

# Preparation and characterisation of aggregating comblike poly(propylene oxide)

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## Abstract

Poly(propylene oxide)s with a comblike architecture were prepared by using an ethylene–vinyl alcohol copolymer as a macroinitiator for anionic graft polymerisation of propylene oxide. The densely grafted polymers were subsequently modified by capping the terminal hydroxyl groups with hexadecanoyl chloride to produce aggregating polymers. Dilute solution viscometry showed that the hydroxyl and hexadecanoyl content of the uncapped and capped polymers, respectively, largely determined their state of aggregation in methanol and toluene. Thermal analysis of the uncapped polymers in the solid state showed a decrease in glass transition temperature with increasing average molecular weight of the grafts. Analysis of the capped polymers revealed crystallisation and melting of the hexadecanoyl chain ends in connection with the glass transition of the poly(propylene oxide) phase. It is conceivable that in the solid state the comblike poly(propylene oxide) chains were interconnected by ‘micellar-like’ microdomains formed by the hexadecanoyl chain ends. © 2000 Elsevier Science Ltd. All rights reserved.

*Keywords:* Comb polymers; Graft copolymerisation; Propylene oxide

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## 1. Introduction

Aggregating polymers have been extensively studied over the years, both from practical and theoretical points of view. The bulk of this work has been done on water soluble polymers in water based systems. An obvious reason for this is the many industrial applications for these polymers, including surfactants, associative thickeners, gelling and flocculating agents, etc. However, polymer aggregation in non-aqueous systems is also of considerable interest. One important emerging area is the use of aggregating polymers in anhydrous electrolytes [1,2]. These electrolytes can for example be used as electrolytic separators between the electrodes in lithium polymer batteries [3,4]. To enhance ionic conductivity, the polymer electrolytes may be plasticised by an electrolyte solution consisting of a lithium salt dissolved in an organic solvent. The primary role of the polymer component in these gel-type electrolytes is to immobilise the electrolyte solution and to provide mechanical stability. Although the mechanical stability of most of the studied gels has relied either on entanglements, as a result of high molecular weight, or on chemical crosslinks, stability can also be obtained by interpolymer aggregation as a result of phase separation of specific structural parts of the polymer.

This type of physical interpolymer linking may offer advantages in the preparation and performance of gel electrolytes.

Polymers investigated for application as gel electrolytes include poly(methyl methacrylate), poly(vinylidene difluoride), polyacrylonitrile, and poly(ethylene oxide) [3–7]. Another attractive candidate is poly(propylene oxide) (PPO), a flexible and completely amorphous polymer with a glass transition temperature of approximately  $-75^{\circ}\text{C}$ . Studies of PPO in electrolytic systems have almost exclusively been carried out using linear low molecular weight samples employed as solid polymer electrolytes, that is, without the presence of a plasticising solvent [8,9]. When used as a solid polymer electrolyte, PPO can be expected to have a poorer ability to dissolve salts and form ion–polymer complexes as compared to poly(ethylene oxide) [10]. However, these drawbacks should be of minor importance if PPO is employed in gel electrolytes where the solvent facilitates ion solvation and conductivity.

The present paper reports on the preparation and characterisation of some aggregating high molecular weight PPO polymers having a comblike architecture. The ability of these polymers to aggregate in organic solvents is important for their intended use in gel electrolytes. Comblike polymers are generally characterised by having high concentrations of chain ends, and by forming brushlike conformations. Because the backbone polymer of these

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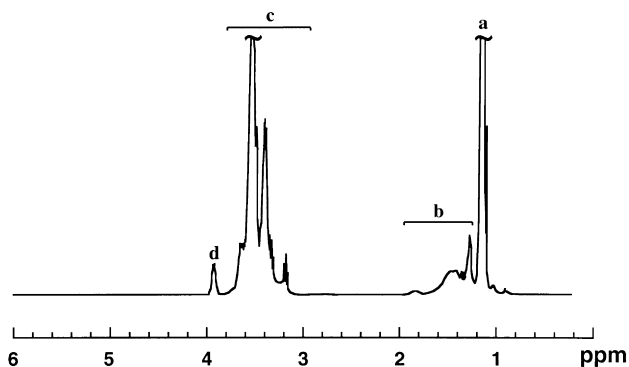


Fig. 1.  $^1\text{H}$  NMR spectra for CPPO690 showing shifts from: (a) PPO methyl protons; (b) PPO methylene and methine protons; (c) backbone methylene protons; and (d) methine protons closest to the terminal PPO hydroxyl group.

copolymers is sterically shielded, they do not normally aggregate in solution. Aggregating polymers may however be obtained by for example attaching chain segments with a dissimilar degree of polarity at the ends of the grafts. The comblike PPO polymers in the present study were prepared by first grafting an ethylene–vinyl alcohol backbone copolymer with propylene oxide. Subsequently, hexadecanoyl units were attached to the ends of the grafts through esterification. The behaviour of the polymers was studied by DSC in the solid state and by viscometry in solution. The aggregation and performance of these polymers in gel electrolytes will be reported in future communications.

## 2. Experimental

### 2.1. Preparation and purification

The comblike poly(propylene oxide)s (CPPO) were prepared by grafting an ethylene–vinyl alcohol copolymer (EVOH,  $M = 55\,000$ , containing 55 mol% vinyl alcohol, du Pont) with propylene oxide (PO). A 200 ml reactor consisting of a glass cylinder fitted between a stainless steel top and bottom, and equipped with a high speed stirrer was used in the grafting reactions. The reactor was further equipped with a gas inlet/outlet, a thermocouple, and a pressure transducer. EVOH was dried in vacuum for 48 h at  $60^\circ\text{C}$ , and dimethyl sulfoxide (DMSO, Merck,  $<0.05\%$   $\text{H}_2\text{O}$ ), was dried over molecular sieves. NaH (Aldrich, 60% dispersion in mineral oil) and PO (Acros, p.a.) were used as received.

The reactor was charged with DMSO, EVOH, and NaH and carefully degassed. A 100 ml glass vessel containing a specific amount of degassed PO was connected to the gas inlet/outlet of the reactor. PO was thereafter transferred to the reactor all at once, and the mixture was heated to  $80^\circ\text{C}$ . The polypropoxylation was allowed to proceed until all the PO in the reactor had been consumed, that is, until the pressure had dropped to a constant value. After that, the reaction mixture was cooled, carefully degassed, and kept at  $8^\circ\text{C}$  until the product was purified.

The CPPO polymers were first precipitated in water from the reaction mixture and dried in vacuum. Purification of the polymers was performed by fractionation in water/methanol solutions at ambient temperature. Water was slowly added to clear methanol solutions until a separate cloudy phase was formed. This cloudy phase was collected and dried to obtain the purified CPPO polymer. The purity was finally checked by gel permeation chromatography (GPC) after drying in vacuum at ambient temperature. GPC analyses were run with THF on Waters ultra-Styrigel columns with pore sizes  $10^5$ ,  $10^4$ ,  $10^3$  and  $500\text{ \AA}$ , using an RI-detector. The flow rate was 1.0 ml/min at  $25^\circ\text{C}$ .

The hydroxyl chain ends of all the CPPO polymers except the sample with the lowest PPO content were capped by hexadecanoyl units. Purified CPPO was dissolved in toluene (Merck, p.a.) in an  $\text{N}_2$  purged glass reactor to form a 10% (wt/v) solution. After heating to  $50^\circ\text{C}$ , a 10% excess of hexadecanoyl chloride (Acros, 98%) was added. The degree of esterification was followed by IR spectroscopy. After reaction, the reaction mixture was dried and the hexadecanoyl capped CPPO, designated hCPPO, was purified by successive extractions in methanol/isooctane mixtures. The sample hCPPO690 was purified by direct precipitation in MeOH.

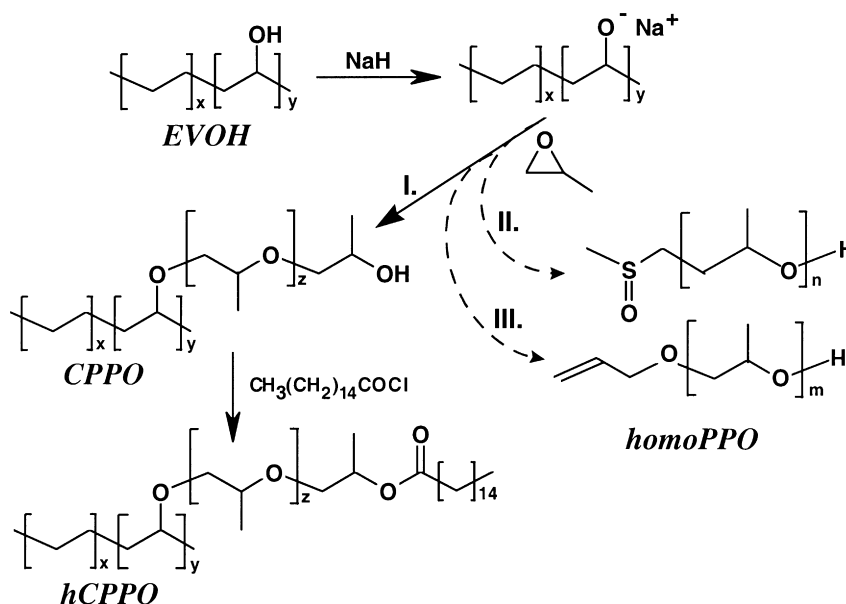
### 2.2. Structural characterisation

Infrared spectra were recorded with a Bruker IFS 66 FTIR spectrometer, using films cast onto KBr prisms from chloroform solutions. The capping reaction was monitored by IR analysis of reaction mixtures placed on KBr prisms.

$^1\text{H}$  NMR spectra of CPPO and hCPPO dissolved in chloroform- $d$  were recorded at ambient temperature using a Bruker ARX500 instrument. Chemical shifts are reported as ppm downfield from tetramethyl silane. A typical NMR spectrum of the CPPO polymers is shown in Fig. 1. It is characterised by shifts from PPO methyl protons at  $\delta = 1.1$ , from EVOH methylene protons at  $\delta = 1.2\text{--}1.75$ , from PPO main chain protons at  $\delta = 3.2\text{--}3.75$ , and from methine protons closest to the terminal PPO hydroxyl groups at  $\delta = 3.9$ . After capping, new shifts appeared at  $\delta = 0.9$ , and at  $\delta = 1.2$  originating from hexadecanoyl methyl and methylene protons, respectively. The compositions of the polymers were calculated by integration and comparison of the characteristic signals. A spectrum of EVOH was recorded using the same conditions, but with DMSO- $d_6$  as solvent. The vinyl alcohol content of the EVOH copolymer was calculated to be 55 mol% by comparing the integrated signals of the methylene protons at  $\delta = 1.2\text{--}1.6$ , and the combined integrated signals from the methine and hydroxyl protons at  $\delta = 3.3\text{--}4.4$ .

### 2.3. Viscometry

Viscometric properties of CPPO and hCPPO were investigated in dilute methanol (Merck, p.a.) and toluene (Merck, p.a.) solutions (0.5–8 g/l) at  $25^\circ\text{C}$  using Ubbelohde



capillary viscometers. Before measurements the solutions were filtered through 0.2  $\mu\text{m}$  Millipore PTFE filters. Limiting viscosities ( $[\eta]$ ) were evaluated from Huggins equation.

#### 2.4. Differential scanning calorimetry

The thermal properties of the pure CPPO and hCPPO polymers were analysed with a Mettler TA 3000 DSC system under  $\text{N}_2$  purge. The samples were contained in aluminium pans and were first annealed at 100°C for 5 min. After cooling down to  $-150^\circ\text{C}$ , the samples were heated to 100°C. The scan rate was in both cases 10°C/min. Glass transition temperatures ( $T_g$ ) were evaluated from the heating scan.

### 3. Results and discussion

Comblike PPO polymers were prepared by anionic polymerisation of PO from an EVOH backbone copolymer, followed by end capping of the terminal hydroxyl groups by using hexadecanoyl chloride (Scheme 1, Route I). The uncapped and capped polymers are designated CPPO and

hCPPO, respectively, followed by their average PPO graft molecular weight,  $M_{\text{graft}}$ . The amounts charged in the polymerisations, and the molecular data of the resulting polymers are shown in Table 1. Copolymers having PPO grafts have previously been prepared by copolymerisation of monoacrylate functional PPO macromonomers with styrene [11,12] and methyl methacrylate [13]. The macromonomer method gave graft copolymers with well-defined  $M_{\text{graft}}$ . However, in some cases the overall molecular weight of the copolymers had to be kept low in order to avoid crosslinking and subsequent gel formation [12]. In contrast, quite different polymers were obtained by the present grafting method. The original EVOH copolymer had  $M = 55\,000$  and contained 55 mol% vinyl alcohol. This led to the formation of densely grafted CPPO polymers with an average of  $\sim 1$  graft chain attached to every fourth carbon atom in the backbone. As a consequence of the dense grafting, the CPPO polymers were quite large molecules with  $M$  ranging from  $\sim 2 \times 10^5$  for CPPO200 to over  $\sim 1 \times 10^6$  for CPPO1700. Moreover, the backbone EVOH copolymer constituted only a minor part of the CPPO polymers.

The PO grafting yields shown in Table 1 were defined as

Table 1  
Preparation of CPPO polymers

Sample	Charged amounts				$M_{\text{graft}}^a$ (g/mol)	PPO graft content <sup>a</sup> (wt%)	Grafting yield <sup>a</sup> (%)	$I_d/I_m^b$
	EVOH (g)	PO (g)	NaH (mg)	DMSO (ml)				
CPPO200	18.00	53.20	90	60	200	75	$\sim 100$	$\sim 0$
CPPO690	3.00	32.20	90	80	690	91	95	0.5
CPPO1500	1.80	48.60	90	60	1500	96	82	0.9
CPPO1700	0.90	49.50	90	60	1700	96	46	1.2

<sup>a</sup> Evaluated by  $^1\text{H}$  NMR analysis of purified samples.

<sup>b</sup> Evaluated by  $^1\text{H}$  NMR analysis of dried reaction mixtures.

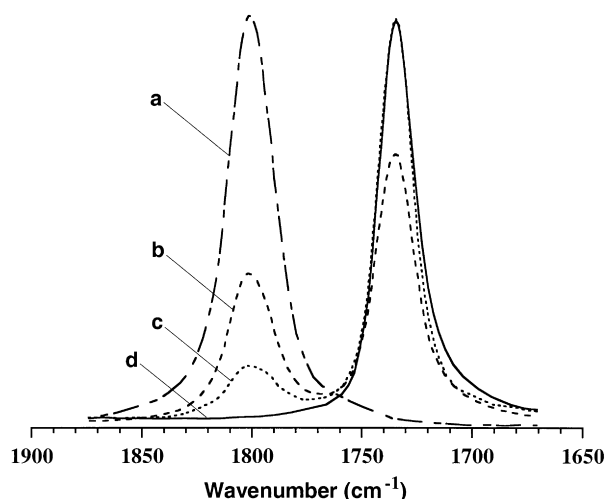


Fig. 2. IR spectra showing the gradual change in the carbonyl region during the preparation of hCPPO690. Spectra are shown for hexadecanoyl chloride (a), for reaction mixtures isolated during the preparation of hCPPO690 after 30 (b), and 120 min. (c) reaction time. Also shown is the spectrum of the purified polymer after reaction (d). An absorption band at  $1380\text{ cm}^{-1}$  was used as internal reference for the spectra b–d.

the percentage of the charged PO actually grafted onto the EVOH backbone. As seen, the yield decreased sharply from essentially 100%, for CPPO200, down to only 46% for CPPO1700. GPC analysis of reaction mixtures revealed that the low yields were due to formation of homopolymer (homoPPO). Base catalysed anionic polymerisations of epoxy monomers other than ethylene oxide are known to be plagued by chain transfer to monomer [14]. This type of chain transfer process converts PO to allyl alcohol anions which are able to initiate further polymerisation (Scheme 1, Route III). Thus, the maximum molecular weight of homoPPO obtained by base catalysed polymerisations is limited by the ratio of the rates of propagation to chain transfer, and has been found to be approximately 6000 at operable temperatures [14]. However,  $^1\text{H}$  NMR analysis of dried reaction mixtures showed only very small traces of unsaturation (at  $\delta = 5.1\text{--}5.3$ ) and it was concluded that the degree of homoPPO formation observed could not be a result of chain transfer to monomer alone.

Another route for the formation of homoPPO is via chain transfer to solvent, in this case to DMSO. In this process dimsyl ions capable of initiating polymerisation of PO are formed (Scheme 1, Route II). EVOH copolymers have previously been grafted with ethylene oxide in the presence of DMSO [15]. One conclusion from these experiments was that high graft yields can be obtained provided that the catalyst load, defined as  $\text{mol NaH/mol hydroxyl} \times 100\%$ , was kept low. Thus, yields exceeding 95% were obtained if catalyst loads of less than 8% were employed. In the present study, the catalyst loads were 1.4, 8.5, 14, and 28% for the preparation of CPPO200, CPPO690, CPPO1500, and CPPO1700, respectively, keeping a concentration of  $\sim 0.03$  mol active deprotonised hydroxyl

groups per litre reaction mixture. The data in Table 1 indicates that the yield decreased sharply with increasing catalyst load.  $^1\text{H}$  NMR analysis of dried reaction mixtures showed quite large shifts at  $\delta = 2.5$  arising from dimsyl end groups on homoPPO. Table 1 shows values of the index  $I_d/I_m$ , where  $I_d$  is the integrated signal arising from the dimsyl protons, and  $I_m$  is the integrated signal from the EVOH methylene protons at  $\delta = 1.2\text{--}1.75$ . As seen, the index increased with increasing catalyst load. In conclusion, the poor grafting yields were mainly a consequence of chain transfer to DMSO caused by high catalyst loads. In this context it should be mentioned that the graft polymerisation of PO was not initiated at lower catalyst concentrations than  $\sim 0.03$  mol/l. The successful removal of homoPPO by fractionation was confirmed by chromatography.

At least two ways to improve the grafting yield can be envisaged from the grafting results obtained. The first is simply to avoid the use of DMSO. Unfortunately, the semi-crystalline and strongly hydrogen bonding character of EVOH limits the number of potential solvents available. Furthermore, the solvents that are available, such as dimethyl formamide and triethyl phosphate, contain acidic protons and can thus be expected to act as chain transfer agents in a similar way as DMSO. The second, more feasible, way to increase the yield is to increase the concentration of EVOH. Consequently, the catalyst load will decrease while the concentration of deprotonised and reactive hydroxyl groups is kept constant in the reaction mixture. The maximum EVOH concentration that can be employed is in practice limited by the viscosity of the mixture.

End capping of the CPPO polymers was achieved through esterification of the terminal hydroxyl groups using a 10% excess of hexadecanoyl chloride. The consumption of the acid chloride and the formation of ester bonds were conveniently monitored by IR spectroscopy of the reaction mixtures, as shown in Fig. 2. In the carbonyl region, bands arising from the acid chloride carbonyl were observed at  $1800\text{ cm}^{-1}$ , and bands from the ester carbonyl groups were present at  $1735\text{ cm}^{-1}$ . An ether absorption band at  $1380\text{ cm}^{-1}$  was used as an internal reference for spectra b–d to offset differences in film thickness. The ester band gradually increased relative to the acid chloride band as the reaction proceeded. No further change in the carbonyl region of the reaction mixtures was noted after approximately 2 h reaction time. After removing the excess hexadecanoyl chloride by extraction in methanol/isooctane mixtures, capping was found to be essentially 100% by  $^1\text{H}$  NMR. The polymers hCPPO690, hCPPO1500, and hCPPO1700 thus contained 26, 14, and 13 wt%, respectively, of hexadecanoyl units.

Typical IR spectra of the uncapped and capped polymers, and of hexadecanoyl chloride are shown in Fig. 3. Characteristic bands in the spectrum of hexadecanoyl chloride (4a) are alkyl bands at  $2800\text{--}3000\text{ cm}^{-1}$  together with the carbonyl band at  $1800\text{ cm}^{-1}$ . The spectra of the CPPO polymers (4b) showed bands from ether units around  $1100\text{ cm}^{-1}$ ,

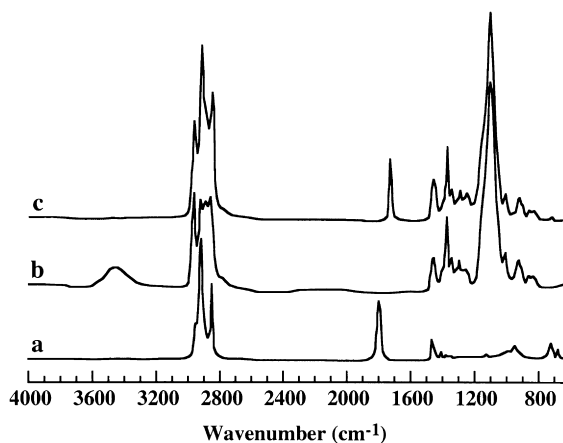


Fig. 3. IR spectra for: (a) hexadecanoyl chloride; (b) CPPO690; and (c) hCPPO690.

bands from alkyl units at  $2800\text{--}3000\text{ cm}^{-1}$ , and broad bands from hydrogen bonded hydroxyl groups at  $3400\text{--}3600\text{ cm}^{-1}$ . After end capping (4c), the carbonyl band was shifted to  $1735\text{ cm}^{-1}$ , as noted above. Further, the shape of the alkyl bands was modified, and the hydroxyl band had completely disappeared.

The solubility of the CPPO and hCPPO polymers was examined in a number of solvents, as shown in Table 2. While toluene and THF are good solvents for PPO, having Mark–Houwink exponential constants ( $a$ ) of 0.75 and 0.62 at 25 and  $20^\circ\text{C}$ , respectively, methanol must be regarded as a rather poor solvent with  $a$  equal to 0.55 at  $25^\circ\text{C}$  [16]. PPO has a theta temperature of  $50^\circ\text{C}$  in isooctane, and thus isooctane is a nonsolvent at  $25^\circ\text{C}$  [17]. In general the CPPO and hCPPO polymers had solubility properties similar to linear PPO. The observed discrepancies from this were most probably effects of the chain ends of the polymers, and were consequently found for the samples having the highest concentrations of hexadecanoyl and hydroxyl groups. Thus, the insolubility of CPPO200 in toluene was probably due to aggregation through hydroxyl groups, and the insolubility of hCPPO690 in methanol may be explained by aggregation through hexadecanoyl units.

To study further the solution properties of the polymers,

Table 2  
Solubility of the CPPO and hCPPO polymers at room temperature (+ : soluble, - : not soluble)

Sample	Solvent			
	THF	Methanol	Toluene	Isooctane
CPPO200	+	+	-	-
CPPO690	+	+	+	-
CPPO1500	+	+	+	-
CPPO1700	+	+	+	-
hCPPO690	+	-	+	-
hCPPO1500	+	+	+	-
hCPPO1700	+	+	+	-

the viscosity of dilute solutions was evaluated. The limiting viscosity for the CPPO and hCPPO polymers in toluene and methanol at  $25^\circ\text{C}$  are shown in Fig. 4 as functions of  $M_{\text{graft}}$ . The behaviour in toluene will be considered first. For the hCPPO polymers, a weak increase in viscosity with increasing  $M_{\text{graft}}$  was observed. This may reflect the increase in overall molecular weight, as  $M_{\text{graft}}$  increased. A sharper increase in viscosity was noted for the CPPO polymers, however starting from a lower viscosity. The steeper increase may be explained by an overall increase in molecular weight in combination with decreased hydroxyl contents. In methanol on the other hand, the viscosity of the CPPO polymers decreased with increasing  $M_{\text{graft}}$ , presumably as a result of decreasing hydroxyl content, and thereby poorer solubility. The viscosity of the hCPPO polymers was lower than for the CPPO polymers, indicating limited solubility and aggregation in methanol. The viscosity of both hCPPO and CPPO polymers seemed to be largely determined by the content of hexadecanoyl and hydroxyl groups. At higher values of  $M_{\text{graft}}$ , the viscosities of the polymers in both toluene and methanol can be expected to converge because of the diluting effect on the concentration of chain ends.

The phase behaviour of the CPPO and hCPPO polymers in the bulk state was studied by calorimetry. Typical DSC thermograms of samples preannealed at  $100^\circ\text{C}$  for 5 min are shown in Fig. 5. The CPPO polymers all showed distinct glass transitions, both during cooling and heating. The glass transition temperatures ( $T_g$ ) of the CPPO polymers evaluated from heating traces are shown in Fig. 6 as a function of  $M_{\text{graft}}$ . As seen, the  $T_g$  gradually decreased with increasing molecular weight, contrary to what is normally observed for linear polymers. This observation may be explained by two effects, namely an increasing plasticising effect on the backbone polymer, and a decreasing hydroxyl concentration. The  $T_g$  of linear PPO is close to  $-75^\circ\text{C}$ , although conflicting data have been reported [18]. It is conceivable that if  $M_{\text{graft}}$  is increased further, the  $T_g$  of the CPPO polymers will approach the value of linear PPO.

DSC analysis of the hCPPO polymers showed clear glass transitions at approximately the same temperatures as the corresponding CPPO polymers (Fig. 5). However, in connection to the glass transitions, small exotherms and endotherms were observed during cooling and heating, respectively. These transitions originated from the crystallisation and melting, respectively, of the hexadecanoyl units. The position of the transitions was shifted down in temperature, together with the  $T_g$  of the PPO phase, as  $M_{\text{graft}}$  increased. It is conceivable that the melting of the hexadecyl phase was induced by the increased segmental mobility of the PPO phase when  $T_g$  was passed during the heating scan. Similarly, crystallisation of the same phase was promoted by the decrease in PPO mobility when  $T_g$  was passed during the cooling scan. Also seen in Fig. 5 are traces from methyl hexadecanate, a model compound for the hexadecanoyl end groups, which crystallised and melted at 15 and  $35^\circ\text{C}$ ,

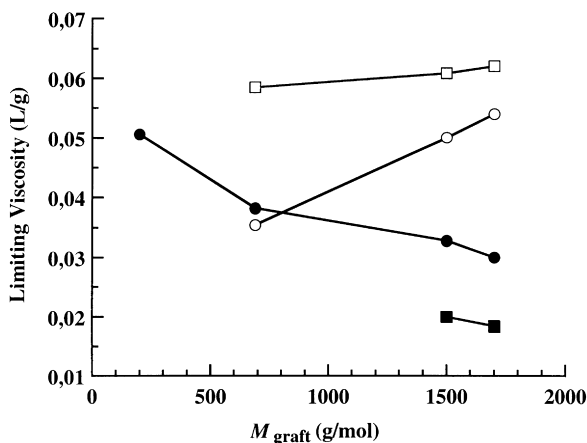


Fig. 4. Effect of the average molecular weight of the PPO grafts,  $M_{\text{PPO}}$ , on the limiting viscosity of the CPPO copolymers in methanol (●) and in toluene (○) solutions, and of the hCPPO copolymers in methanol (■) and toluene (□) solutions at 25°C.

respectively. These temperatures were far above the corresponding values for the hexadecanoyl units of the hCPPO polymers. Thus, the thermal behaviour of the PPO phase in these polymers was seemingly unaffected by the presence of the hexadecanoyl end caps. In contrast, the behaviour of the hexadecanoyl end groups was strongly influenced by their connectivity to the PPO chains. The hexadecanoyl units were obviously phase separated from PPO, at least at temperatures below their melting point. hCPPO samples stored under  $\text{N}_2$  atmosphere at room temperature were slightly hazy, indicating phase separation also at temperatures above the melting points of the hexadecanoyl phase. No crystallinity could however be detected in the temperature range  $-100$  to  $100^\circ\text{C}$  when hCPPO690 was studied by optical microscopy using cross-polarised light.

It is feasible that the hexadecanoyl chain ends formed ‘micellar-like’ microdomains surrounded by PPO grafts.

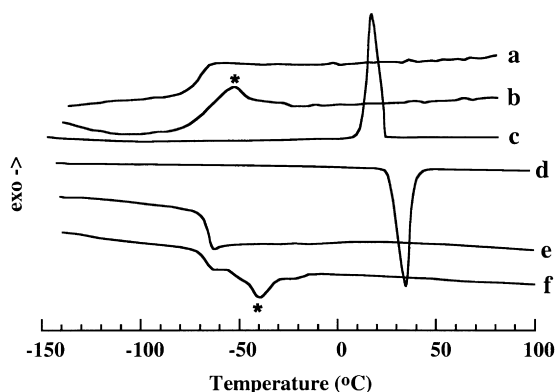


Fig. 5. DSC cooling traces for: (a) CPPO1500; (b) hCPPO1500; (c) methyl hexadecanate; and DSC heating traces for (d) methyl hexadecanate; (e) CPPO1500; and (f) hCPPO1500. The samples were preannealed at  $100^\circ\text{C}$  for 5 min before the cooling–heating cycle. Crystallisation and melting peaks of the hexadecanoyl units are marked with asterisks in trace (b) and (f), respectively.

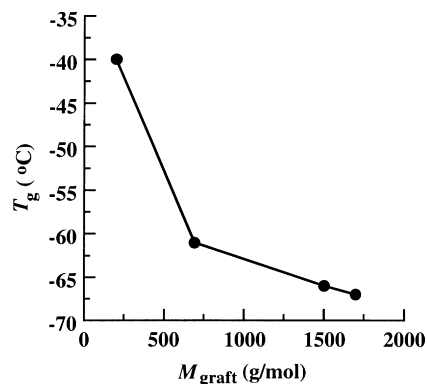
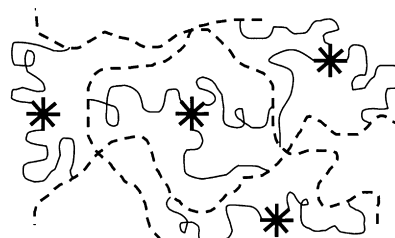


Fig. 6. Effect of the average molecular weight of the PPO grafts,  $M_{\text{PPO}}$ , on the  $T_g$  of the CPPO copolymers.

Scheme 2 shows a graphic representation of the structure of the hCPPO polymers in the solid state (thick, thin, and dashed lines denote hexadecanoyl units, PPO grafts, and EVOH backbones, respectively). Most of the PPO grafts have been omitted for clarity). A single hCPPO polymer chain carried  $\sim 800$  hexadecanoyl units. Hexyl end capped polymers have previously been shown to aggregate with 20–28 hexyl units per microdomain [19]. Assuming a similar aggregation number in the present case and a density similar to that of linear PPO ( $\sim 1$  g/ml), the sample hCPPO1700 can for example be expected to have a microdomain concentration of  $\sim 10^7$  species/ $(\mu\text{m})^3$ . Thus, the high concentration of hexadecanoyl units enables the formation of quite densely interconnected backbone polymer chains.

#### 4. Conclusions

High molecular weight comblike PPO polymers were prepared by grafting EVOH with PO. The reaction conditions used in the present work gave rise to the formation of quite large amounts of homoPPO, primarily as a consequence of chain transfer to DMSO. This led to low yields in the grafting process. It may be possible to increase the grafting yields by increasing the concentration of EVOH in the reaction mixtures, as compared to the concentrations used in the present work. Although homoPPO was present in the reaction mixtures after grafting, it was easily removed by



Scheme 2.

fractionation. Capping the terminal hydroxyl groups with hexadecanoyl chloride was found to be essentially quantitative when an excess of 10% of the acid chloride was used. Unreacted acid chloride was conveniently removed by extraction.

Capping the chain ends strongly affected the viscosity and the state of aggregation of the polymers. Thus, the concentration and nature of the chain ends controlled to a high degree the solubility and the viscosity of dilute solutions. In the bulk state the length of the grafts seemingly determined the glass transition temperature of the PPO polymers, and thereby also influenced the melting temperature of the hexadecanoyl phase. It is likely that the capped comblike polymers had a structure consisting of a PPO matrix in which the chains were interconnected by discrete hexadecanoyl microdomains. This type of polymer structure is interesting for use as a host for suitable electrolyte solutions in polymer gel electrolytes.

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