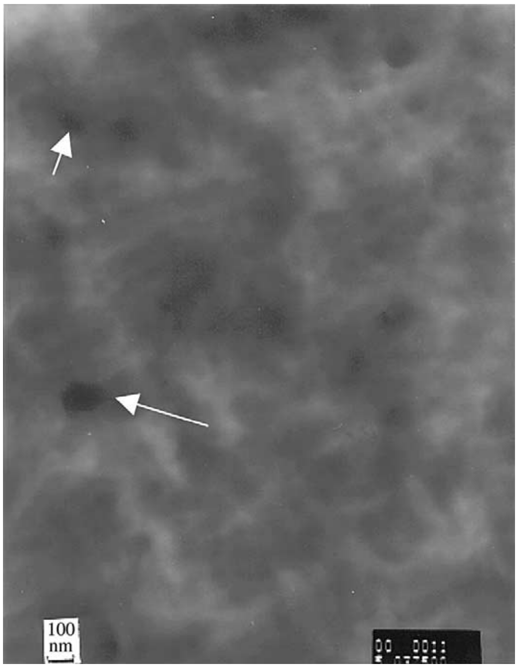


Fig. 10. TEM analysis of PET-C-5 complex of telechelic phosphine oxide PET (5 mol% phosphine oxide end groups) and 2.5 mol% cobalt(II) chloride.

Polar inorganic components tend to aggregate in polymer–inorganic hybrid materials via nonspecific dipole–dipole interactions. The inorganic aggregates are clearly observed using TEM as the electronic density of the inorganic aggregates is significantly different from the polymer matrix [8]. TEM showed no significant aggregation of the inorganic component in the PET-Co(II) salt hybrid materials (PET-C-3) with 3.0 mol% phosphine oxide endcapper and 1.5 mol% Co(II) chloride. This result indicated that the cobalt salt was dispersed in the PET matrix on the molecular level. When the concentration of cobalt salt was increased to 2.5 mol% (PET-C-5), a few small aggregates (∼100 nm) were randomly distributed in the PET matrix (Fig. 10). These results indicated that the introduction of telechelic phosphine oxide containing groups effectively dispersed a high level (up to ∼1.5 wt%) of polar metal salt homogeneously in polyester matrices without significant aggregation.

4. Conclusions

A novel phosphine oxide containing endcapper, 4-carboxyphenyl biphenyl phosphine oxide, was synthesized, and the purity of the endcapper was verified using NMR spectroscopy, mass spectroscopy, and elemental analysis. Phosphine oxide endcapped polyester macroligands were quantitatively prepared via the copolymerization of moderate molecular weight PET oligomer precursor and endcapper. The quantitative incorporation of phosphine oxide functionality was confirmed using ^{1}H NMR spectroscopy and elemental analysis. Complexes of macroligands and cobalt(II) salt were prepared via charging the cobalt(II) chloride at the onset of polymerizations. NMR spectroscopy, FT-IR, and UV–vis indicated that the cobalt(II) ion preferentially coordinated with the phosphine oxide end groups. The complexes exhibited higher melt viscosity than analogues without cobalt salts, and the phosphine oxide end groups aided the dispersion of cobalt(II) chloride in a PET matrix.

Acknowledgements

The authors thank Eastman Chemical Company for financial and analytical support and Mr Thomas Glass for assistance with solid state ^{31}P NMR spectroscopy. The authors also thank Prof Jim McGrath for many years of insightful discussions, inspiration, and friendship.

References

[1] (a) Manners I. Science 2001;294:1664.
(b) Schubert US, Eschbaumer C. Angew Chem Int Ed 2002;41:2892.
(c) Lohmeijer BGG, Schurbert US. J Polym Sci, Part A: Polym Chem 2003;41:1413.
(d) Gohy JF, Lohmeijer BGC, Varshney SK, Schubert US. Macromolecules 2002;35:7427.
[2] (a) Smith AP, Fraser CL. Macromolecules 2002;35:594.

(b) Bender JL, Corbin PS, Fraser CL, Metcalf DH, Richardson FS, Thomas EL, et al. J Am Chem Soc 2002;223:408.
(c) McAlvin JE, Scott SB, Fraser CL. Macromolecules 2000;33:6953.
(d) Fraser CL, Smith AP, Wu XF. J Am Chem Soc 2000;122:9026.
(e) Wu XF, Fraser CL. Macromolecules 2000;33:4053.
(f) Wu XF, Collings JE, McAlvin JE, Fraser CL. Macromolecules 2001; 34:223.

[3] Vitalini D, Mineo P, DiBella S, Fragala I, Maravigna P, Scamporrino E. Macromolecules 1996;29:448.

[4] Yang JM, Hsiue GH. Macromolecules 1991;24:4010.

[5] (a) Chen L, Xu H, Yu XH, Yang CZ. J Polym Sci, Part A: Polym Chem 1996;34:721.
(b) Lin Q, Cheng D, Yu X. Chin J Inorg Chem 1998;14:287.

[6] Peters MA, Belu AM, Linton RW, Dupray L, Meyer TJ, DeSimone JM. J Am Chem Soc 1995;117:3380.

[7] (a) Hechet S, Ihre H, Fréchet JMJ. J Am Chem Soc 1999;121:9239.
(b) Giannelis EP. Adv Mater 1996;8:29.

[8] (a) Bonaplata E, Smith CD, McGrath JE. ACS Symp Ser 1995;603:227.
(b) Wang S, Zhuang H, Sankarapandian M, Shoba HK, Ji Q, Shultz AR, et al. Polym Prepr 2000;41(2):1350.
(c) Spinu M, McGrath JE. J Org Inorganomet Chem Polym 1992;2:103.
(d) Wang S. PhD Dissertation, Virginia Polytechnic Institute and State University; 2000.

[9] (a) Grohn F, Bauer BJ, Akpalu YA, Jackson LC, Amis EL. Macromolecules 2000;33:6042.
(b) Sooklal K, Hanus LH, Ploehn HJ, Murphy CJ. Adv Mater 1998;10: 1083.

[10] Jungmann N, Schmidt M, Maskos M. Macromolecules 2003;36:3974.

[11] (a) Cheng H, Horton PN, Hursthouse MB, Hii KK. Tetrahedron: Asymmetry 2004;15:2241.
(b) Hursthouse MB, Levason W, Ratnani R, Reid G. Polyhedron 2004; 23:1915.
(c) Priya S, Balakrishna MS, Mague JT. Inorg Chem 2003;42:1272.
(d) Paine RT, Bond EM, Parveen S, Donhart N, Duseler EN, Smith KA, et al. Inorg Chem 2002;42:444.
(e) Hasegawa Y, Yamamuro M, Wada Y, Kanehisa N, Kai Y, Yanagida S. J Phys Chem A 2003;107:1697.
(f) Hasegawa Y, Kimura Y, Murakoshi K, Wada Y, Kim J, Nakashima N, et al. J Phys Chem 1996;100:10201.

[12] Green M, O'Brien P. Chem Mater 2001;13:4500.

[13] (a) Wan I, Keifer LA, McGrath JE, Kashiwagi T. Polym Prepr 1995; 36(1):491.
(b) Wang S, Zhuang H, Shobba HK, Glass TE, Sankarapandian M, Ji Q, et al. Macromolecules 2001;34:8051.
(c) Ji Q, Muggli M, Wang F, Ward TC, Burns G, Sorathia U, et al. Polym Prepr 1997;37(2):120.
(d) Smith CD, Grubbs HJ, Webster HF, Gungor A, Wightman JP, McGrath JE. High Perform Polym 1991;4:211.
(e) Riley DJ, Gungor SA, Srinivasan S, Sankarapandian M, Tchatchoua CN, Muggli MW, et al. Polym Eng Sci 1997;37:150.
(f) Lin Q, Long TE. J Polym Sci, Part A: Polym Chem 2001;38:3736.
(g) Czupik M, Fossum E. J Polym Sci, Part A: Polym Chem 2003;41: 3871.
(h) Rusch-Salazar LA, Sheares VV. J Polym Sci, Part A: Polym Chem 2003;41:2277.
(i) Bernal DP, Bankey N, Cockayne RC, Fossum E. J Polym Sci, Part A: Polym Chem 2002;40:1456.
(j) Kim JP, Kang JW, Kim JJ, Lee JS. J Polym Sci, Part A: Polym Chem 2003;41:1503.

[14] (a) Goodman I, Sheanan RJ. Eur Polym J 1990;26:1081.
(b) Goodman I, Rodriguez MT. Macromol Chem Phys 1994;195:1705.
(c) Lawton EL. Polym Eng Sci 1985;25:348.

[15] Simionescu C, Vasiliu-Opre C. Polym Prep 1972;13(1):584.

[16] Simionescu C. Makromol Chem 1973;163:75.

[17] Lin Q, Wang ZH, Ratta V, Wilkes GL, Long TE. Polym Int 2002;51:540.

[18] Kang H, Lin Q, Armentrout RS, Long TE. Macromolecules 2002;35: 8738.

[19] Lin Q, Unal S, Fornof A, Wei Y, Li H, Armentrout RS. Macromol Symp 2003;199:163.

[20] (a) Nelson CJ. J Polym Sci Chem Ed 1974;44:2905.
(b) Youk JH, Kambour RP, MacKnight WJ. Macromolecules 2000;33: 3594.
(c) Zhang B, Weiss RA. J Polym Sci, Polym Chem 1992;30:91.
(d) Zhang B, Weiss RA. J Polym Chem 1992;30:989.

[21] (a) McAuliffe CA, Pritchard RG. J Chem Soc, Dalton Trans Inorg Chem 1995;1095.
(b) Godfrey SM, McAuliffe CA, Ranger GC, Kelly DG. J Chem Soc, Inorg Chem 1993;2089.
(c) Cotton SA, Franckevicius V. Transition Met Chem 2002;27:38.

[22] Kato H, Akimoto K. J Am Chem Soc 1974;96:1351.

[26] Cotton EA, Soderberg RH. J Chem Soc 1960;82:5771.

[27] (a) Watson EK, Rickelton WA, Robertson AJ, Brown TJ. Solvent Extr Ion Exch 1988;6:207.
(b) Lagier CM, Olivirei AC, Hariss RK. J Chem Soc, Perkin Trans 2 Phys Org Chem 1998;1791.

[28] Rosen SL. Fundamental principles of polymeric materials. New York: Wiley; 1993.

[29] Blyer LL, Hass TW. J Appl Polym Sci 1969;13:2721.