Macromolecules **1993,** *26,* 3245–3246

Surface Graft Polymerization on Polyethylene Using Macroinitiators

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Received December 29, 1992

Postpolymerization polymer surface modification is a broadly used synthetic scheme to alter a polymer's chemical and physical properties.[1,2] Grafting onto the surface of a polymer fiber or film is an example of such an approach.[3] Surface grafting onto unreactive non-cross-linked polymers like polyolefins faces several problems. First, the introduction of such an initiator site can be a problem. Typically a polymer like polyethylene must be oxidized or otherwise modified so that radicals or radical precursors are generated at the surface.[4–8] Subsequent addition of a polymerizable monomer with heat or light then produces a graft. Second, if reactions are limited to the surface, the grafted polymer is not a true graft with homopolymer blocks attached to every constituent polyethylene molecule in the polyethylene film. Only polymer moieties with functional groups at the surface are actually modified in a surface-grafted polyolefin. The foreign graft polymer is, in such cases, more like a block copolymer anchored in the polyethylene matrix by noncovalent binding. Finally, difficulties in quantifying the number of oxidation sites, the extent of grafting, and side reactions like homopolymerization complicate such chemistry. We here report a different approach. Our approach depends on physically entrapping relatively short terminally functionalized ethylene oligomers into a host polymer film. Given suitably thermally stable initiator groups, this route can be used in either radical or anionic polymerization chemistry. Anionic polymerization, while chemically compatible with the hydrocarbon groups of polyethylene, has not previously been used for surface grafting onto polyethylene because of the absence of suitable methodology to incorporate initiation sites into the polymer.

Synthesis of appropriately functionalized oligomers and their incorporation into polyethylene used chemistry we had developed earlier to prepare functionalized polyethylene surfaces with spectroscopic probes.[9–11] This approach, which we termed entrapment functionalization, relies on anionic oligomerization of ethylene, terminal functionalization of the lithiated oligomer so formed, and then blending of low concentrations of the functionalized oligomer with a host polyolefin. In the first instance, anionic oligomerization of ethylene[12] was followed by quenching of the oligomer 1 with 1,1-diphenylethylene (eq 1) yielding oligomer 2 after protonation with methanol.

$$\mathrm{H_2C{=}CH_2} \xrightarrow[\substack{\text{TMEDA}\\ \text{heptane}}]{n\text{-BuLi}} \underset{\mathbf{1}}{\mathrm{Bu(CH_2CH_2)}_n\mathrm{CH_2CH_2Li}} \xrightarrow{\mathrm{H_2C{=}CPh_2}}$$

$$\mathrm{Bu(CH_2CH_2)}_{n+1}\mathrm{CH_2CLiPh_2} \xrightarrow{\mathrm{MeOH}}$$

$$\underset{\mathbf{2}}{\mathrm{Bu(CH_2CH_2)}_{N+1}\mathrm{CH_2CHPh_2}} + \text{PE-H} \xrightarrow[130\ ^\circ\mathrm{C}]{o\text{-}\mathrm{C_6H_4Cl_2}} \xrightarrow[\text{casting}]{\text{solution}}$$

$$\underset{\text{PE/2}}{\text{PE-H/PE}_{\text{Olig}}\text{-CHPh}_2} \quad (1)$$

About 75% of the oligomers so formed were functionalized with diphenylmethyl groups. The polyethylene degree of polymerization varied in different experiments but ranged between 1600 and 2500. Polyethylene films containing this oligomer were then formed by solution casting from a solution of 2 and virgin polyethylene.[14] Surface grafting chemistry was effective with loadings of the functionalized oligomer to the host polyethylene that varied from 0.2 to 10 wt %. On the basis of prior examples, we expected most of the diarylmethyl groups of the entrapped oligomers in these films to be at the polyethylene solution interface and accessible to a soluble strong base like *n*-BuLi in THF.[9,10] Separate experiments showed that a soluble analog of PE/2-Li, 1-lithio-1,1-diphenylhexane prepared from the reaction of BuLi·TMEDA and 1,1-diphenylethene, successfully polymerized methacrylonitrile.[13]

A suitable radical precursor was prepared using the chemistry in eq 2. In this example, the lithio oligomer 1

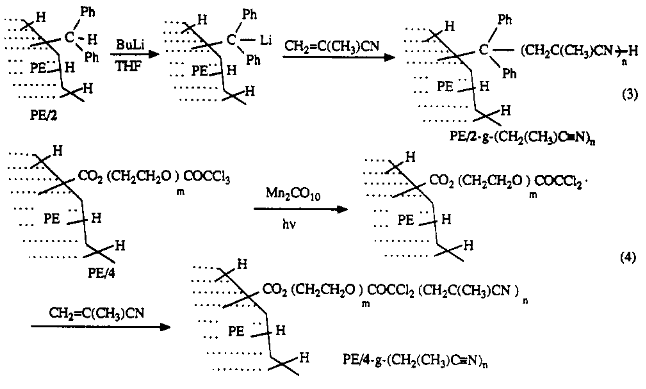
$$1 \xrightarrow[2.\ \mathrm{H_3O^+}]{1.\ \mathrm{CO_2}} \underset{\mathbf{3}}{\mathrm{Bu(CH_2CH_2)}_{n+1}\mathrm{CO_2H}} \xrightarrow[2.\ \mathrm{HO(CH_2CH_2O)_nCH_2CH_2O_2CCl_3}]{1.\ \mathrm{SOCl_2}}$$

$$\underset{\mathbf{4}}{\mathrm{Bu(CH_2CH_2)}_{n+1}\mathrm{CO_2(CH_2CH_2O)}_n\mathrm{CH_2CH_2O_2CCl_3}}$$

$$\xrightarrow[\substack{o\text{-}\mathrm{C_6H_4Cl_2}\\ 130\ ^\circ\mathrm{C}}]{\text{+PE-H}} \xrightarrow[\text{casting}]{\text{solution}} \underset{\text{PE/4}}{\text{PE/PE}_{\text{Olig}}\mathrm{CO_2}\text{-PEG-}\mathrm{O_2CCl_3}} \quad (2)$$

was made into a carboxylic acid 3. This acid was first separated (basic Al_2O_3) from unfunctionalized oligomers so that >95% of the oligomers were functionalized. An acid chloride derivative was then used to esterify a monoester of poly(ethylene glycol). This yielded the thermally stable radical precursor oligomer 4 which was entrapped in polyethylene by solvent-casting films from mixtures of 4 and pure polyethylene. The incompatibility of the poly(ethylene glycol) block with the host polyethylene was expected to favor surface incorporation of the diblock such that the end group would be available for polymerization.[11] The molecular weight of the polyethylene block varied but was typically in the range 1600–2500.

Surface grafting of either PE/2 or PE/4 with methacrylonitrile proceeded as shown in eqs 3 and 4. Treatment of PE/2 with 0.04 N BuLi in THF produced a faint pink color on the film characteristic of 1,1-diphenyl-1-lithiohexane. Removal of the excess BuLi solution and washing twice with fresh THF followed by addition of a 4 M THF solution of methacrylonitrile then yielded a surface-grafted product. The pink color immediately disappeared on addition of the monomer. Radical polymerization onto PE/4 was carried out by irradiating the film PE/4 suspended in a DMSO solution of methacrylonitrile containing 0.7 mM $Mn_2(CO)_{10}$ with a tungsten lamp.[15]



Evidence for surface graft formation was obtained from ATR-IR spectroscopy, transmission IR spectroscopy, XPS spectroscopy, and contact angle measurements. These

0024-9297/93/2226-3245$04.00/0

Table I. ATR-IR Spectroscopic, XPS Spectroscopic, and Contact Angle Data for Films PE/2 and PE/5 Grafted with Methacrylonitrile[a]

	time (h)	monomer (M)	degree of polymn of Graft[b] (n)	$C_{N\,1s}/C_{C\,1s}$[c]	Θ_a[d] (deg)
starting film	0	4.0	0	0.001	110
PE/2-*g*-$(CH_2C(CH_3)C{\equiv}N)_n$	1	4.0	14	0.033	92
PE/2-*g*-$(CH_2C(CH_3)C{\equiv}N)_n$	2	4.0	21	0.045	81
PE/2-*g*-$(CH_2C(CH_3)C{\equiv}N)_n$	8	4.0	51	0.092	71
PE/4-*g*-$(CH_2C(CH_3)C{\equiv}N)_n$	2	5.5	16	0.013	*e*
PE/4-*g*-$(CH_2C(CH_3)C{\equiv}N)_n$	2	3.5	10	0.011	84
PE/4-*g*-$(CH_2C(CH_3)C{\equiv}N)_n$	2	1.5	6	0.007	87

[a] Anionic grafting used a 3 wt % loaded lithiated film in a THF suspension at 25 °C. Radical grafting used a 0.7 wt % loaded film suspended in DMSO with 0.7 mM $Mn_2(CO)_{10}$ and irradiation from a 150-W tungsten lamp. [b] The degree of polymerization was measured by IR or XPS spectroscopy (see text). [c] Surface atomic ratios for nitrogen to carbon were measured with a Perkin-Elmer PHI Model 5500 XPS spectrometer with a Mg Kα source and 45° X-ray incident irradiation. Relative atom percent calculations used the instrument's software and were corrected for relative atom sensitivity. [d] Advancing water contact angles have an error of ±2° and are the average of 6–8 measurements using doubly distilled water. [e] This value was not measured.

data are summarized in Table I. In the case of the anionic grafting, the amount of surface grafting increased with increasing reaction time. However, our initial efforts at continuing polymerization beyond 8 h have not been successful. We believe this reflects adventitious quenching of anionic sites. Analysis of the extent of surface grafting by transmission IR spectroscopy through measurement of the integrated absorbances of the nitrile $-C{\equiv}N$ peak (2240 cm^{-1}) to a polyethylene $-CH_2-$ peak (2020 cm^{-1}) and calculations using a Beer's law plot for known mixtures of polyethylene and polymethacrylonitrile and the amount of 2 showed that the average degree of polymerization of the surface graft was ca. 50 after 8 h. This is likely a minimal value since some of the initiator sites in PE/2 probably are not effective participants in the surface polymerization chemistry. In any case, XPS spectroscopy suggests that the surface was largely polymethacrylonitrile. Further, contact angle analysis using water showed that the surface hydrophilicity (Θ_a 71°) was comparable to that of a pure cast polymethacrylonitrile film (Θ_a 68°). In the case of the radical polymerization, the extent of polymerization was linearly related to the square root of the dimanganese decacarbonyl ($[Mn_2CO_{10}]^{1/2}$), suggesting that the degree of polymerization was limited by chain termination through coupling or disproportionation. The degree of polymerization onto PE/4 was estimated to be only 16 based on the N/Cl ratio from XPS spectroscopy. This estimate assumed that every trichloroacetate group successfully initiated a polymerization and is likely a minimal value. Comparison of the ratio of absorbances for the $\nu_{C\equiv N}/\nu_{CH_2}$ peaks in the transmission and ATR-IR spectra of the product films for the $Mn_2(CO)_{10}$ procedure with similar ratios for the anionic procedure also suggested that a lower amount of surface polymerization occurred in the $Mn_2(CO)_{10}$ procedure. A more direct assay of the degree of polymerization by dissolution and solution-state analysis of the modified film was impractical because of the low concentration of modified polyethylene in a typical 1-cm^2 piece of film.

The absence of homopolymerization in either anionic or radical surface grafting was confirmed by ^{1}H NMR or IR spectroscopic analysis of the residue of the evaporated supernatent. In all cases, the surface-grafted films were extracted with acetone in a jacketed Soxhlet apparatus for 6 h. These extractions and control experiments which showed that polymethacrylonitrile prepared in solution in the presence of an unfunctionalized polyethylene film using either *n*-butyllithium, 1-lithio-1,1-diphenylhexane, or ethyl trichloroacetate/$Mn_2(CO)_{10}$ ($h\nu$ initiation) was not adsorbed on polyethylene film established that the surface grafts were firmly attached to the polyethylene. Additional control experiments showed no surface modification occurred when polyethylene films without 2 or 4 were treated with either *n*-BuLi or $Mn_2(CO)_{10}$. The dispersity of the graft polymerization was not measurable in either the anionic or radical polymerization chemistry.

Preliminary work indicates that other monomers like acrylonitrile and acrylate esters can be substituted for methacrylonitrile in this chemistry. These studies and additional spectroscopic studies of the details of this surface-grafting chemistry and of the surface-grafted surfaces are ongoing.

Acknowledgment. Support of this research by the National Science Foundation (DMR 8917810) is gratefully acknowledged.

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