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Control of Surface Functionalization of Polyethylene Powders Prepared by Coprecipitation of Functionalized Ethylene Oligomers and Polyethylene

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ABSTRACT: Techniques for functionalization of polyethylene by entrapment of terminally functionalized ethylene oligomers in a host polymer powder or film are described. The effects of varying the oligomer microstructure, the host polymer morphology, and the entrapment procedure on the eventual location of the entrapped nitroxyl groups were examined by ESR spectroscopy and reactivity studies. The results show that the extent of surface functionalization in the product polymer formed in entrapment functionalization can be varied in a controllable and predictable manner.

Chemical modification of preformed polymers is both a desirable and useful way of improving a given polymer's properties in various applications.[1-3] Many processes including adhesion, printing, grafting, composite formation, and biocompatibility depend more on the chemical and physical interactions at a polymer–solution interface than on bulk properties of a polymer. Ideally such chemical modifications are designed so that they only result in surface derivatization of the substrate polymer with little or no functionalization occurring in the bulk. In an earlier report we described a new procedure leading to surface functionalized polyethylene powders.[4] In this procedure, we successfully entrapped short functionalized polyethylene oligomers into higher molecular weight polyethylene such that the oligomer's functional groups were readily accessible to solvents and polyethylene-incompatible reagents. In this paper, we have expanded on this earlier study, demonstrating that the degree of "surface" functionalization attainable in this so-called entrapment functionalization method can be experimentally varied and controlled.

Most other procedures designed to surface derivatize unreactive polymers rely on phase differences between the reagents and the bulk polymer and the incompatibility of reagents with bulk polymer to ensure that functional groups are only introduced at the polymer's surface. This approach is exemplified by the procedures used by Dias and McCarthy to functionalize poly(chlorotrifluoroethylene).[5] Etching procedures that have been successfully used to produce surface functionalized polyethylene films similarly use polar oxidants which cannot readily permeate into bulk polyethylene.[6,7] In other cases such as corona discharge treatment of polyethylene, surface functionalization is attained because the reagent's diffusion into bulk polymer is slower than the rate of its reaction with the polymer surface.[8]

Unlike these sorts of procedures, the entrapment functionalization procedure we have developed for polyethylene functionalization does not rely on diffusion of a reagent to achieve surface vs. bulk functionalization. Entrapment functionalization involves initial dissolution of a host polymer along with a smaller amount of a terminally functionalized oligomer in a solvent like toluene at 100 °C. Cooling of this solution containing polymer and oligomer to room temperature leads to coprecipitation of the polymer and oligomer such that the oligomer's terminal functional group ends up at the polymer–solution interface or surface. While the actual mechanisms responsible for achieving surface vs bulk functionalization during this precipitation step are not known, there are several experimental parameters which we can easily vary which should affect the degree of surface functionalization in the product entrapment functionalized polyethylene. More specifically, we have achieved a modest measure of control of surface functionalization by varying the host polymer's morphology, the precipitation conditions, the oligomer's microstructure, the terminal functional groups' size and polarity, and the oligomer's size as discussed below.

Results and Discussion

In this paper we have attempted to examine the effect of several experimentally controllable parameters on the surface selectivity of entrapment functionalization. We have in particular examined the effects of solvent polarity, oligomer microstructure, oligomer end group, and polyethylene morphology. The results show that it is possible to manipulate these variables and to thus control whether a functional group in an entrapment functionalized polymer powder or film is or is not accessible to solvents and reagents external to the polyethylene.

In the procedure we describe as entrapment functionalization we first prepare a polyethylene-like oligomer with an ESR spin label attached to a terminal functional group for use as a spectroscopic reporter group. This oligomer is then codissolved with virgin polyethylene in a solvent like toluene or xylenes. Cooling the solution then coprecipitates the polymer, entrapping the oligomer and its functional group in the host polyethylene. In typical procedures, 1 g of virgin (additive free) polyethylene is dissolved in 25 mL of toluene at 110 °C along with 0.01 g of an oligomer whose M_N ranges from 1200 to 6000. This solution can then be cooled to form a precipitate of an entrapment functionalized polyethylene powder. Alternatively, a polyethylene film can be prepared from these solutions by solvent casting. These general procedures, which successfully produced surface functionalized polyethylene powders in our earlier work, were used throughout this present work with modifications as necessary to test how experimental changes affect the extent of "surface" functionalization in the product polymer.

Once an entrapment functionalized polyethylene powder (or film) had been prepared, we analyzed it using ESR spectroscopy. ESR experiments involved suspending a polymer sample in an ESR tube in oxygen-free solvent. Rotational correlation times were calculated from these ESR spectra.[9] In some cases, the reactivity of the nitroxyl group toward solutions of various reagents was examined.

One objective of our work was to determine how terminally functionalized ethylene oligomers derived from the reactions shown below can be coprecipitated with high

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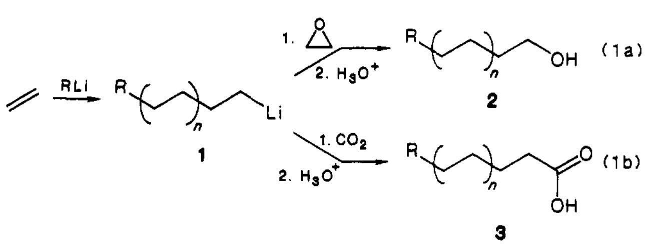
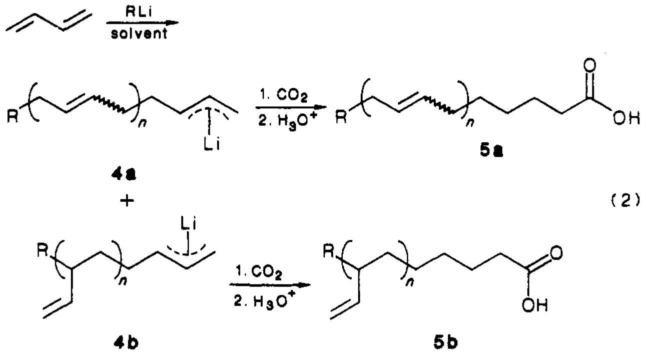
density polyethylene to form surface-functionalized powders. "Surface functionalized" in reference to a non-cross-linked polymer like polyethylene is a vague term whose meaning has been defined differently by different groups.[10] This ambiguity reflects the fact that the phase boundary between polyethylene and solution is a very poorly defined and environmentally dependent phase boundary unlike the sort of phase boundary seen at the surface of a well-defined solid such as a metal. This issue has been dealt with at length in other papers. For example, Whitesides has described experiments with heterogeneously etched preformed polyethylene films in which there is a clear differentiation between so-called surface functional groups which affect contact angle measurements and functional groups which can react readily with reagents which are expected to be incompatible with polyethylene.[10] Since we cannot measure contact angles for powders prepared by using these entrapment procedures, we cannot directly compare our results to his. In any case, our long-range goals are to study chemistry at polyethylene–solution interfaces where the solvent is an organic solvent. The significance of water contact angles in such cases is unclear. However, it is likely that the functionality introduced by the entrapment functionalization procedure we have described here resembles the deeper type of surface functionality described by Whitesides. Thus, in this paper when we discuss functional groups at the surface of a polyethylene powder in contact with any given solvent, we are primarily questioning if the functional groups either behave spectroscopically as if they are in the solvent in question and/or if they react within several hours with reagents which are unlikely to diffuse rapidly into bulk polyethylene. Solution-like spectroscopic behavior is manifested by a_N values like similar spin labels in solution and, more importantly, by τ_c values of ca. 2×10^{-10} s for freely tumbling nitroxyl groups. Rotational correlation times of ca. 150×10^{-10} sec are characteristic of immobilized nitroxyl groups.[11]

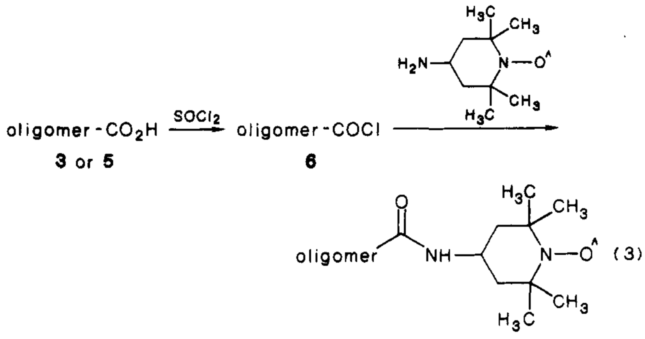
There are many aspects of the entrapment functionalization we developed which are amenable to experimental control. However, one of the most obvious ways to affect some control is to vary the structure of the oligomer or its end group through synthesis. Thus, in this paper we have explored variation through synthesis of both the size and extent of branching (microstructure) in the oligomer and the effects of these changes in entrapment functionalization. These variations followed literature precedent for control of these types of anionic oligomerizations.[12,13] In addition, we briefly examined the effect of adding short segments of a second, polyethylene-incompatible polymer to these oligomers prior to the step in which the functional group (and eventual spin label) is added.

Functionalized ethylene oligomers capable of being entrapped in polyethylene powders and films were prepared by anionic polymerization of ethylene using *n*-butyllithium and *N,N,N,N*-tetramethylethylene diamine initiator or by anionic polymerization of 1,3-butadiene using *sec*-butyllithium as an initiator (eq 1 and 2).[13,14] Electrophilic substitution of the living polymers produced in these polymerization reactions introduced the terminal functional group (or a precursor to the penultimate spectroscopic probe). Complete removal of the carbon–carbon double bonds in the polybutadiene was achieved by hydrogenation.[15] By using the butadiene route and by changing the basicity of the solvent used for the anionic polymerization, it was possible to vary the amount of pendant vinyl groups in the intermediate polybutadiene and hence the amount of branching in the penultimate saturated polymer.[12] The percentage of 1,2-polybutadiene in the intermediate functionalized polybutadiene was measured by IR and NMR spectroscopy and was presumed to be equal to the amount of ethyl branching in the final product.[16] Thus, a range of molecular weights of polyethylene-like oligomers could be attained, and the microstructure of the oligomers could be varied. Ethylene derived oligomers ranging in M_V from 1500 to 4000 were prepared in this manner. Butadiene derived oligomers with 12%, 22%, 49%, and 80% branching and M_V's ranging from 2000 to 8000 were also prepared.





Once the carboxyl-terminated oligomers had been prepared, they were further derivatized by reduction (in the case of 5) and introduction of a spin label. Reduction of the polybutadiene oligomer was accomplished by using both Wilkinson's catalyst and a heterogeneous cobalt catalyst.[15] This reaction was carried out until no carbon–carbon double bonds remained by NMR spectroscopy. The spin label was then introduced by intermediate formation of an acid chloride (eq 3).



7a: no ethyl branching
b: 12% ethyl branching
c: 22% ethyl branching
d: 49% ethyl branching
e: 80% ethyl branching

Entrapment of nitroxyl-terminated oligomer **7b** was carried out by using several different types of host polymer powders under a range of entrapment conditions as discussed below. Host polymers varied in morphology and density. Two HDPE samples (A and B, densities of 0.97 and 0.96, respectively) and three LDPE samples (C, D, and E, densities of 0.92, 0.925, and 0.93, respectively) were used whose crystallinity as measured by IR was 72%, 77%, 58%, 50%, and 59% (A, B, C, D, and E). In general,

Table I
Effect of Solvent on Nitroxyl Motion in PE/4 Using Various Host Polyethylenes (τ_C, $\times 10^{10}$ s)[a]

solvent	PE(A)/ **7b**	PE(B)/ **7b**	PE(C)/ **7b**	PE(D)/ **7b**	PE(E)/ **7b**
no solvent	148	120	107	114	106
n-hexane	115	102	9	8	8
carbon tetrachloride	74	85	4	4	2
toluene	22	18	4	3	3
diethyl ether	21	25	4	3	3
tetrahydrofuran	2	3	2	2	1
ethanol	1	1	68	69	66

[a] The rotational correlation times were calculated from spectra of the entrapment functionalized polymer suspended in the indicated solvent at 25 °C according to the method in ref 9.

Table II
Effect of Solvent on a_N Values of Entrapped Spin Labels in Polyethylene A[a]

solvent	a_N (G)	τ_C ($\times 10^{10}$ s)
no solvent	31.0[b]	148
n-hexane	14.5	115
carbon tetrachloride	14.7	74
toluene	15.1	22
diethyl ether	15.1	21
tetrahydrofuran	15.3	2
ethanol	15.4	1

[a] The a_N values were measured in the indicated solvent at 25 °C using a suspension of high-density polyethylene containing oligomer **7b** (12% ethyl branching). [b] This value is an estimate because of the line broadening in this ESR spectrum.

similar behavior was observed for the two high-density polyethylene samples and amongst the three low-density samples. Coprecipitation of nitroxyl-terminated oligomer **7b** by cooling a toluene solution of the oligomer and host polyethylene yielded entrapment-functionalized powders. Suspension of these powders in various solvents produced ESR spectra of the entrapped nitroxyl group which varied depending on the identity of the suspending solvent. These solvent effects are summarized by the τ_c values in Table I. The mobility of the nitroxyl probe in the low density samples in nearly all solvents other than ethanol was quite high. We believe this reflects the lower crystallinity of the host polymer in these cases (vide infra) and swelling of the polymer by solvent. In comparison, ethanol is a poor solvent for polyethylene and its effects are likely to be more localized to the polymer–solution interface. On the basis of work discussed below, we feel the τ_c values of these powders in ethanol suspensions are the most useful measure of how changes in experimental conditions and substrates affect topological selectivity in entrapment functionalization.

The degree to which nitroxyl groups entrapped in polymer powders or films are at the surface or interface is quantitatively and qualitatively difficult to evaluate. This in part reflects the likelihood that the phase boundary between polyethylene and a solvent is ambiguous as discussed above. In our previous paper we emphasized the use of τ_c values to evaluate the degree to which the entrapped nitroxyl groups we were examining were at a polyethylene-solution interface. We also reported preliminary data which seemed to correlate reactivity with these ESR data. This paper expands on these observations. In addition, we also tried to use the effect of solvent on a_N values to evaluate the environment of spin labels.[11,17] Table II lists these results. While the data support our earlier interpretation that the nitroxyl groups of oligomer **7b** are in a position to feel the effects of solvent, the differences in a_N values are too small to be relied on as a general way to evaluate the extent to which a nitroxyl group is located in a polyethylene–solution interfacial region.

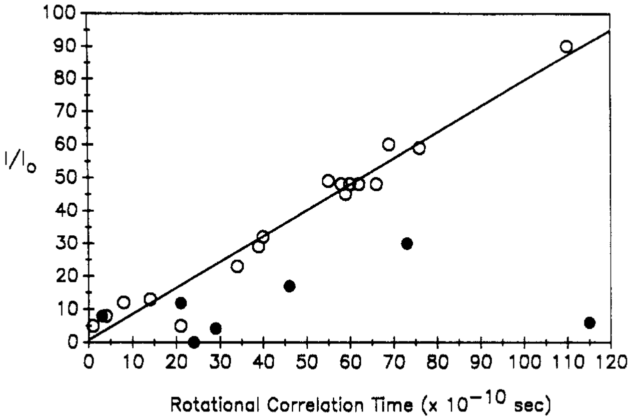


Figure 1. Relationship between entrapped spin label reactivity and rotational correlation time for spin labels entrapped in polyethylene powders and films: dithioerythritol in ethanol as a reducing agent plotted versus τ_c values for an ethanol suspension of the entrapped spin label, ○; *n*-butyllithium in hexanes as a reducing agent plotted versus τ_c for an ethanol suspension of the entrapped spin label, ●.

In contrast to the small differences observed in measurement of a_N values of PE(A)/**7b** suspended in different solvents, comparison of τ_c values for the nitroxyl groups of PE(A)/**7b** in ethanol suspensions were more useful. Further, the values measured for τ_c correlated with the reactivity of entrapped nitroxyl groups toward reagents in solution. In general, entrapped nitroxyl groups with τ_c values of less than 5×10^{-10} s suspended in ethanol were >90% reduced by reagents like dithioerythritol in 12 h. This is illustrated by the data in Figure 1. The data in Figure 1 were collected over an extended period by using all the types of host polymer described in this paper and with oligomers **7a**, **7b**, **7c**, and **11**. The good correlation seen between dithioerythritol reactivity and τ_c holds regardless of the host polymer's crystallinity or its physical form (powder, thin or thick film). On the basis of these reactivity data, we have arbitrarily defined spin labels with $\tau_c < 5 \times 10^{-10}$ s in an ethanol suspension as being in what we have called the interfacial region or at the "surface" of the polymer since they both have freedom of motion as if they were in solution and react readily with reagents in solution. Additional evidence that the assumption that dithioerythritol/ethanol reactivity correlates with a nitroxyl's location at the surface is correct comes from other experiments studying the reactivity of other reagents such as alkyllithium reagents toward polyethylene-entrapped nitroxyl groups. This is shown by data for the reactivity of *n*-butyllithium which is hexane soluble and which has reactivity toward entrapped nitroxyl groups which is not correlated with the nitroxyl's τ_c value. In the case of butyllithium, high reactivity was generally noted for nitroxyl groups entrapped in polyethylene powders. The ability of *n*-butyllithium to react with entrapped nitroxyl groups did not correlate with the τ_c values of entrapped nitroxyl groups in either ethanol or hexane (the solvent used for the *n*-BuLi reaction). Thus, while dithioerythritol reactivity is correlated with nitroxyl group mobility, other reagents which can diffuse into polyethylene do not have reactivities which are similarly related to τ_c values. These *n*-BuLi data are also shown in Figure 1. It is significant that the residual ESR signal left after these reactions was characteristic of a completely immobilized or buried nitroxyl in accord with our interpretation that nitroxyl

Table III
Effects of Oligomer Microstructure on Rotational Correlation Times of Entrapped Nitroxyl Radicals[a,b]

	rotational correlatn times ($\times 10^{10}$ s)								
solvent	PE(A)/7a	PE(A)/7b	PE(A)/7c	PE(B)/7a	PE(B)/7b	PE(B)/7c	PE(E)/7a	PE(E)/7b	PE(E)/7c
no solvent	124	148	131	120	120	139	121	106	114
n-hexane	80	115	64	86	102	59	6	8	7
carbon tetrachloride	60	74	39	52	85	38	4	3	3
toluene	15	20	8	16	18	6	2	3	3
diethyl ether	17	21	10	19	25	10	3	3	3
tetrahydrofuran	2	2	2	2	3	2	1	1	2
ethanol	34	1	1	30	1	1	60	66	9

[a] Rotational correlation times were calculated from ESR spectra of entrapment-functionalized powders suspended in the indicated solvent at 25 °C using the method described in ref 9. [b] Oligomers with more than 22% ethyl branching (i.e. oligomers with 49% or 80% ethyl branching) were not entrapped. In these cases ESR spectroscopy showed all the nitroxyl group remained in the filtrate after an attempted entrapment experiment.

Table IV
Effects of Solvent and Entrapment Method on Rotational Correlation Times of Entrapped 7[a]

		measured rotational correlatn time ($\times 10^{10}$ s) (solvent used in suspensn of PE/7)						
polymer	precipitatn solvent	no solv	*n*-hexane	carbon tetrachloride	toluene	diethyl ether	tetrahydrofuran	ethanol
PE(A)/7b	toluene	148	115	74	20	21	2	1
PE(A)/7b	dibutyl ether	132	54	39	7	15	2	1
PE(A)/7b	toluene–HOAc[b]	123	59	41	14	17	2	1
PE(A)/7b	hexanes[c]	141	25	14	6	9	3	99
PE(A)/7b	methanol[d]	131	12	9	5	7	3	69
PE(B)/7b	hexanes[c]	139	20	13	5	7	3	103
PE(B)/7b	methanol[d]	129	10	4	3	4	2	62
PE(E)/7b	hexanes[c]	113	6	2	1	3	1	61
PE(E)/7b	methanol[d]	108	3	2	2	2	1	66
PE(B)/7a	hexanes[c]	114	33	18	10	11	3	104
PE(B)/7a	methanol[d]	118	25	14	7	8	3	76
PE(E)/7a	hexanes[c]	106	7	6	2	3	2	68
PE(E)/7a	methanol[d]	104	7	5	2	3	2	63
PE(B)/7c	hexanes[c]	130	21	13	6	7	2	89
PE(B)/7c	methanol[d]	128	10	7	3	5	2	43
PE(C)/7c	hexanes[c]	105	5	4	3	4	2	58
PE(C)/7c	methanol[d]	109	4	3	2	3	2	50

[a] Rotational correlation times measured from spectra taken of degassed suspensions of the entrapment-functionalized powder suspended in the indicated solvent. Unless otherwise indicated, the entrapment was achieved by thermal precipitation. [b] This solvent mixture was 90:10 (v/v) toluene and acetic acid. [c] Entrapment was achieved by pouring a hot toluene solution of the host polymer and oligomer into room temperature hexanes. [d] Entrapment was achieved by pouring a hot toluene solution of the host polymer and oligomer into room-temperature methanol.

groups which can tumble freely in ethanol suspension are located at the polymer–solution interface.

Changes in oligomer microstructure and size also affected the location of the nitroxyl group in the final entrapment functionalized polyethylene powder. With use of both high-density polyethylene and low-density polyethylene as host polymers (PE(A), PE(B), or PE(E)), we carried out entrapment experiments with similarly sized oligomers which differed only in the their extent of branching. First, we had already noted that the oligomer's size had an effect. Spin-labeled amides derived from octadecanoic acid are not entrapped in polyethylene under conditions where similar linear C_{120}–C_{200} oligomeric amides are quantitatively entrapped. Further increases in oligomer size led to an entrapment functionalized polymer whose nitroxyl groups were increasingly located in the bulk polymer and inaccessible to solvent or DTE in ethanol. Second, the structure of the oligomer has a significant effect on the degree of surface functionalization. The results of some of these experiments are shown in Table III. Oligomers with more than 30% ethyl branching and M_V of 2500–5000 were not entrapped under conditions where the same sized oligomers with <30% ethyl branching were entrapped. In addition, comparison of linear (0% branching) oligomers (**7a**) with oligomers with more ethyl branching (**7b** and **7c**) shows that more bulk functionalization was observed with the linear oligomers in entrapment experiments using either high- or low-density polyethylene. This trend is most evident in comparison of τ_c values in ethanol for both high density polyethylenes. The trend is similarly seen with the low-density host polymer though in this case increased surface selectivity is only seen when oligomer **7c** versus **7a** or **7b** is entrapped. The overall conclusion is that increased branching favors surface functionalization so long as the branching is not too extensive. If there is too much branching, no entrapment occurs. Oligomer size seems equally important. Small oligomers are not entrapped in polyethylene. Larger oligomers tend to yield increasing amounts of bulk functionalization.

Starting with various types of polyethylene and nitroxyl functionalized oligomers of similar size and with similar branching, we next examined the effect of changing the solvent and the entrapment method on the surface selectivity of entrapment functionalization. In our earlier report, we simply coprecipitated functionalized oligomers and the host polyethylene in toluene. In this paper we varied this procedure in several ways. First, we tried changing the polarity of the solvent either by substituting other solvents or by addition of cosolvents. Precipitation of the host polyethylene and the functionalized oligomer then was accomplished by allowing the reaction mixture to cool to room temperature as before. The powders formed in this way were then examined by ESR spectroscopy as suspensions in various solvents. These ESR spectra, like those seen before,[4] consisted of mixtures of

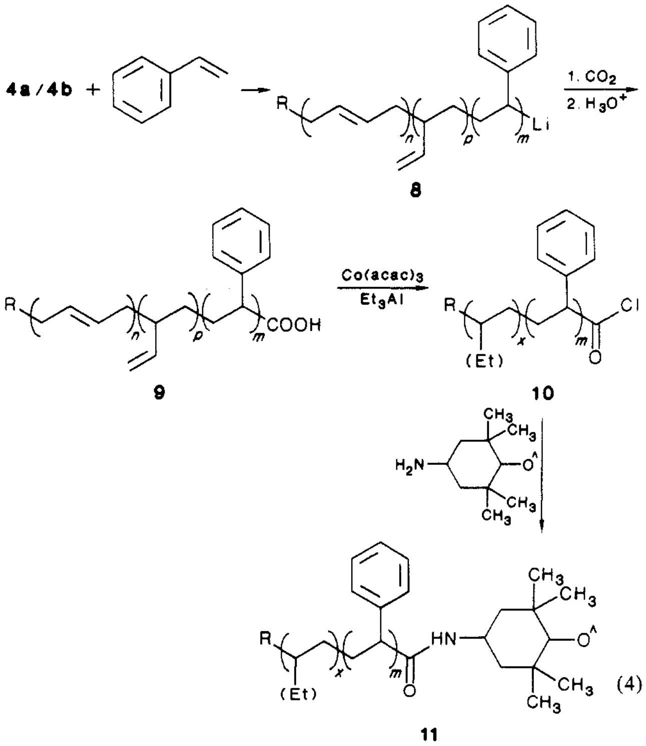
Table V
Effects of Oligomer End Group Structure on Rotational Correlation Times of Entrapped Nitroxyl-Labeled Oligomers 7b and 11[a]

	rotational correlatn times ($\times 10^{10}$ s)									
solvent	PE(B)/ **7b**	PE(B)/ 11	PE(D)/ **7b**	PE(D)/ 11	PE(E)/ **7b**	PE(E)/ 11	PE(B)/ 11[b]	PE(B)/ 11[c]	PE(E)/ 11[b]	PE(E)/ 11[c]
no solvent	120	126	114	100	106	101	115	117	101	102
n-hexane	102	43	8	2	8	3	7	14	2	4
carbon tetrachloride	85	27	4	2	4	2	4	7	2	2
toluene	18	5	3	1	3	1	2	4	1	2
diethyl ether	25	8	3	2	3	2	3	6	2	2
tetrahydrofuran	3	1	2	1	2	1	2	2	1	1
ethanol	1	1	69	9	69	8	40	75	42	53

[a] Rotational correlation times were measured in the indicated solvent at 25 °C for degassed suspensions of the entrapment-functionalized polymer which had been prepared by thermal precipitation in toluene. [b] Entrapment-functionalized powder prepared precipitation of oligomer and host polymer using methanol. [c] Entrapment functionalized polymer powder which had been prepared precipitation of oligomer and host polymer using hexane.

broadened and sharp three-line spectra characteristic of a mixture of motionally restricted and freely rotating nitroxyl groups. Rotational correlation times were estimated from these spectra and are listed in Table IV. Comparison of the first three entries in Table IV shows that surface selectivity was not greatly changed by using a more polar solvent or solvent mixture. However the small changes seen for τ_c values in most solvents is in accord with the notion that a more polar solvent afforded slightly greater surface selectivity. We then examined entrapment-functionalized polyethylene powder that was formed by more rapidly quenching solutions of host polymer and oligomer. In these cases, the 100 °C solution of polyethylene and oligomer was poured into room-temperature methanol or hexane. Once again, ESR spectra were obtained for the powders so formed. Table IV lists rotational correlation times estimated from ESR spectra of nitroxyl labels in these samples as well. We again saw small differences among these experiments. In these cases, the effects of several factors are present. First there is an effect due to the polarity of the solvent used in this sort of rapid solvent quenching. Comparison of the τ_c values in ethanol suspension for the same polymer plus oligomer quenched with methanol versus hexanes generally shows that methanol quenching produces a more "surface"-functionalized powder. Second, the effect of increased branching in the oligomer noted in Table III is also seen here. For example, comparison of $\tau_{c(\text{ethanol})}$ values for PE(B) with **7a**, **7b**, or **7c** once again indicates that greater branching in the oligomer favors surface selectivity. Finally, rapid quenching leads to major differences between the morphology of powders formed in this way and those formed by simple cooling and precipitation. The product polymers formed in rapid quenching are less crystalline. Using IR spectroscopy the changes vary for each host polymer.[18] Specific values are (polymer, thermal precipitation, rapid methanol precipitation and rapid hexane precipitation): PE(A), 72, 61, 67; PE(B), 77, 62, 67; PE(C), 58, 43, 47; PE(D), 50, 37, 46; PE(E), 59, 40, 46. These morphological changes induced by rapid versus slow quenching account for the qualitative similarity of the τ_c values in Table IV and for the samples of PE(C or D or E)/7.

In our earlier work, we had examined small changes in end group structure and had noticed that an oligomer terminated with an ether-bound nitroxyl group versus an amide-bound nitroxyl group interacted with solvent to a smaller extent and was presumably located deeper in the entrapment functionalized polymer. In this work we extended these studies. Extensions of these studies were facilitated by the control over the nature of the terminal functional group in these oligomers we could achieve. This control was the result of the synthetic versatility of the organolithium end group present in the living polymerizations. In this case, we also prepared a block copolymer in which a short polystyrene block ($m \cong 8$ by ^{1}H NMR spectroscopy) was added onto the original polybutadiene living polymer by continuing the anionic polymerization of butadiene with a small amount of styrene. The living polystyrene so obtained (eq 4) was then quenched with CO_2 and subsequently acidified to yield a carboxylated polystyrene. Derivatization of the carboxyl group so-formed by acid chloride formation ($SOCl_2$) followed by reaction with 4-amino-2,2,6,6-tetramethylpiperidinyl-1-oxy yielded a spin-labeled polymer.



Comparison of τ_c values listed in Table V for oligomers **7b** or **11** entrapped in the same host polymer by thermal precipitation shows that the end group can have significant effects. Significant surface selectivity is achieved with **11** even in the case of the low-crystallinity, low-density polymer sample PE(E). The effects of having a less polyethylene miscible end group as in **11** were even seen in solvent precipitation as noted in Table V.

Finally, we have briefly examined the potential for entrapment functionalization of films. These studies used all the sorts of oligomers described above and a high-

Table VI
Rotational Correlation Times of Entrapment Functionalized Films Containing Entrapped Nitroxyl-Terminated Oligomers[a]

	rotational correlatn times ($\times 10^{10}$/s)			
solvent	PE(B)/ **7b**[b]	PE(B)/ **7b**[c]	PE(B)/ **7c**[c]	PE(B)/ **11**[c]
no solvent	136	137	125	128
n-hexane	85	73	63	55
carbon tetrachloride	69	82	27	23
toluene	14	13	6	5
diethyl ether	18	23	11	8
tetrahydrofuran	3	4	2	2
ethanol	110	69	58	55

[a] Rotational correlation times were measured from degassed suspensions of films in the indicated solvents at 25 °C according to the procedure of ref 9. [b] This film was prepared by a molten casting procedure and was 10 mil thick. [c] This film was 2 mil thick and was prepared by solvent casting technique.

density polymer. Table VI lists some τ_c values for suspensions of these films. While complete surface selectivity was not achieved by using solution cast films, the same trends noted above for polymer powders appear to be present here.

In summary, entrapment functionalization is a viable synthetic procedure for incorporating spectroscopic labels at polyethylene–solution interfaces. Host polymer morphology, oligomer microstructure, oligomer end group, and entrapment conditions can all be used to increase or decrease the extent of surface functionalization in the product functionalized polyethylene powder or film in predictable, controllable ways.

Experimental Section

General Methods. Butadiene and carbon dioxide were obtained from Matheson Co. Ethylene was purchased from Air Products. Cobalt(III) acetylacetonate was obtained from Strem Chemical Inc. 4-Amino-2,2,6,6-tetramethylpiperidinyl-1-oxy was purchased from Sigma Chemical Co. All other chemicals used were obtained from Aldrich Chemical Co. Hydrocarbon and ethereal solvents were distilled under nitrogen from sodium benzophenone ketyl immediately prior to use. Other solvents used were reagent grade and were generally not further purified. Tetramethylethylenediamine was distilled from potassium metal and stored under nitrogen until use. Nitrogen was purified by passage through a calcium chloride drying tower. Butadiene was purified by successively passing it through two columns containing calcium sulfate (Drierite) and 4-Å molecular sieves, respectively. Hydrogen and ethylene were reagent grade and used without further purification. Thionyl chloride was purified according to a literature method.[20] Styrene was purified by a procedure described by Collman.[21] All glassware was dried in an oven at 130 °C overnight prior to use. Magnetic stirring or shaking on a wrist-action shaker was generally used for agitation of reactions. Syringes and stainless-steel cannulae were utilized to transfer water- and air-sensitive solvents and reagents. The column for GPC analysis was a 30-cm long by 7.8-mm in diameter and packed with fully porous, highly cross-linked styrene–divinylbenzene copolymer (Waters, 500-Å STYRAGEL). GPC was carried out with degassed toluene at room temperature. Infrared spectra of polymer powders (i.e., polyethylene or entrapment-functionalized polyethylene) were taken by using thin translucent disks prepared by a pressed-disk technique. Infrared spectra of polybutadiene and other cooligomers (i.e., ethylene–butene cooligomers, strictly linear ethylene oligomers, and (ethylene–butene)–styrene block cooligomers were obtained as thin films prepared by melting these oligomers between two sodium chloride plates. All IR spectra were recorded on a Pye Unicam SP3-200 or Bruker Model 30 FT-IR spectrometer at room temperature. Band positions are reported in cm^{-1}. ^{1}H NMR spectra were obtained by using a Varian EM-390 instrument. Chemical shifts are reported relative to TMS. The percent vinyl branching in the functionalized polybutadienes (hence the contents of ethyl branching in the functionalized ethylene–butene cooligomers) was calculated from data obtained by either IR spectroscopy or ^{1}H NMR spectroscopy.

Polymer Materials. PE(A) having a density of 0.97 was obtained from Gulf Chemical Co. PE(B), PE(C), PE(D), and PE(E) were obtained from Dow Chemical Co. Characterization data supplied by Dow Chemical Co. for these four polyethylene samples were as follows. Density: 0.960 for PE(B), 0.920 for PE(C), 0.925 for PE(D), and 0.930 for PE(E). Melt index: 42 for PE(B), 25 for PE(C), 50 for PE(D), and 87.5 for PE(E). Contents of comonomers during preparation: <10% of propylene for PE(B), <10% of octene for PE(C), PE(D), and PE(E). Although these samples supposedly were additive-free, these polyethylenes were still dissolved in toluene at 110 °C and then precipitated from the solution after cooling to room temperature. Subjecting these polyethylene samples to several precipitation cycles did lead to loss of a small amount of low molecular weight material as determined by GPC. However, no soluble material could be detected in the filtrates after four dissolution–precipitation cycles for high-density (i.e., PE(A) and PE(B)) or after seven dissolution–precipitation cycles for the low-density polyethylenes (i.e., PE(C), PE(D), and PE(E)). The polyethylene samples were therefore pretreated to four such dissolution–precipitation cycles for high-density polyethylene or seven dissolution–precipitation cycles for low-density polyethylene before use in the entrapment experiments.

Preparation of Ethylene–Butene Cooligomers. Butadiene was oligomerized following the general procedure of Grassley starting with 10 g of butadiene and *sec*-butyllithium as an initiator.[16] The solvent generally used was cyclohexane except that THF was added in order to vary the extent of 1,2-polybutadiene (and hence the % ethyl branching in the eventual product).[13] The amounts of THF used for each different oligomer were as follows: **4b** (none); **4c** (0.12 mL); **4d** (0.3 mL); and **4e** (THF as solvent). In a typical procedure, 10 g of butadiene was added into a 1-L, round-bottomed flask equipped with a magnetic stirrer. After addition of 400 mL of cyclohexane and 0.12 mL of THF, 4.7 mL of 1.3 N *sec*-butyllithium was added by using a syringe. Heating the reaction mixture up to 50 °C for 24 h yielded a solution of the living oligomer. After this solution cooled to room temperature, the cyclohexane solution of the intermediate lithiated polybutadiene was transferred by forced siphon through a cannula under nitrogen into a 2-L flask containing a large amount of freshly crushed dry ice. Vigorous agitation during this addition was required to avoid formation of ketone product. This flask was then equipped with a drying tube containing anhydrous calcium sulfate (Drierite) and stored in a refrigerator for 24 h. Protonation of the lithium salt of this carboxylated polybutadiene was accomplished by mixing this cyclohexane solution with 200 mL of 1 N aqueous HCl at 50 °C for 2 h. After the solution was cooled to room temperature, the organic phase was separated by centrifugation and removed by forced siphon through a cannula under a nitrogen pressure. The resultant polymer was then precipitated by addition of 300 mL of methanol, isolated by centrifugation, and finally dried at 25 °C under reduced pressure for 48 h. The products were characterized by IR and NMR spectroscopy. A typical IR spectrum had peaks at (**4b**) 3090 (m), 3010 (s), 2920 (s), 2840 (s), 1830 (w), 1710 (s), 1640 (m), 1465 (s), 1405 (m), 1380 (w), 1360 (m), 1315 (m), 1275 (w), 1250 (w), 1170 (w), 1080 (m), 1000 (s), 965 (s), 910 (s), 730 (s), and 700 (s) cm^{-1}. Other carboxylated polybutadiene samples had similar IR spectra with minor changes in peak location and/or relative intensity. ^{1}H NMR spectra of the various carboxylated polybutadienes were also similar with a typical spectrum (e.g. for **4b**) being ($CDCl_3$) δ 10.5 (removed by D_2O), 7.1, 5.4, 5.0, 4.8, 3.1, 2.3, 2.1, 1.4, and 0.9. The carboxylated polybutadiene **4b** was ca. 12% 1,2-vinyl, 46% 1,4-cis, and 42% 1,4-trans based on IR spectroscopy[17] and was ca. 10% 1,2-vinyl and 90% 1,4-trans and -cis based on integration of the area under the peaks at 5.4 (1,4-trans and -cis) and 5.0 (1,2-vinyl) of this polymer's ^{1}H NMR spectrum. The M_v of this polybutadiene was ca. 2500. M_v values for this polymer and **4c–e** were determined by using a Ubbelohde viscometer using a solution of 0.03 g of polymer in 25 mL of toluene at 30 °C according to

$$[\eta] = \frac{3(\eta_r^{1/3} - 1)}{C} = 3.24 \times 10^{-4} M_v^{0.7}$$

where η = relative viscosity and C = concentration of the solution in grams of polybutadiene per 100 mL of solution.[22] Other carboxylated polybutadienes were similarly prepared with M_v values of 2600 (**4c**), 2800 (**4d**), and 2200 (**4e**). Polymer **4c** was ca. 22% 1,2-vinyl, 39% 1,4-cis, and 39% 1,4-trans by IR spectroscopy and 19% 1,2-vinyl and 81% cis and trans by ^{1}H NMR spectroscopy. Polymer **4d** was 49% 1,2-vinyl, 25% 1,4-cis, and 26% 1,4-trans by IR spectroscopy, and polymer **4e** was 80% 1,2-vinyl, 9% 1,4-cis, and 11% 1,4-trans by IR spectroscopy.

Hydrogenation of carboxylated polybutadienes was carried out either with $RhCl(PPh_3)_3$ as described previously or with $Co(acac)_3$ as a catalyst.[23] In the latter case, 5 g of polybutadienecarboxylic acid was dissolved in 50 mL of toluene and transferred by forced siphon through a cannula to a 250-mL centrifuge tube containing a 2 mol % triethylaluminum/cobalt acetylacetonate catalyst having a triethylaluminum/cobalt acetylacetonate molar ratio of 6. Hydrogenation was then carried out by using a Parr shaker-type hydrogenation apparatus under 70 psi of hydrogen pressure at 70 °C for 48 h. After the reaction mixture had cooled to room temperature, 500 mL of toluene and 250 mL of 1 N aqueous HCl were added to dilute the polymer solution and to decompose the catalyst. This heterogeneous mixture was stirred at 80 °C for 3 h. After the organic and aqueous phases were separated by centrifugation, another 250 mL of 1 N aqueous HCl was added to the organic phase and stirred at 80 °C for an additional 3 h. These aqueous HCl treatments were repeated four times, and the organic layer was isolated each time by centrifugation. This organic solution was then treated with 200 mL of 0.125 M aqueous EDTA (disodium salt) with stirring at 60 °C for 1 h. After the organic and aqueous phases were separated by centrifugation, 800 mL of methanol was added to the organic phase to precipitate the hydrogenated polymer. This resultant solid polymer was separated by centrifugation, washed with 600 mL of methanol, and finally dried under reduced pressure at 80 °C for 48 h to yield the product which was characterized by IR and ^{1}H NMR spectroscopy. A typical IR spectrum had peaks at 2910 (s), 2840 (s), 1710 (s), 1405 (s), 1380 (m), 1275 (w), 1040 (w), 965 (w), 770 (w), 730 (s), and 720 (s) cm^{-1} (**5b**), and a typical ^{1}H NMR spectrum showed no peaks at δ 5.1 or 5.4 indicating that complete hydrogenation had occurred. The resulting ethylene–butene cooligomers were waxy solids or viscous oils and were soluble in toluene at 25 °C at a level of ca. 1.0 g/10 mL of toluene. Atomic absorption spectroscopy showed that these ethylene–butene cooligomers contained small amounts of residual cobalt, ca. 14.1×10^{-6} mmol of cobalt/g of cooligomer **5b**.

Preparation of Spin-Labeled Oligomers. The linear carboxylated ethylene oligomer or ethylene–butene cooligomers **5a–e** were made into acid chlorides with $SOCl_2$. Then 4-amino-2,2,6,6-tetramethylpiperidinyl-1-oxy spin label was added to form a carboxylic acid amide as previously described.[4] The spin-labeled oligomers were characterized by ESR spectroscopy and by IR spectroscopy ($\nu_{C=O}$ at 1670 cm^{-1}) with no detectable absorption at 1710 cm^{-1} (where any ketone byproduct would be) or at 1700 cm^{-1} where the starting carboxylic acid group absorbed.

Procedure for Entrapment Functionalization by Thermal Precipitation. This entrapment procedure was carried out in a manner similar to that described previously.[4] One change in procedure employed when low-density polyethylenes were used as host polymers was that centrifugation was used instead of filtration (i.e. for PE(C), PE(D), or PE(E)).

Procedure for Entrapment Functionalization by Solvent Precipitation. To a 100-mL round-bottomed flask equipped with a magnetic stirring bar and a condenser was added 0.6 g of the host polyethylene, 0.2 g of functionalized oligomer, and 30 mL of toluene. After this mixture was heated to 110 °C by using an oil bath with stirring, a homogeneous solution formed. The solution was allowed to stir at this temperature for 20 min and immediately poured into 300 mL of the desired cool solvent (i.e., methanol or hexane) which was stirred vigorously for an additional 30 min. The polyethylene precipitate so formed was separated by centrifugation and placed in a 250-mL flask equipped with a magnetic stirrer. Addition of 100 mL of toluene (or 50/50 (v/v) toluene–hexane for low-density polyethylene) formed a suspension which was stirred at 25 °C for 1 h. This washing process was repeated two times, and the polymer sample was separated each time by centrifugation. After these procedures, the resultant polyethylene was recovered by centrifugation, rewashed with 200 mL of toluene and 50 mL of diethyl ether, and finally dried in vacuo at room temperature for 24 h.

Film Formation of Entrapment-Functionalized Polyethylene Using a Solvent Casting Technique. A 0.8-g sample of entrapment-functionalized polyethylene powder was added to a 50-mL round-bottomed flask which contained 15 mL of *o*-dichlorobenzene. The polymer suspension was heated to 120 °C oil bath with stirring to effect dissolution of the polymer. After all the polymer was dissolved, the polymer solution was immediately poured into a preheated 14-cm outer diameter petri dish sitting in an oven held at 120 °C. The oven had been modified so that a constant stream of nitrogen gas with pressure of 10 psi was being swept over the polymer solution in the petri dish. After the solvent had evaporated for 45 min, the petri dish was placed in a vacuum oven held at 60 °C for an additional 1 h to remove the last traces of solvent. The polymer film was finally peeled out of the bottom of dish, cut into pieces (ca. 20 × 30 mm), and rolled into the ESR tube prior to use in ESR measurement. During the rolling process and insertion of polymer film into the ESR tube, a pair of clean thin gloves were used to avoid putting fingerprints on the film. The procedure described above produced a film with an average thickness of 2 mils measured with a micrometer.

Film Formation of Entrapment-Functionalized Polyethylene Using a Molten Casting Technique. A 1-g sample of entrapment-functionalized polyethylene powder was evenly dispersed diameter circle on a sheet of aluminum foil which was placed on a hot plate. The hot plate was then gently heated until the polymer sample melted. At this point, the polyethylene sample was immediately covered with another sheet of aluminum foil and pressed by a hand-operated metal roller to make a film. This polyethylene film sandwiched between aluminum foil was then removed from the hot plate and cooled to room temperature, and the film was peeled off. After cutting the film into strips (ca. 2 × 30 mm), it was placed in an ESR tube with a pair of forceps for ESR spectral studies. The procedure described above produced a film with an average thickness of 10 mils as measured with a micrometer.

General ESR Measurements. ESR spectra were recorded at ambient temperature by using a Varian E-6S spectrometer operating at a microwave frequency of 3.3 KG with a modulation amplitude of 1 G and with attenuation power set low enough to avoid saturation. In study of the solvent effects, each polymer sample was allowed to contact an excess of solvent in a 4-mm outer diameter ESR tube. This ESR tube capped with a septum was vacuum degassed three times by using freeze–thaw techniques and then allowed to stand at room temperature for 2 h prior to spectral analysis.

General Procedure for Reactions of Entrapment-Functionalized Polyethylene with Soluble Reagents. After the entrapment-functionalized polyethylene as a suspension in the solvent of choice had been recorded, a large excess of the desired reagent was added to the ESR tube via a syringe. Agitation was accomplished by stirring with a Vortex mixer for 2 min. The ESR spectrum was recorded periodically and intensity of the largest peak in the ESR spectrum was measured. In the cases of very polar solvents such as *N,N*-dimethylformamide or water, the high dielectric constant of these solvents precluded direct ESR monitoring of a suspension of the entrapment-functionalized polyethylene. In these cases, an ESR spectrum of a standard amount of entrapment-functionalized polyethylene in the dry state was first obtained, and, in a series of separate flasks, samples from the same batch of entrapment-functionalized polyethylene were allowed to contact with excess amount of the desired solvent. In a typical procedure, the flask was capped with a septum, degassed in vacuo, and shaken with the desired reaction solution by using a wrist-action shaker. After the desired period of time, the polymer sample was isolated by filtration, washed with water, ethanol, and acetone successively, and finally dried under reduced pressure for 48 h. After a thorough drying, a new ESR spectrum was recorded by using the same amount of the entrapment-functionalized polyethylene as in the original case. Control experiments using entrapment-functionalized polyethylene in ESR tubes in procedures analogous to these but without addition of reagents which could react with this entrapment-functionalized polyethylene showed that ESR intensities measured in successive experiments varied by ±6%.

Digestion of Polymer Samples. The procedure used was a modification of Shanina's.[24] To a 20-mL quartz crucible was added 0.2 g of the polymer sample and 4 mL of concentrated H_2SO_4. The polymer mixture was gently heated on a hot plate until the polymer sample was completely decomposed. Then, 10 mL of concentrated HNO_3 was added dropwise to the decomposed polymer sample, followed by further heating on the hot plate for an additional 24 h with occasional shaking. A brownish homogeneous solution was finally obtained after this acidic digestion. After this solution was cooled to 25 °C, the solution was diluted with distilled water in a 25-mL volumetric flask and analyzed for cobalt content by atomic absorption spectroscopy by the Agricultural Analytical Services Laboratory at Texas A&M University. A blank cobalt analysis using the same amount of reagents excluding the polymer sample was also carried out. These analyses showed that oligomer **4b** contained 14.1×10^{-6} mmol of Co/g while the host polymer and blank supposedly contained 9×10^{-8} mmol of Co/g. This small amount of cobalt did not directly affect our studies. However, prolonged heating of the oligomers that contained cobalt once the spin label had been incorporated resulted in apparent oxidation of the spin label.

Preparation of Carboxylated Butadiene–Styrene Block Cooligomer 9. In a typical procedure, 10 g of butadiene was passed into a 1000-mL round-bottomed flask equipped with a magnetic stirring bar which contained 400 mL of cyclohexane. To this solution was added 4.8 mL of 1.3 N *sec*-butyllithium in cyclohexane as an initiator through a syringe. Polymerization was then carried out at 50 °C with stirring under nitrogen for 24 h. To this living lithiated polybutadiene was in turn added 4.2 g of distilled styrene via a syringe. After an additional 24 h of further block polymerization, this solution was cooled to room temperature and 200 mL of THF was added with a syringe. The polymer solution was immediately transferred by forced siphon through a cannula under nitrogen into a 2-L flask which contained a large amount of freshly crushed dry ice.[25] The flask was then equipped with a drying tube containing anhydrous calcium sulfate (Drierite) and stored in a refrigerator for 24 h. After the solvents were removed at reduced pressure by using a rotary evaporator, the lithium salt of this carboxylated butadiene–styrene block cooligomer was dissolved in 350 mL of toluene. Protonation of this cooligomer was accomplished by mixing this toluene solution with 150 mL of 1 N aqueous HCl at 55 °C for 2 h. after the solution was cooled to room temperature, the two phases were separated by centrifugation and the organic phase was removed by using a cannula under nitrogen. The resultant cooligomer 15 was precipitated by addition of 300 mL of methanol and dried at room temperature under vacuum for 48 h. An IR spectrum of this block cooligomer showed absorptions at 3080 (m), 3070 (s), 3010 (s), 2920 (s), 2850 (s), 1940 (w), 1870 (w), 1805 (w), 1710 (s), 1640 (m), 1605 (w), 1495 (m), 1465 (s), 1405 (w), 1380 (w), 1360 (w), 1305 (m), 1235 (w), 1150 (w), 1030 (w), 995 (m), 965 (s), 910 (s), 760 (m), 730 (s), and 700 (s) cm^{-1}. The M_v of this carboxylated butadiene–styrene block cooligomer **9** so prepared was ca. 3500. A ^1H NMR spectrum of this polymer in CCl_4 using TMS as an internal standard showed peaks at δ 10.5, 7.0, 6.5, 5.3, 5.0, 4.8, 3.0, 2.3, 2.0, 1.4, and 0.9. The olefin content of polybutadiene segment in this block cooligomer **9** was ca. 10% 1,2-vinyl and 90% 1,4-trans and -cis as by integration of peaks at δ 5.3 (1,4-trans and -cis) and 5.0 (1,2-vinyl) in this cooligomer's ^1H NMR spectrum. The styrene content of this block cooligomer was ca. 9 units of styrene in each polymer chain on the basis of ^1H NMR spectrum and was estimated by integration of the area under the peaks at δ 5.0 (1,2-vinyl), 5.3 (1,4-trans and -cis), 6.5 (ortho protons in styrene), and 7.0 (meta and para protons in styrene) using the M_v measured previously.

Hydrogenation of Carboxylated Butadiene–Styrene Block Cooligomer 9 To Prepare (Ethylene–Butene)–Styrene Block Cooligomer 10 Using Co(acac)$_3$ as a Catalyst. This procedure used in the hydrogenation of **10** was the same as that used in the hydrogenation of carboxylated polybutadiene above. The product polymer **10** (M_v = 3500) was a soft, waxy material and was soluble in toluene at room temperature at a level of 0.8 g of polymer in 10 mL of toluene. IR spectrum (neat, cm^{-1}, intensity): 3080 (m), 3060 (m), 3030 (s), 2920 (s), 2850 (s), 2540 (w), 1950 (w), 1710 (s), 1601 (m), 1495 (m), 1465 (s), 1375 (m), 1300 (w), 1245 (w), 1160 (w), 1120 (w), 1070 (w), 1035 (m), 965 (w), 910 (w), 850 (w), 760 (m), 735 (s), 720 (s), and 700 (s). ^1H NMR analysis of **10** in CCl_4 (TMS was used as an internal standard) confirmed the completion of hydrogenation due to the absence of peaks at δ 5.0 and 5.3 attributable to the protons of vinyl groups.

Preparation of 4-Carboxamido-2,2,6,6-tetramethylpiperidinyl-1-oxy Labeled (Ethylene–Butene)–Styrene Block Cooligomer 11. This preparation was carried out in a manner similar to that for the other carboxylated oligomers described above. An IR spectrum of this spin-labeled (ethylene–butene)–styrene block cooligomer had a characteristic band at 1675 cm^{-1}, suggesting the formation of an amide linkage. An ESR spectrum of **11** in a dry state showed a broad three-line signal with a_N value of 31.0 G.

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Registry No. PE, 9002-88-4; (ethylene)(propylene) (copolymer), 9010-79-1; (octene)(propylene) (copolymer), 70800-37-2.

References and Notes

(1) Feast, W. J., Munro, H. S., Eds. *Polymer Surfaces and Interfaces*; Wiley: 1987.
(2) Wu, S. *Polymer Interfaces and Adhesion*; Marcel Dekker: New York, 1982.
(3) Brewis, D. M.; Briggs, D. *Polymer* **1981**, *22*, 7–16.
(4) Bergbreiter, D. E.; Chen, Z.; Hu, H.-P. *Macromolecules* **1984**, *17*, 2111–2114.
(5) Dias, A. J.; McCarthy, T. J. *Macromolecules* **1987**, *20*, 2068–76.
(6) Holmes-Farley, S. R.; Reamey, R. H.; Nuzzo, R.; McCarthy, T. J.; Whitesides, G. M. *Langmuir* **1987**, *3*, 799–815 and references therein.
(7) Fonseca, C.; Perena, J. M.; Fatou, J. G.; Bello, A. *J. Mater. Sci.* **1985**, *20*, 3283–8.
(8) Nuzzo, R. G.; Smolinsky, G. *Macromolecules* **1984**, *17*, 1013–19.
(9) Likhtenshtein, G. I. *Spin Labeling Methods in Molecular Biology*; Wiley: New York, 1976; Chapter 1. The rotational correlation times calculated from the line width and peak height of ESR spectra had errors of ±20%.
(10) Holmes-Farley, S. R.; Whitesides, G. M. *Langmuir* **1987**, *3*, 62–76.
(11) Dodd, G. H.; Barratt, M. D.; Rayner, L. *FEBS Lett.* **1970**, *8*, 286–288.
(12) Rozantsev, E. G. *Free Nitroxyl Radicals*; Plenum: New York, 1970; Chapter 4. Keana, J. F. W. *Chem. Rev.* **1978**, *78*, 37–64. Whitesides, G. M.; Newirth, T. L. *J. Org. Chem.* **1975**, *40*, 3448–3450.
(13) Halasa, A. F.; Lohr, D. F.; Hall, J. E. *J. Polym. Sci., Polym. Chem. Ed.* **1981**, *19*, 1357–1360.
(14) Young, R. N.; Quirk, R. P.; Fetters, L. J. *Adv. Polym. Sci.* **1984**, *56*, 1–90.
(15) Hay, J. N.; Harris, D. S.; Wiles, M. *Polymer* **1976**, *17*, 613–617. Magnin, H.; Rodriguez, F.; Abadie, M.; Schue, F. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 901–912.
(16) Rachapudy, H.; Smith, G. G.; Raju, V. P.; Graessley, W. W. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 1211–1222. Rochefort, W. E.; Smith, G. G.; Rachapudy, H.; Raju, V. R.; Graessley, W. W. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 1197–1210.
(17) The relative percentage of 1,4-*cis*, 1,4-*trans*, and 1,2-vinyl groups in the intermediate polybutadiene was determined by measuring the corresponding optical densities in the IR spectrum of the polybutadiene at the 735 (1,4-cis), 910 (1,2-vinyl), and 965 (1,4-trans) cm^{-1}: cf. Morero, D.; Santambrogio, A.; Porri, L.; Ciampelli, F. *Chim. Ind. (Milan).* **1959**, *41*, 758–762.
(18) Rasmussen, J. R.; Stedronsky, E. R.; Whitesides, G. M. *J. Am. Chem. Soc.* **1977**, *99*, 4736–4745. Rasmussen, J. R.; Bergbreiter, D. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1977**, *99*, 4746–4756.
(19) Wunderlich, B. *Macromolecular Physics*; Academic: New York, 1973/1976; Vol. 1 and 2. (b) Tobin, M. C.; Carrano, M. J. *J. Polym. Sci.* **1957**, *24*, 93–103.
(20) Friedman, L.; Wetter, W. P. *J. Chem. Soc. A* **1967**, 36–37.
(21) Collman, J. P.; Kosydar, K. M.; Bressan, M.; Lamanna, W.; Garrett, T. *J. Am. Chem. Soc.* **1984**, *106*, 2569–2579.
(22) Yang, J.-H.; Ou-Yang, J. *Sci. Sin.* **1980**, 734–743. (b) Sheng, T.-C.; Ou-Yang, C. *Chem. Abstr.* **1975**, 8343762. (c) Shen, Z.; Gong, Z.; Zhong, C.; Ou-Yang, J. *Sci. Sin.* **1974**, *17*, 656–660.
(23) Falk, J. C. In *Catalysis in Organic Syntheses*; Rylander, P. N., Greenfield, H., Eds.; Academic: New York, 1976; pp 305–324.

Macromolecules **1989**, *22*, 662–665

(24) Shanina, T. M.; Gel'man, N. E.; Mikhailovskaya, V. S.; Kabaeva, N. M. *Zh. Anal. Khim.* **1981**, *36*, 414–417.

(25) It was found that if THF was added before block polymerization of styrene with polybutadienyllithium as an initiator, no carboxylation occurred after the introduction of dry ice on the basis of IR analysis of the resultant product. This was probably due to the THF-induced decomposition of lithium chain ends of cooligomers under such block polymerization conditions: cf. Wakefield, B. J. *The Chemistry of Organolithium Compounds*; Pergamon: Elmsford, NY, 1974; Chapter 14.

Catalytic Hydrogenation of Polymers in the Bulk

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ABSTRACT: Although research on the catalytic hydrogenation of polymers historically has focused on solution studies,[1,2] the *bulk* hydrogenation of polymers using molecular catalysts is reported here. In spite of slow reaction rates, high conversions (>90%) can be obtained at moderate temperatures and pressures. Samples were prepared by evaporating solutions containing the catalyst ($Rh(PPh_3)_3Cl$, $[Ir(COD)(PMePh_2)_2]PF_6$) and a reducible hydrocarbon polymer. The initial hydrogen uptake rates are shown to be sensitive to catalyst loading and the resulting distribution of catalyst in the polymer. The implications of the results with respect to catalyst mobility are discussed.

Introduction

One advantage of homogeneous catalysis over heterogeneous catalysis is its greater ability to effectively catalyze reactions on polymeric substrates.[3,4] The slow rates and low yields observed when heterogeneous catalysts are used in such reactions are generally ascribed to the difficulty of orienting the long polymer chain on the immobile active site.[3] In contrast, homogeneous catalysis offers catalytic mobility and circumvents such orientational problems. Catalytic hydrogenation has been one proving ground for these ideas. While hydrogenations of olefin-containing polymers and solvent-swelled networks were slow and did not go to completion when catalysts such as Pd/C or Rh/Al_2O_3 were used, the hydrogenations proceeded well with homogeneous catalysts.[5]

During a search for a material effective at irreversibly gettering hydrogen gas,[6,7] we became interested in learning whether the mobility of homogeneous catalysts was sufficient to permit effective hydrogenation of polymers in the *absence of solvent*. The synthesis of polymers within a bulk polymer matrix using Zeigler catalysts has been reported by others.[8] This paper describes the bulk hydrogenation of olefinic polymers using molecular catalysts.

Two catalysts were selected for this study from the large number of known homogeneous hydrogenation catalysts. Wilkinson's catalyst,[9] $Rh(PPh_3)_3Cl$, is the best understood of all such catalysts. Each step of its catalytic cycle has been elucidated by painstaking studies.[10] Most relevant to this work is the unambiguously homogeneous nature of the catalyst[11] and its previous use in solution hydrogenations of polymers.[12] Additionally, its low sensitivity to air simplified sample preparation and manipulation. In contrast, the mechanism of the relatively new series of hydrogenation catalysts $[Ir(COD)(L)_2]PF_6$ (COD = 1,5-cyclooctadiene; L = PR_3, R = alkyl, aryl), developed by Crabtree et al.,[13] is less definitive. These catalysts are notable for their great reactivity in hydrogenations even with highly substituted olefins. They differ from all other known hydrogenation catalysts in that their activity is unaffected by the presence of oxygen. For these reasons, and because of evidence supporting the homogeneous nature of its chemistry,[12] the Crabtree catalyst $[Ir(COD)(PMePh_2)_2]PF_6$ was chosen for this study.

Several factors contributed to the selection of olefinic polymers as substrates. Double bonds with low steric hindrance and a low number of substituents were required to enhance reactivity toward catalytic hydrogenation. Only thermoplastic polymers were considered because of their structural integrity and processibility. The polybutadiene polymers readily satisfy the first two requirements. Obtaining the desired material characteristics limited the available choices. Polystyrene-*block*-polybutadiene-*block*-polystyrene (PS–PB–PS) is a thermoplastic rubber. The low T_g of its polybutadiene continuous phase provides elasticity while the phase-separated polystyrene domains afford physical cross-linking. A related nonchemical cross-linking scheme is found in the partially crystalline polymer syndiotactic 1,2-polybutadiene (1,2-PB). In this case, crystalline domains cohere the amorphous regions of the polymer.

Experimental Section

Materials and Sample Preparation. The syndiotactic 1,2-polybutadiene was purchased from Polysciences, Inc. Nuclear magnetic resonance (NMR) analysis indicates an olefinic to aliphatic proton ratio of 0.9:1.0. Shell Chemical Co. supplied the butadiene–styrene triblock copolymer (Kraton D1102) with a 72% by weight butadiene center block. The proton NMR spectrum confirms the specified styrene:butadiene ratio. Based on carbon NMR analysis, the butadiene center block contains a mixture of 1,4-cis, 1,4-trans, and 1,2-vinyl additional units in the approximate ratio of 40:45:15, respectively. $Rh(PPh_3)_3Cl$ was obtained from Aldrich Chemical Co. Research grade chemicals, polymers, and solvents were used without further purification. $[Ir(COD)(PMePh_2)_2]PF_6$ was prepared by literature methods.[15]

Samples for hydrogenation studies were cast from solution. For example, 1.0 g of the triblock copolymer was dissolved in 50 mL of toluene. The solution was degassed, 0.1 g of $Rh(PPh_3)_3Cl$ was added, and the solvent was then removed under vacuum. The resulting polymer/catalyst mixture (9.1% by wt catalyst) was analyzed by capillary gas chromatography to confirm that there is less than 0.1% residual solvent. Samples containing Wilkinson's catalyst were cast from toluene while those containing $[Ir(COD)(PMePh_2)_2]PF_6$ were cast from dichloromethane.

Hydrogenations. Hydrogenations were performed in a pressure reaction apparatus purchased from Lab Glass Inc. and modified to include a pressure guage (0–100 psig) and gas inlet ports. The total volume of the system was 120 mL. For those experiments requiring low hydrogen pressures, an absolute

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