

# Preparation and Characterization of Poly(ethylene-graft-ethylene oxide)

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## SYNOPSIS

Graft copolymers containing poly(ethylene oxide) side chains attached to a polyethylene backbone were prepared by coupling of poly(ethylene-co-acrylic acid) (PEAA) and poly(ethylene oxide) monomethyl ethers (MPEO) by esterification in *o*-xylene at 140°C. The MPEO side chains had molecular weights of 750 to 5000. The chemical composition of the graft copolymers was analyzed by NMR and FT-IR spectroscopy. The weight fraction of the MPEO grafts in the graft copolymers was found to be around 0.4. The graft copolymers exhibited a phase-separated morphology with the backbones and the MPEO grafts forming separate crystalline phases. The MPEO phase had a melting temperature 8–25°C lower than the corresponding MPEO homopolymers, as determined by DSC. The melting point of the crystalline phase formed by the PEAA main chains was close to that of the pure PEAA. Crystallinity was also confirmed by x-ray diffraction. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

Graft copolymers containing poly(ethylene oxide) (PEO) side chains is an interesting group of copolymers due to their solution and surface properties as well as their ability to form phase-separated morphologies. Because of their amphiphilic nature, the PEO graft copolymers have many potential applications, for example, as compatibilizers in polymer blends, as surface modifiers in biomedical materials, as surfactants, and as stabilizers in emulsions and dispersions.

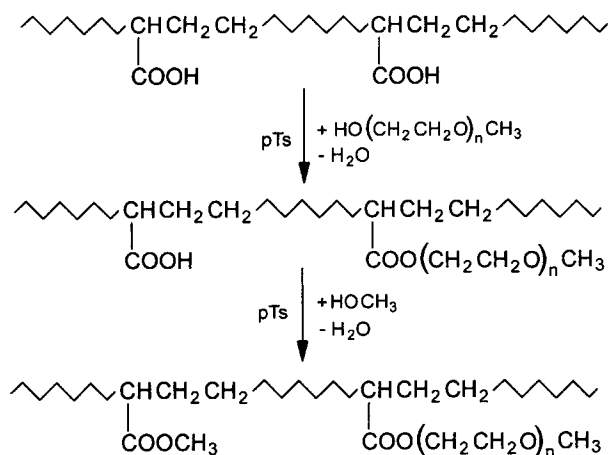
Preparation and properties of many different types of graft copolymers containing PEO side chains have been reported on during the past years.<sup>1,2</sup> At our laboratory, the synthesis and characterization of PEO block and graft copolymers has been a research topic for several years.<sup>3–5</sup> Recently, we have reported on the preparation of poly(styrene-graft-ethylene oxide) by anionic ethoxylation of reactive polystyrene backbones.<sup>6</sup> In the present article we wish to report on the preparation and characterization of an amphiphilic graft copolymer consisting

of a polyethylene (PE) backbone grafted with poly(ethylene oxide) (PEO).

Polyolefins have low surface energies, which is a drawback in many applications, for example, in surface treatments such as painting, printing, and glueing. Polyolefin films are generally surface modified in order to improve the adhesion properties, for example, through surface oxidation by corona treating or by chemical means. In the biomedical field, surface grafting with hydrophilic polymers has been explored.<sup>7,8</sup> Surface properties of polymers may also be changed by the adsorption of amphiphilic block and graft copolymers, or by incorporation of a suitable amphiphilic polymer in the polymer matrix by blending.<sup>9,10</sup> We have previously reported on the surface properties of polyurethanes modified by amphiphilic block and graft copolymers, and the effects on biomedical properties such as protein adsorption and bacterial adhesion.<sup>11,12</sup>

The aims of the present work were to prepare graft copolymers suitable for surface modification of polyolefins such as polyethylene and polypropylene, and to study the interfacial and bulk properties of blends of the graft copolymers and polyolefins. In the current article we describe the preparation and characterization of poly(ethylene-graft-ethylene oxide) (PE-PEO). The graft copolymers were syn-

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**Figure 1** Grafting of PEAA with MPEO by esterification.

thesized by coupling of poly(ethylene-*co*-acrylic acid) (PEAA) and poly(ethylene oxide) monomethyl ethers (MPEO) of varying molecular weights via esterification reactions. In forthcoming articles we will report on the use of the graft copolymers as surface modifiers for polyolefins.

## EXPERIMENTAL

### Materials

A copolymer of polyethylene and acrylic acid (PEAA, density 0.945 g/cm<sup>3</sup>) with an acrylic acid content of 13.5% w/w was obtained from Exxon Chemical Norden AB, Sweden. The molecular weight ( $M_n$ ) was estimated at 16,000, according to GPC in TCB (trichloro benzene) at 135°C, using linear polyethylenes as standards. Poly(ethylene oxide) monomethyl ethers, MPEO, with  $M_n = 750$  (Janssen Chimica), 2000 (Aldrich Chemical Company), and 5000 (EGA Chemie), were used. *p*-Toluene sulfonic acid mono hydrate (pTs, Merck, *pro*

*analysis*) was used as a catalyst, and Irganox 1010 (Ciba-Geigy) as an antioxidant. *o*-Xylene (Janssen Chimica, 99%) was used as the reaction medium, and methanol (Merck, *pro analysis*) as a solvent in the purification procedure. All chemicals were used as received.

### Instruments

FT-IR spectra were obtained by using a Bruker IFS-66 FT-IR spectrometer. Films for infrared analysis were solvent cast onto KBr discs from *o*-xylene or THF. Differential scanning calorimetry (DSC) analyses were run under N<sub>2</sub> using a Mettler DSC 30 instrument equipped with a low temperature cell. <sup>1</sup>H-NMR spectra were run in CDCl<sub>3</sub> at 45°C for PE-PEO<sub>5000</sub> and at ambient temperature for PE-PEO<sub>750</sub>, using a Varian XL-300 instrument. PE-PEO<sub>2000</sub> was analyzed at 50°C using a Bruker ARX 500 instrument. A Seifert x-ray 3000 instrument was used for x-ray diffraction analyses.

### Grafting Procedure

PEAA and MPEO were allowed to react under N<sub>2</sub> at 140°C in *o*-xylene in the presence of pTs. The reaction scheme is given in Figure 1. The reaction was carried out in a five-neck glass flask equipped with a stirrer, thermometer, nitrogen gas inlet, and a condenser. During the reaction the solvent was distilled off and allowed to pass through a layer of molecular sieves before reentering the reactor in order to remove any water formed during the reaction. The PEAA copolymer was first dissolved in refluxing *o*-xylene, and then the catalyst, the antioxidant, and the MPEO were added. Methanol was added in excess after the reaction between PEAA and MPEO was finished, in order to esterify residual acid groups. In all experiments 0.5% w/w of an antioxidant was added to the reaction medium. All experimental data are collected in Table I.

**Table I** Preparation of Poly(ethylene-*graft*-ethylene oxide)

Sample	Charged Amounts				Molar Ratio OH/COOH	Reaction Time (h)		Yield <sup>b</sup> (g)
	<i>o</i> -Xylene (mL)	PEAA (g)	MPEO (g)	pTs <sup>a</sup> (g)		MPEO	Methanol	
PE-PEO <sub>750</sub>	200	6.01	8.46	0.720	1.00	9	7	4.2
PE-PEO <sub>2000</sub>	300	20.00	30.00	2.334	0.40	3.5	17	17.1
PE-PEO <sub>5000</sub>	500	24.99	35.00	2.522	0.15	6	17	19.6

<sup>a</sup> pTs = *p*-Toluenesulfonic acid.

<sup>b</sup> Purified graft copolymer.

### Purification of the Graft Copolymers

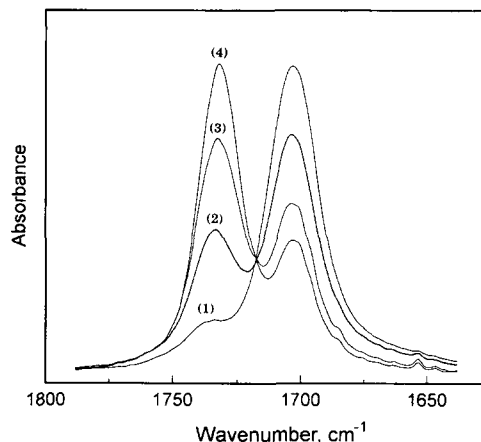
On cooling of the reaction mixture the graft copolymer precipitated as a strongly swelled gel, while the unreacted poly(ethylene oxide) stayed in solution. The solution was decanted and the residue treated with cold methanol under stirring. The solid polymer phase was allowed to settle, and the methanol supernatant removed and evaporated. The residue after evaporation was analyzed by FT-IR. The washing of the graft copolymer with methanol was repeated until no traces of MPEO could be detected by IR spectroscopy in the methanol supernatant. The graft copolymer was then dried under vacuum at room temperature.

### Conversion of Acid Groups

The conversion of carboxylic acid groups in the esterification reaction was monitored by FT-IR spectroscopy in order to evaluate the extent of grafting as a function of time. A few drops of the hot reaction mixture were put onto a KBr disc. The solvent was evaporated in an oven at 100°C for 5 min, and the residue was analyzed in the carbonyl stretching region (1650–1800 cm<sup>-1</sup>). The conversion of the acid groups was calculated by measuring the decrease of the the absorption peak at 1700–1705 cm<sup>-1</sup>, which is attributed to carboxylic acid.<sup>13,14</sup> A peak at 720 cm<sup>-1</sup> originating from the backbone was used as an internal standard. The results from the analyses are presented in Figure 2.

### Characterization

The chemical compositions of the graft copolymers were analyzed by <sup>1</sup>H-NMR and FT-IR spectroscopy. The MPEO content in the copolymers was calculated from <sup>1</sup>H-NMR spectra by comparing the integrated signals from the methylene protons in the MPEO grafts ( $\delta = 3.65$ ) and the methylene protons in the polyethylene backbone ( $\delta = 1.25$ ). Glass transition temperatures, melting points, and heats of melting ( $\Delta H_m$ ) were determined by differential scanning calorimetry (DSC). In the DSC measurements the samples were first heated at 10°C/min up to 150°C, cooled down to -100°C at 10°C/min, and then reheated at 10°C/min. The heating-cooling cycle was repeated two or three times until reproducible scans were obtained. The crystallinity of the graft copolymers was also demonstrated by x-ray diffraction run at room temperature.



**Figure 2** Esterification of PEAA with MPEO. Absorbance FT-IR spectra of the reaction mixture (carbonyl region) after various reaction times: (1) 5 min; (2) 60 min; (3) 310 min; (4) 535 min.

## RESULTS AND DISCUSSION

### Preparation of Graft Copolymers

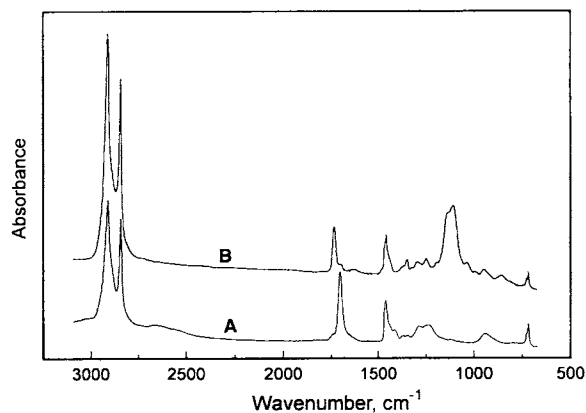
We have previously reported on the preparation of amphiphilic graft copolymers by transesterification of acrylic copolymers with PEO monomethyl ethers (MPEO).<sup>3</sup> In the present work we have utilized grafting by esterification by using the carboxylic acid groups of a PEAA copolymer as reactive sites in reactions with MPEO of different molecular weights. The reaction path is shown in Figure 1.

At a relatively low acrylic acid content PEAA is a semicrystalline polymer similar to polyethylene, with a melting point of 95°C. The PEAA polymer used as a backbone in our experiments had an acrylic acid content of 5.7 mol %, and a number-average molecular weight of 16,000, according to GPC measurements. The carboxylic acid groups of PEAA are intermolecularly hydrogen bonded, and this fact, in addition to the effects of the crystalline morphology of the polymer, makes a true solution difficult to obtain. The PEAA granules will swell strongly at room temperature in a polar solvent such as THF, and will give a solution only at the boiling point of the solvent, for instance, 60–65°C. The polymer also dissolves in *o*-xylene at 140°C, and in order to obtain high reaction rates we chose to carry out the esterification under these conditions.

The accessibility and reactivity of the functional groups may limit the esterification reaction rates. In the present case, the reactive carboxylic acid groups are relatively few, for instance, one group in 35 methylene units in the backbone, and, consequently, the reaction rates should be rather low. The

low rate can be compensated for by increasing the concentration of hydroxyl groups, but because a content of MPEO grafts of less than 40–50% by weight was wanted, the amounts of MPEO was kept relatively low. As shown in Table I, OH/COOH ratios of 0.15 to 1.0 were used. The progress of the reaction was observed by measuring the decrease of the  $1705\text{ cm}^{-1}$  peak (acid carbonyl) and the increase of the  $1735\text{ cm}^{-1}$  peak (ester carbonyl) in the IR spectra of the reaction product. These results are presented in Figure 2, and as evident from the figure quite long reaction times had to be used in order to reach reasonable conversions. The reactions were allowed to proceed for 3.5–9 h, as shown in Table I. In the preparation of PE-PEO<sub>750</sub>, a reaction time of 9 h was necessary in order to reach the high conversion of the carboxylic acid groups required for the MPEO content wanted. With MPEO 5000 as a reactant, the reaction was carried to a substantially lower conversion of the carboxylic acid groups, but still a reaction time of 6 h was necessary because of the low OH/COOH molar ratio used (0.15).

A factor that may limit the reactivity of the functional groups is the large difference in polarity between the PEAA backbone and the MPEO reactant. The two homopolymers are not compatible on a molecular scale, and segregation and phase separation may, thus, occur. Because of these and other limitations arising from polymer–polymer interactions, the maximum conversion of the carboxy groups may be lower than in the corresponding reactions between small molecules. However, these aspects of the reaction were not studied. Another factor to be considered is that esterification is an equilibrium reaction, and the removal of the water formed in the reaction is important in order to reach high yields. In the present case, the reaction medium was



**Figure 3** Absorbance FT-IR spectra of (A): pure PEAA, and (B): graft copolymer PE-PEO<sub>750</sub>.

continuously distilled off and passed through molecular sieves before reentering the reactor, which should ensure high conversions.

It has previously been noted that graft copolymers prepared from PEO or MPEO very easily crosslink, either in connection with the synthesis or at the separation of the reaction products.<sup>4,15,16</sup> PEO is relatively reactive towards free radicals, and may crosslink due to radical coupling reactions, which has been noted in the preparation of graft copolymers by radical polymerization of PEO macromonomers. However, polymers prepared via transesterification or esterification reactions may also crosslink because of radical reactions. At the high temperatures used in the reactions, autooxidation of the PEO as well as of the PEAA chains may occur if oxygen is available. In order to avoid these problems, an antioxidant was used in the reactions, together with a nitrogen atmosphere.

A more likely reason for crosslinking during the grafting reaction is the presence of difunctional or polyfunctional polyether species. Commercial MPEO samples, especially those having molecular weights higher than 2000, are known to contain small amounts of difunctional PEO formed by impurities, for example, water, in the ethoxylation reaction.<sup>17</sup> Because of the presence of two active polymerization sites in the molecule, a molecular weight twice that of the monofunctional MPEO will be obtained. The content of difunctional PEO in the MPEO used in the present reactions was, thus, analyzed by GPC measurements, for instance, by determining the polymer fraction having twice the molecular size of the main fraction. In MPEO of molecular weight 750, no difunctional PEO was detected. In MPEO 2000 and 5000, the contents of difunctional PEO were estimated at 4 and 17%, respectively. However, because of the relatively low grafting efficiency and the reaction limitations at high MPEO molecular weights, crosslinking does not seem to have any importance in the present study.

Carboxylic acid groups may interact with one another via hydrogen bonding, and are known to form strongly hydrogen bonded complexes with PEO.<sup>13,14</sup> We have previously shown that MPEO graft copolymers containing carboxylic groups prepared from styrene–maleic anhydride copolymers form complexes insoluble in most solvents.<sup>18</sup> In order to decrease the hydrogen bonding ability of the present copolymers, the residual carboxylic acid groups were converted to methyl ester groups by adding an excess of methanol to the reaction mixture after the reaction with MPEO was finished and continuing the esterification reaction for a prolonged period of time

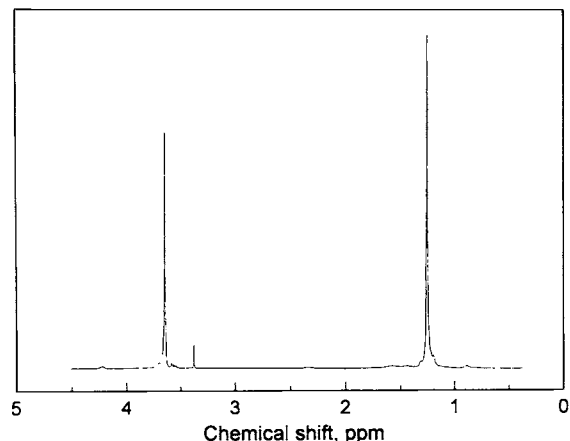
(Table I). The resulting copolymers were soluble in THF at 55°C and *o*-xylene at 90°C. The methanol treatment may, however, result in an acid-catalyzed transesterification between methanol and the MPEO ester groups on the polymer backbone, which would reduce the number of MPEO grafts in the copolymer.

All graft copolymers prepared contained unreacted MPEO and had to be purified before characterization. Because of the relatively small weight fraction of MPEO grafts present in the copolymers they were not soluble in water or methanol, which gave an opportunity for removing the excess of MPEO by extraction with methanol. However, graft copolymer molecules having degrees of grafting higher than the average can be expected to dissolve during this treatment. The low yields observed may, thus, be a consequence of such losses.

### Characterization

The purified copolymers were analyzed by FT-IR spectroscopy. Spectra of the PEAA backbone and a purified graft copolymer sample are shown in Figure 3. In the spectra, the shift of the carbonyl peak from 1705  $\text{cm}^{-1}$  in PEAA to 1735  $\text{cm}^{-1}$  in the graft copolymer is indicative of the conversion of carboxylic acid groups into ester groups. Furthermore, the occurrence of a distinct peak at 1100  $\text{cm}^{-1}$ , attributed to ether bonds, shows that the copolymer contains MPEO grafts.

The grafting efficiency, for instance, the relative number of acid groups esterified with MPEO, was measured by FT-IR as the decrease of the peak at 1705  $\text{cm}^{-1}$  attributed to carboxylic acid groups. The grafting efficiency was also measured by  $^1\text{H-NMR}$  spectroscopy after treatment of the residual carboxylic acid groups with methanol (Table II). A typical



**Figure 4**  $^1\text{H-NMR}$  spectrum of graft copolymer PE-PEO<sub>750</sub>.

NMR spectrum is shown in Figure 4. By comparing the integrated signals from the methylene protons in the PEO sidechains at  $\delta = 3.65$  and the methylene protons in the polyethylene backbone ( $\delta = 1.25$ ), the MPEO contents in the graft copolymers were determined, as also shown in Table II. In general, the grafting efficiency values obtained by NMR were lower than those obtained by FT-IR, which may be a consequence of transesterification in the methanol treatment step.

The PEAA polymer used as a backbone for the graft copolymers is a semicrystalline material with a melting point of 95°C. Because of the large difference in polarity between the backbone and the MPEO grafts, a phase-separated morphology was obtained for all the graft copolymers irregardless of the chain length of the MPEO grafts. In Figure 5, DSC traces for the graft copolymers are shown. The backbone polymer formed a crystalline phase with a melting temperature of 90–95°C according to DSC

**Table II** Characterization of Poly(ethylene-graft-ethylene oxide): MPEO Content and Grafting Efficiency

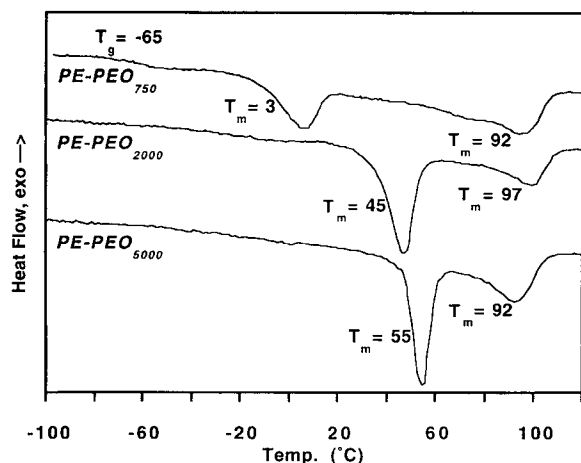
Sample	MPEO Grafts <sup>a</sup> (% w/w)	Grafting Efficiency (%)		Conversion of COOH <sup>d</sup> (%)
		NMR <sup>b</sup>	FT-IR <sup>c</sup>	
PE-PEO <sub>750</sub>	40	47	58	81
PE-PEO <sub>2000</sub>	45	22	30	78
PE-PEO <sub>5000</sub>	37	6	8	71

<sup>a</sup> Measured by NMR.

<sup>b</sup> Acid groups reacted with MPEO measured by NMR.

<sup>c</sup> Acid groups reacted with MPEO measured by FT-IR.

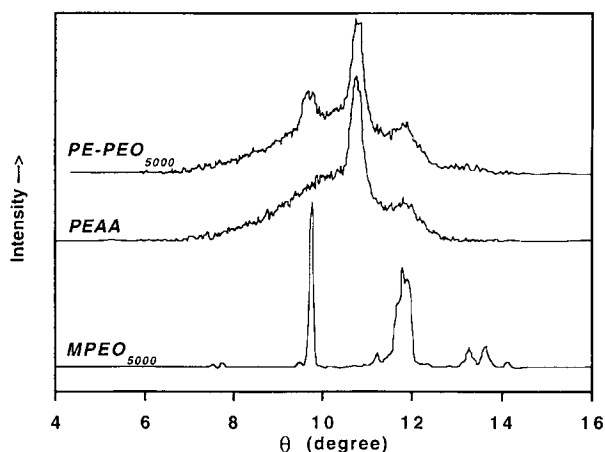
<sup>d</sup> Measured by FT-IR after reaction with methanol.



**Figure 5** DSC traces obtained for graft copolymers PE-PEO<sub>750</sub>, PE-PEO<sub>2000</sub>, and PE-PEO<sub>5000</sub>.

analyses (Table III). X-ray diffraction patterns of all the graft copolymers contained lines that could be identified as belonging to the PEAA diffractogram, as shown in Figure 6. The crystal structure should accordingly be similar to that of pure PEAA, and to polyethylene.<sup>19,20</sup>

The separate phase formed by the MPEO grafts was found to be crystalline for chain lengths of 15 EO units (MPEO 750) or larger, as noted previously for graft copolymers containing MPEO grafts.<sup>4</sup> In the DSC traces shown in Figure 5, melting endotherms were noted for all polymers. The melting temperatures were 8–25°C lower than those of the corresponding MPEO homopolymers (Table III). MPEO crystallinity was also observed by x-ray diffraction, except for the MPEO 750 graft copolymer, which had a MPEO melting point below room temperature. In this case the diffractogram was similar



**Figure 6** X-ray diffraction patterns for PE-PEO<sub>5000</sub>, PEAA, and MPEO<sub>5000</sub>.

to that of pure PEAA. In the x-ray diffractograms for PE-PEO<sub>2000</sub> and PE-PEO<sub>5000</sub> the lines assigned to MPEO appeared at similar positions as in the pure crystalline material, but they were significantly broader. In the graft copolymers, the MPEO grafts seem to crystallize with a crystal lattice similar to that of pure MPEO, but the morphological order seems to be much less. Similar conclusions have previously been drawn from x-ray data obtained from MPEO-grafted acrylic copolymers exhibiting side chain crystallinity.<sup>4</sup>

The degree of crystallinity for the MPEO grafts was found to depend on the chain length of the grafts. The graft copolymers prepared from MPEO 2000 and 5000 were shown by DSC to have high crystallinities and sharp MPEO melting points, and as shown in Figure 5, no glass transitions could be detected. In PE-PEO<sub>750</sub>, a glass transition assigned

**Table III** Characterization of Poly(ethylene-*graft*-ethylene oxide): Glass Transition Temperatures, Melting Temperatures, and Crystallinity

Sample	$T_g$ (PEO) (°C)	$T_m$ (PEO) (°C)	$T_m$ (PE) (°C)	Crystallinity (%)	
				PEO <sup>a</sup>	PE <sup>b</sup>
PE-PEO <sub>750</sub>	-65	3	92	40	90
PE-PEO <sub>2000</sub>	—	45	97	60	50
PE-PEO <sub>5000</sub>	—	55	92	60	60
PEAA	—	—	95	—	—
MPEO <sub>750</sub>	—	28	—	—	—
MPEO <sub>2000</sub>	—	58	—	—	—
MPEO <sub>5000</sub>	—	63	—	—	—

<sup>a</sup> Crystallinity of the MPEO phase compared to pure MPEO ( $\Delta H_m$  [MPEO grafts]/ $\Delta H_m$  [MPEO]).

<sup>b</sup> Crystallinity of the PE phase compared to pure PEAA ( $\Delta H_m$  [PE backbone]/ $\Delta H_m$  [PEAA]).

to MPEO was clearly observed at  $-65^{\circ}\text{C}$ , as evident from Figure 5. Data for the thermal transitions are collected in Table III, together with relative degrees of side chain crystallinity estimated from the DSC measurements.

## CONCLUSIONS

This work has shown that poly(ethylene-*graft*-ethylene oxide) can be prepared by grafting MPEO onto a backbone of ethylene-acrylic acid copolymer. The graft copolymers synthesized have a phase-separated morphology, with the backbone as well as the grafts forming crystalline phases.

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