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Entrapment of Functionalized Ethylene Oligomers in Polyethylene

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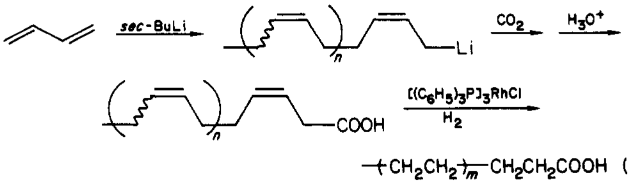
Received November 28, 1983

ABSTRACT: Functionalization of polyethylene by entrapment of functionalized ethylene oligomers in precipitates of polyethylene is described. The reactivity of the resulting entrapped functionalized ethylene oligomers toward various reagents and the degree of mobility of these entrapped ethylene oligomers in the presence of various solvents were evaluated by using ethylene oligomers containing spin labels as reporter groups. The results show that ethylene oligomers of $\bar{M}_v = 2500$ can be quantitatively and reproducibly entrapped in polyethylene powders by coprecipitation with high-density polyethylene and that the polar functional groups of these ethylene oligomers can interact with solvents and with reagents in solution when these functionalized polyethylene powders are suspended in various solutions. Studies of the reactivity and dynamics of the entrapped oligomer's functional groups toward reagents in solution also show the effect of solvation on reactions of functionalized polyethylene and demonstrate that the dimensions of the interfacial region of polyethylene (i.e., the effective surface dimensions of polyethylene in contact with solutions) are dependent on the parameters of the particular experiment being conducted.

Procedures for functionalization of polymers are of interest in many aspects of polymer science. In the particular case of relatively unreactive polymers such as polyolefins, such functionalization procedures assume considerable importance as a way of altering the surface chemistry of these hydrocarbon polymers or as a means of increasing these polymers' utility and durability in various practical applications. Consequently, many methods have been developed to accomplish functionalization of these polymers. Useful methods include both surface-selective treatments such as chemical etching,[2,3] irradiation,[3] absorption,[3] and polymerization of surfactants at the polymer–solution interface,[4] as well as the simple expedient of addition of low molecular weight additives to polymer melts during processing. Copolymerization is yet another procedure which can be used to modify a polymer, although in this latter case alteration of a polymer's bulk properties is unavoidable. An unresolved issue in most of this work is a clear understanding of exactly what constitutes the "surface" of a hydrocarbon polymer such as polyethylene. In this paper, we describe a new entrapment procedure which can be used as a versatile means of preparing functionalized polyolefin powders. These procedures permit the introduction of relatively complicated functionality into solid polyethylene powders in a single step and have several desirable features. First, the various chemical manipulations leading to the formation of the functional groups which are to be incorporated in the polymer can be accomplished on comparatively low molecular weight materials in homogeneous solution. Since all functional groups are accessible to reagents in a homogeneous solution, incomplete reaction of functional groups and some side reactions can be minimized. Incorporation of mixtures of functional groups into the product functionalized polymer is thus less of a problem. Second, characterization of the products of synthetic sequences is simplified. Third, in these entrapment procedures, functionalized ethylene oligomers are entrapped in polyolefins like polyethylene reproducibly. Thus, successive preparations of functionalized polyolefins with a similar distribution of and level of incorporation of functional groups is possible. Fourth, although the entrapment process leads to only modest levels of incorporation of functional groups on a millimole of functionality per gram of polymer basis (typical levels are 0.01 mmol of functionality per gram of polymer), these levels of functionalization are sufficient for subsequent spectroscopic studies as described below. Fifth, the manner in which these functionalized ethylene oligomers are entrapped in polyethylene precipitates could be controllable as described in more detail below. Potentially, this makes entrapment functionalization a uniquely selective process for derivatizing an unreactive polymer. Finally, the practical result of these entrapment functionalization procedures, at least with high-density polyethylene and the functionalized ethylene oligomers described below, is that polyethylene powders can be prepared with reactive nitroxyl spin labels located near the polyethylene's surface. Studies of dynamics of these spin labels by ESR and studies of the reactivity of these nitroxyl radicals as a function of the reagent and solvent used then provide a demonstration of how various experimental parameters can affect the accessibility of functional groups at a polyethylene "surface".

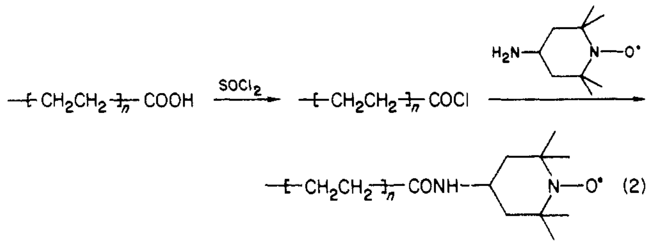
The ethylene oligomers we used in these studies were prepared by the reaction shown in eq 1. Graessley has previously shown that anionic polymerization of butadiene followed by protonation of the intermediate anionic



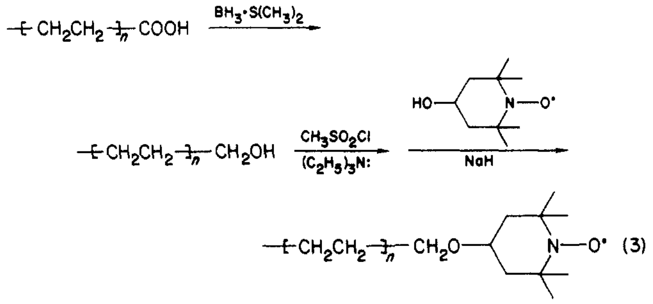
$$\text{—(}CH_2CH_2\text{)}_m\text{—}CH_2CH_2COOH \quad (1)$$

1

polymer and hydrogenation of the carbon–carbon double bonds is a useful way to prepare unfunctionalized ethylene oligomers with good control of molecular weight of the product oligomers.[5,6] The resulting ethylene oligomers are not strictly linear however, since the the 1,4-polybutadiene produced in this reaction consists of 88% 1,4-polybutadiene and 12% 1,2-polybutadiene. Thus, the oligomers produced in eq 1 have some ethyl branching which may affect the location of their incorporation in polyethylene precipitates. In our case, we modified Graessley's procedures by carboxylating the intermediate lithiated polybutadiene to introduce a carboxyl functional group on the ethylene oligomer precursor. Hydrogenation and further derivation of this carboxylated polybutadiene then produced the desired ethylene oligomer. Further derivation of these carboxylated ethylene oligomers to produce spin-labeled polymers is illustrated by the reactions in eq 2 and 3.



2



3

Carboxylated ethylene oligomers or spin-labeled ethylene oligomers prepared by the above procedures were both soluble in toluene solutions at room temperature to the extent of ca. 0.1 g of oligomer/mL of toluene. The $\bar{M}_v$ of the carboxylated polybutadiene (and hence the $\bar{M}_v$ of the derived ethylene oligomers) was typically ca. 2500 and ranged in different preparations from 2000 to 3500. Heating 20 mL of a toluene solution of either **1**, **2**, or **3** and 0.5 g of high-density polyethylene[8] to 110 °C produced a slightly viscous homogeneous solution of polyethylene and ethylene oligomer which formed a filterable polyethylene precipitate (**1**-PE, **2**-PE, or **3**-PE, respectively) on cooling to room temperature. Examination of the recovered polyethylene powder by IR spectroscopy showed a $\nu_{C=O}$ at 1710 and 1670 cm^{-1} when ethylene oligomers **1** and **2** were used, respectively. Control experiments using polyethylene alone showed no carbonyl absorption in the infrared. Repeated dissolution and precipitation of these polyethylene precipitates could be carried out without any measurable decrease in the relative intensity of the $\nu_{C=O}$ in the polyethylene precipitates containing **1** or **2** respectively, suggesting that once **1** and **2** were entrapped that they were quantitatively entrapped in subsequent precipitations.

The course of these entrapment procedures was also monitored by GPC of the filtrates of these cycles of precipitation of the polyethylene powder.[10] On the basis of control experiments, RI detection could have detected as little as 1×10^{-5} g of **1**/mL of filtrate. After dissolution of **1**-PE in toluene and precipitation on cooling, the filtrate was examined by GPC. No ethylene oligomer could be detected. On the basis of the detection limits of our GPC experiments and the sensitivity of the ESR experiments described below, we concluded that <1% of the entrapped **1**–**3** was lost to solution in subsequent dissolution/precipitation cycles of **1**-PE, **2**-PE, or **3**-PE after the initial entrapment process had occurred.

Separate experiments in which known amounts of **1** were added to polyethylene allowed us to estimate that up to 0.09 g of **1** could be entrapped in 1 g of polyethylene powder based on the weight difference between the amount of **1** in the starting solution and the amount of **1** recovered. Ethylene oligomers **2** and **3** were entrapped to similar extents.

Control experiments in which **2** was added to toluene suspensions of polyethylene powder at room temperature led to no detectable absorption of **2** by polyethylene as verified by IR and ESR spectroscopic studies of the polyethylene powder recovered from these control experiments. This established that what we describe as entrapment was not merely absorption of **2** by polyethylene. The functionalized polyethylene powders **2**-PE were stable as ethanol or toluene suspensions for at least 1 week at room temperature. As dry powders, they behaved identically in solvation and reactivity experiments (vide infra) even after months of storage. However, these functionalized polyethylene powders were not stable to hot solvent. Extraction of **2**-PE with hot ethanol for 24 h in a Soxhlet apparatus led to loss of 82% of the entrapped oligomer **2**. Continuous extraction of **2**-PE with ethanol at room temperature for 24 h in contrast led to loss of only 3% of the entrapped **2** in **2**-PE.

ESR spectroscopy studies of polyethylene powders containing **2** or **3** corroborated the above conclusions about the quantitative nature of the entrapment process. No **2** or **3** was detectable in filtrates from dissolution–precipitation of polyethylene-entrapped **2** and **3**. ESR spectroscopy also provided detailed information about the location, accessibility, and reactivity of **2** and **3** as described below.

Figure 1 illustrates the effect of various solvents on the nitroxyl groups of **2**-PE. On the basis of the effect of solvent on the line shape of these ESR spectra of polyethylene entrapped **2**, the nitroxyl groups of **2** are apparently entrapped such that they can achieve significant mobility when **2**-PE is suspended in suitable solvents. Interestingly, addition of a solvent such as ethanol, which is expected to be a poor solvent for polyethylene, changed the ESR spectrum of **2** from one characteristic of immobilized **2** into a spectrum more characteristic of soluble **2**. In contrast, addition of toluene, which is a good solvent for polyethylene, produced a spectrum which was characteristic of a mixture of both soluble **2** and immobilized **2** while a hexane suspension of **2**-PE gave rise to an ESR spectrum which contained even less of the sharp three-line spectrum characteristic of soluble **2**. The rotational correlation times calculated from these ESR spectra[11] are listed in Table I and indicate that the polar nitroxyl amide groups of **2**-PE are located near the polymer/solution interface and that the nature of this interface is solvent dependent.[12] Evidently toluene and hexane are less able to either swell this interfacial region of these polyethylene precipitates or to partially dissolve the polar end groups of the entrapped oligomers **2**.[13]

Although suspending **2**-PE in ethanol did produce a relatively sharp ESR spectrum for the nitroxyl groups in

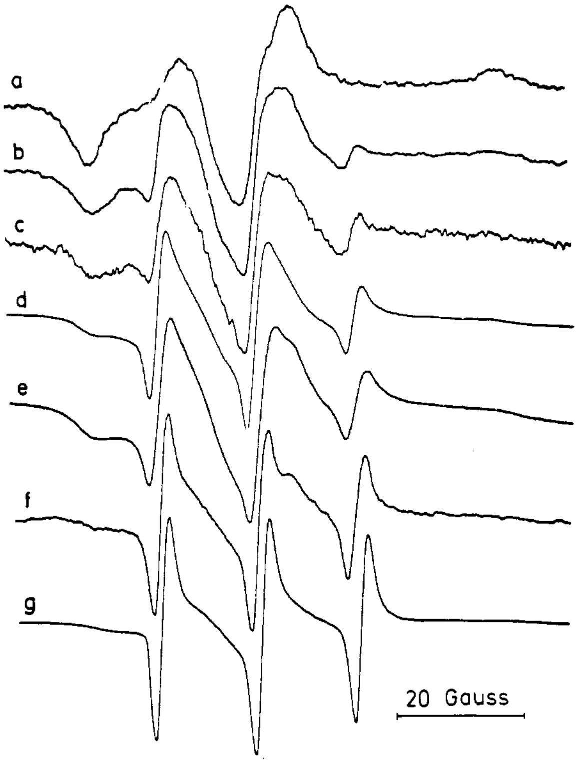


Figure 1. ESR spectra of 2-PE as vacuum-degassed suspensions in various solvents at 25 °C: (a) in the absence of solvent, (b) in hexane, (c) in carbon tetrachloride, (d) in toluene, (e) in diethyl ether, (f) in tetrahydrofuran, and (g) in ethanol.

Table I
Influence of Solvents on Nitroxide Motion in 2-PE and 3-PE

solvent	rotational correlation times ($\times 10^{10}$ s) 2-PE	3-PE
no solvent	148	163
n-hexane	115	48
carbon tetrachloride	74	49
toluene	20	18
diethyl ether	21	22
tetrahydrofuran	2	6
ethanol	1	5

[a] Rotational correlation times measured at 25 °C in the indicated solvent according to the procedure of ref 11.

2-PE, the structure of 2-PE evidently was not altered by this process. If 2-PE were first suspended in ethanol and then suspended in toluene or hexane, the ESR spectrum of 2-PE in toluene or hexane was indistinguishable from the ESR spectrum of 2-PE in toluene or hexane which had not been pretreated with ethanol. We interpret this as meaning that the different spectra seen in ethanol and presumably in other solvents are not due to movement of the nitroxyl groups of 2-PE from bulk polymer to the surface or vice versa. We consider this reversible solvent-dependent behavior instead to be evidence for a comparatively indistinct phase boundary between bulk polyethylene and solution. Thus, the effective surface of polyethylene, i.e., that interfacial region where solvent and soluble reagents can interact with species immobilized in the polyethylene depends on the particular solvent or other experimental parameters used to study it. Further evidence for this premise is provided by the reactivity studies below.

Qualitatively similar ESR spectra were obtained for 3-PE suspended in various solvents. Rotational correlation times calculated from these spectra are also listed in Table I and were slightly different from similar values for 2-PE. The rotational correlation times calculated for 3-PE suspended in ethanol and THF were most noticeably different from those for 2-PE in these solvents and may reflect location of the less polar **3** deeper in the bulk polymer phase of these polyethylene precipitates.

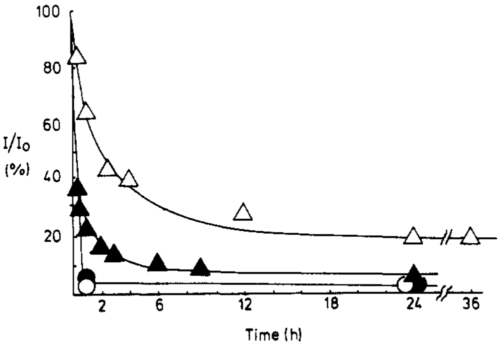


Figure 2. Reaction of 2-PE with various organolithium reagents at 25 °C: (●) with methyllithium in diethyl ether; (○) with *n*-butyllithium in hexane; (▲) with *tert*-butyllithium in pentane; (△) with (triphenylmethyl)lithium in tetrahydrofuran.

Further evidence that the nitroxyl groups of **2** are at the polyethylene solution interface comes from studies of the reactivity of the nitroxyl groups of 2-PE. Addition of alkyllithium reagents such as CH_3Li or n-C_4H_9Li as ether or hexane solutions respectively led to rapid loss of the intensity of the ESR signal association with **2**. Typically the ESR signal of **2** decreased to less than 5% of its original value within the time required to add either of these organolithium reagents to a THF or hexane suspension of 2-PE and to examine the ESR spectrum.[14] In both of these cases, the nitroxyl groups of 2-PE are effectively at the surface of the polymer in the sense that they readily and quantitatively react with methyl- or *n*-butyllithium. The use of more hindered organolithium reagents in place of methyl- and *n*-butyllithium demonstrated that access to the nitroxyl groups of 2-PE is also dependent on the nature of the reagent which is reacting with 2-PE. As is shown in Figure 2, *tert*-butyllithium rapidly reduces about 80% of the **2** in 2-PE and then more slowly reduces most of the rest of the **2** in 2-PE leaving about 6% unreacted **2** in 2-PE after 24 h at 25 °C. (Triphenylmethyl)lithium in THF reacts even more slowly leaving about 20% unreacted **2** in 2-PE after 24 h at 25 °C.[15]

Reduction of the nitroxyl groups of 2-PE could also be accomplished with ethanolic solutions of dithioerythritol and with ether solutions of dithioerythritol under the same conditions in which dithioerythritol quantitatively reduced **2**.[16] A similar, slightly slower reduction of **2** in 2-PE was seen with 2,4-dinitrophenylhydrazine in ethanol.[17] In all cases involving 2-PE, there was a residual ESR signal amounting to ca. 3–6% of the original signal which remained after 48 h of reaction (Figure 3). Since these polar reducing agents should not be very soluble in polyethylene, this residual ESR signal presumably reflects the percentage of **2** in 2-PE located in the bulk polymer which is inaccessible to reagents present in external solutions.

While the above results are generally in agreement with the premise that 2-PE is a "surface" functionalized polymer, it is clear even from these results that the "surface" of these functionalized polyethylene powders is not a distinct phase boundary. Reaction of the nitroxyl groups of 2-PE with various reducing agents dissolved in more polar solvents illustrates this more clearly. Figure 4 shows the results of a series of experiments in which 2-PE was allowed to react with either sodium ascorbate in water,[18]

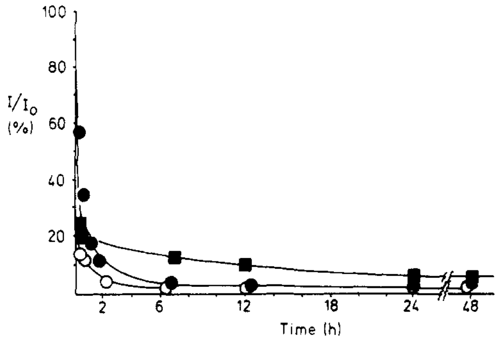


Figure 3. Reduction of the nitroxyl group in **2**-PE with various reagents: (○) with dithioerythritol in diethyl ether; (●) with dithioerythritol in ethanol; (■) with 2,4-dinitrophenylhydrazine in ethanol.

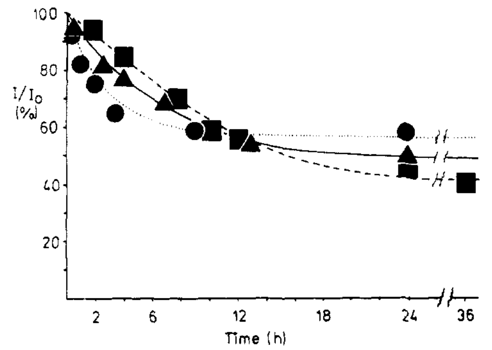


Figure 4. Reduction of the nitroxyl group of **2**-PE with reagents in high dielectric constant solvents: (■) with sodium sulfide in dimethylformamide; (●) with dithioerythritol in water; (▲) with sodium ascorbate in water.

dithioerythritol in water, or with sodium sulfide in dimethylformamide.[19] In each of these cases, approximately 40–60% of the original ESR intensity remained after 24 h at 25 °C. While the decreased rate of reaction seen in these cases may reflect experimental difficulties inherent in contacting a hydrophobic polymer with an aqueous solution, the leveling off of the extent of reaction seen in each case is more likely due to poorer accessibility of the nitroxyl groups of **2**-PE in these more polar solvents and to these polar reagents. Thus, in these latter cases, **2**-PE resembles a bulk functionalized polymer to a greater extent than was the case in the earlier reactivity experiments employing ethanol, ether, or hydrocarbon solutions of reagents which react with **2**.

In summary, entrapment of ethylene oligomers provides a simple entry to functionalized polyethylene powders that contain functional groups at the polyethylene–solution interface. The functionalized polyethylene powders formed by these procedures provide a clear demonstration of the variability of the polyethylene/solution phase boundary (i.e., the "surface" of polyethylene). It is possible to imagine a range of ways in which functional groups of ethylene oligomers can be incorporated into these polyethylene precipitates. Figure 5 illustrates schematically three such ways in which functional groups might be distributed in these polyethylene powders. We think that the above experimental data show that the procedures described in this paper produce polyethylene powders with a distribution of functional groups like that shown in Figure 5b. The ready formation of various types of functionalized ethylene oligomers containing a wide range of functionality under homogeneous conditions and the potential of varying either the structure of the host polymer (e.g., changing from high-density polyethylene to low-density polymer) or the structure or size of the oligomer to be entrapped means that this method of functionalizing an unreactive polymer has the potential of leading to either more or less bulk functionalization (i.e., a functionalized polymer like that shown in Figure 5, part a or b). Entrapment functionalization is thus both a demonstrably useful alternative to existing methods for preparation of derivatives of hydrocarbon polymers for subsequent studies of chemistry in and at the surface of such polymers and a potentially very selective process for functionalization of unreactive polymers.

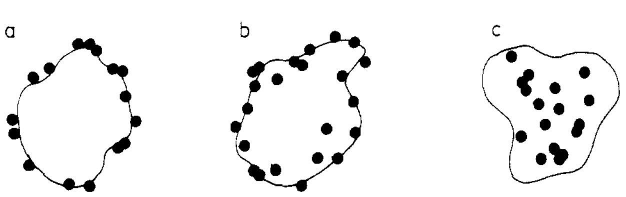


Figure 5. Possible distribution of polar functional groups (●) in hydrocarbon polymer precipitates.

Experimental Section

General Procedures. Ethereal and hydrocarbon solvents used were purified by distillation from a purple solution or suspension of benzophenone and sodium prior to use. Dimethylformamide was dried over 4-Å molecular sieves before use. Other solvents used were reagent grade and generally not further purified. Infrared spectra of polyethylene powders were taken either as KBr pellets or as thin translucent films of polyethylene (prepared under pressure in a pellet press). ESR spectra were recorded on a Varian E-6S spectrometer. 4-Amino- and 4-hydroxy-2,2,6,6-tetramethylpiperidinyl-1-oxy were purchased from Aldrich Chemical Co. as were other reagents. Butadiene was obtained from Matheson Co. (Triphenylmethyl)lithium was prepared from triphenylmethyl chloride by a literature procedure,[20] and sodium ascorbate was prepared *in situ* from ascorbic acid. High-density polyethylene was obtained from Gulf Chemical Co. and had a density of 0.97.

Preparation of Carboxylated Ethylene Oligomer 1. Following the general procedure of Graessley,[5] butadiene was polymerized with *sec*-butyllithium in cyclohexane at 50 °C for 24 h to yield an intermediate lithiated polybutadiene which was in turn quenched with carbon dioxide to yield the lithium salt of a carboxylated polybutadiene. In the carboxylation step, the cyclohexane solution of lithiated polybutadiene was transferred onto crushed dry ice by forced siphon through a cannula. Vigorous agitation was maintained during this addition process. If good mixing was not achieved or if carbon dioxide was passed into the cyclohexane solution of lithiated polybutadiene, the resultant oligomer contained an appreciable amount of ketone functionality apparently formed by reaction of the lithiated polybutadiene with the lithium salt of carboxylated polybutadiene. Protonation of the lithium salt of this carboxylated polybutadiene was accomplished by mixing a toluene solution of this oligomer with 1 N aqueous HCl at 60 °C for 2 h. After cooling and separating the toluene phase, the resultant polymer was precipitated by addition of methanol and dried at 25 °C under reduced pressure. The resultant polymer was characterized by IR spectroscopy and had absorptions at 1710, 965 (trans), 910 (vinyl), and 730 (cis) cm^{-1}. The $\bar{M}_v$ of this oligomer was determined with an Ubbelohde viscosimeter using toluene solutions at 30 °C. Hydrogenation of this polybutadiene was accomplished by using tris(triphenylphosphine)rhodium chloride as a catalyst in toluene at 70 °C. The carboxylated ethylene oligomer produced by this hydrogenation was precipitated from solution with methanol, redissolved in cyclohexane and separated from any insoluble material, and again precipitated with methanol. After drying the product, **1** was characterized by IR spectroscopy and typically had a small absorption at 965 cm^{-1} but no peaks at 910 or 730 cm^{-1}.

Preparation of 4-Carboxamido-2,2,6,6-tetramethylpiperidinyl-1-oxy Functionalized Ethylene Oligomer 2. To a 100-mL three-necked flask equipped with a magnetic stirrer was added 0.2 g of hydrogenated polybutadienecarboxylic acid (1) and 15 mL of freshly distilled thionyl chloride. The reaction was catalyzed by addition of several drops of dimethylformamide and heated to reflux for 12 h. Simple distillation then removed the excess thionyl chloride. After the thionyl chloride had been removed, IR spectroscopy showed complete conversion to the desired oligomeric acid chloride ($\nu_{C=O}$ at 1780 cm^{-1}) which was normally not isolated. Typically, 15 mL of distilled cyclohexane along with 0.02 g of 4-amino-2,2,6,6-tetramethylpiperidinyl-1-oxy (H_2N-TMPO) was added to this crude acid chloride without characterization of the intermediate. The resulting mixture was refluxed an additional 12 h under a nitrogen atmosphere and cooled to room temperature, and the product **2** was precipitated by addition of 150 mL of methanol. The product oligomer **2** was isolated by filtration and washed with methanol (150 mL) and then dried under reduced pressure at 25 °C for 48 h to remove any residual solvent. The product oligomer **2** has an ESR spectrum identical with that of H_2N-TMPO and had an amide absorption in the IR at 1670 cm^{-1} with no detectable absorption at 1700 cm^{-1} where the original oligomeric carboxylic acid was seen.

Preparation of 4-Oxy-2,2,6,6-tetramethylpiperidinyl-1-oxy Labeled Ethylene Oligomer 3. The carboxylated ethylene oligomer **1** (1 g) was dissolved in 50 mL of hot toluene and allowed to react with 0.3 mL of 10.2 M borane–methyl sulfide which was added dropwise with stirring to the solution of **1**. After refluxing the resulting mixture for 12 h, the solution was cooled to 25 °C and the functionalized ethylene oligomer was precipitated with 100 mL of methanol. The product polymer was then converted into a hydroxylated ethylene oligomer by refluxing it in methanol for 2 h. After this suspension cooled to 25 °C, the desired product ethylene oligomer was isolated by filtration, washed with 50 mL of methanol and then 50 mL of acetone, and dried at 25 °C under reduced pressure for 48 h. Analysis of this product by IR spectroscopy showed that the carbonyl peak of **1** was gone. The oligomeric alcohol (0.8 g) was then dissolved in a fresh 50-mL portion of toluene and allowed to react with 0.2 mL of triethylamine and 0.5 mL of methanesulfonyl chloride at reflux for 12 h. The product mesylate resulting from this procedure was isolated as described above for the hydroxylated polymer (IR, 1176 cm^{-1}). The desired spin-labeled ethylene oligomer (**3**-PE) was prepared directly from this mesylate by reaction of 0.5 g of this mesylate in 30 mL of toluene with the sodium salt of 4-hydroxy-2,2,6,6-tetramethylpiperidinyl-1-oxy and isolated as described above by methanol precipitation. The ESR spectrum of this spin-labeled ethylene oligomer was identical with the ESR spectrum of the starting nitroxyl radical in toluene. The final step in this sequence in which the spin label was attached to the ethylene oligomer via an ether linkage was only partly successful based on the relatively lower intensity of the ESR signal of samples of **3**-PE vs. **2**-PE. Presumably elimination occurred during the Williamson ether synthesis (small peaks possibly due to $\nu_{C=C}$ absorptions at 910 and 970 cm^{-1} were seen in the IR spectrum of **3**).

General Procedure for Entrapment Functionalization. To a 100-mL round-bottomed flask equipped with a magnetic stirring bar was added 0.5 g of high-density polyethylene, 0.2 g of functionalized ethylene oligomer, and 20 mL of toluene. After heating this suspension to 110 °C using an oil bath, a solution formed. The solution was stirred for 1 h at this temperature, and the oil bath was removed. After cooling to 25 °C, the polyethylene was recovered by filtration and washed with 150 mL of toluene and finally dried under reduced pressure for 24 h. ESR spectra of the functionalized **2**-PE and **3**-PE prepared in this fashion were taken as suspensions in various solvents (cf. Figure 1 and text) after first degassing a suspension of polyethylene powder and then allowing the suspension to first stand for 2 h.

General Procedure for Reactions of 2-PE or 3-PE with Soluble Reagents. After the ESR spectrum of **2**-PE as a suspension in the solvent of choice had been recorded, a large stoichiometric excess of the desired reagent was added to the ESR tube. Agitation was accomplished with a Vortex mixer. The ESR spectrum was recorded periodically. In reactions with very polar solvents such as water or dimethylformamide, the high dielectric constant of these solvents precluded direct ESR monitoring of a suspension of **2**-PE in these solvents. In these cases, an ESR spectrum of a standard amount of **2**-PE in the dry state was obtained and, in a separate flask, **2**-PE was allowed to react with the reaction solution of interest with vigorous shaking using a wrist-action shaker. After the desired period of time, the **2**-PE was reisolated, washed with water, ethanol, and acetone, and dried under reduced pressure. After thorough drying, a new ESR spectrum was recorded using the same amount of **2**-PE as in the original case. Control experiments using **2**-PE in ESR tubes in procedures analogous to these but without addition of reagents which could react with **2**-PE showed that ESR intensities measured in successive experiments varied by ±5%.

Acknowledgment. Funding of this research by the Texas A&M Center for Energy and Mineral Resources and by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

Registry No. Polyethylene (homopolymer), 9002-88-4.

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(6) The polybutadiene polymers used in this procedure were ca. 88% 1,4- and 12% 1,2- based on IR spectroscopy. Their $\bar{M}_v$ was determined using a Mark–Houwink relationship ($a = 0.7$, $K = 3.24 \times 10^{-4}$)[7] and was typically about 2500. Hydrogenation produced polymers containing ca. 5% residual unsaturation, primarily in the form of trans carbon–carbon double bonds based on IR spectroscopy.

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(8) The high-density polyethylene used in these studies had a density of 0.97 and a degree of crystallinity of 72% based on IR spectroscopy.[9] Entrapment of ethylene oligomers did not change this value and thus suggests that the functionalized oligomers are confined to the amorphous regions of the polyethylene host polymer.

(9) Wunderlich, B. "Macromolecular Physics"; Academic Press: New York, 1973/1976; Vol. 1 and 2.

(10) The high-density polyethylene used in entrapment experiments did not contribute any measurable material to the solutions which were analyzed by GPC. Although treatment of high-density polyethylene to these same dissolution/precipitation cycles did lead to loss of small amounts of low molecular weight material as determined by RI detection, no soluble material could be detected in filtrates after four dissolution–precipitation cycles. The polyethylene used in our studies was thus pretreated to four such dissolution–precipitation cycles before use in these entrapment experiments. Visual examination of these polymeric precipitates after one or more precipitation cycles showed that the polymer precipitates were of similar size (the precipitated polyethylene powder microscopically appeared to be in the form of small platelets with dimensions of ca. 1 × 1 × 0.02 mm).

(11) Likhtenshtein, G. I. "Spin Labeling Methods in Molecular Biology"; Wiley: New York, 1976; Chapter 1.

(12) The term interface is used in several places in this paper as an alternative to the term "surface" to better describe the indefinite and indistinct nature of the surface of these polymers in contact with solvents.

(13) Rasmussen et al. (Rasmussen, J. R.; Bergbreiter, D. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1977**, *99*, 4746–4756) report similar phenomena for surface-functionalized low-density polyethylene films prepared by chemical etching procedures.

(14) Nitroxyl radicals are reportedly reduced rapidly by organolithium reagents: cf. Whitesides, G. M.; Newirth, T. L. *J. Org. Chem.* **1975**, *40*, 3448–3450.

(15) In the case of reaction of **2**-PE with (triphenylmethyl)lithium, the reaction product is the relatively stable triphenylmethyl radical. Therefore, in these experiments, we followed the general procedure described for reactions of **2**-PE with reducing agents in high dielectric solvents, isolating the **2**-PE after reaction to separate the polymer-entrapped polymeric nitroxyl radical species from any triphenylmethyl radicals which were

present in solution. In spite of these precautions, we cannot completely exclude the possibility that the formation of this paramagnetic product in this reaction and its possible inadvertent inclusion into polyethylene could account for the residual ESR signal seen in Figure 2 since ESR is such a sensitive technique.

(16) A diastereomer of dithioerythritol, dithiothreitol, is known to act as a reducing agent toward nitroxyl radicals: cf. Keana, J. F. W. *Chem. Rev.* **1978**, *78*, 37-64.

(17) Several literature reports describe reduction of nitroxyl radicals by hydrazine derivatives: cf. Keana, J. F. W.; Lee, T. D. *J. Org. Chem.* **1975**, *40*, 3145-3147. Daniel, W. E., Jr.; Cohn, M. *Biochemistry* **1976**, *15*, 3917-3924. Rozantsev, E. G. "Free Nitroxyl Radicals"; Plenum Press: New York, 1970; Chapter 4.

(18) Examples of use of sodium ascorbate to reduce nitroxyl groups include ref 13 and Kornberg et al. (Kornberg, R. D.; McConnell, H. M. *Biochemistry* **1971**, *10*, 1111-1120).

(19) Reduction of nitroxyl radicals by sodium sulfide in dimethylformamide is precedented: cf. Kornblum, N.; Pinnick, H. W. *J. Org. Chem.* **1972**, *37*, 2050-2051.

(20) Tomboulian, P. *J. Org. Chem.* **1959**, *24*, 229-234.

Excited-State Annihilation Processes in Poly(vinylaromatics) in Solution: Poly(2-vinylnaphthalene) and Poly(4-vinylbiphenyl)

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ABSTRACT: The triplet yield (measured by T–T absorption) and monomer and excimer fluorescence (measured from integrated intensities) have been determined as a function of laser intensity using a Nd:YAG Q-switched laser at 266 nm for the title polymers. At higher laser intensities the polymer triplet yield and fluorescence tended to saturate to a much greater extent than monomeric model compounds (i.e., naphthalene or 4-methylbiphenyl). This is interpreted to be the result of S–S and S–T intracoil annihilation, which appears to be much more important in polymer photophysics than is usually the case with small molecules in solution. It was also observed that in CH_2Cl_2 solvent (but not methyltetrahydrofuran) the S–S annihilation leads to radical cation formation of the pendent aromatic by virtue of electron capture by the solvent. The implication of these results with respect to general photophysical and energy migration processes in polymers is discussed.

Introduction

In an earlier report the triplet quantum yield of poly(2-vinylnaphthalene) (P2VN) was found to be very low and inversely proportional to the molecular weight.[1] It was postulated that the reduction of the triplet quantum yield relative to the monomeric model compound was the result of singlet excimer formation. But the magnitude of this reduction and the inverse molecular weight effect on the triplet quantum yield left some puzzling questions. There have been other reports of low triplet quantum yields in polymers by Masuhara et al.[2] for carbazole- and pyrene-containing polymers, by Lachish and Williams for poly(vinylcarbazole) (PVCz),[3] and by Gupta et al.[4] for poly(1-vinylnaphthalene) (P1VN). Masuhara et al.[2a] concluded that the reason for the low triplet yield in polymers of PVCz was singlet–singlet annihilation of excitons on the same polymer chain. Thus, the present study was designed to reexamine P2VN and also to understand the general features of singlet–singlet annihilation in poly(vinylaromatic) polymers.

Experimental Section

The synthesis and characterization of P2VN and P4VBP have been described previously.[5-7] The numeration of the polymers is the same as those used in previous experiments. 1,3-$\beta\beta$-Dinaphthylpropane (DNP) was the same material as in an earlier report.[8] 2-Methyltetrahydrofuran (MTHF) was purchased from Aldrich Chemicals. MTHF was filtered through freshly activated alumina and refluxed over lithium aluminum hydride under a nitrogen atmosphere before use. Dichloromethane (spectrograde MCB and Fisher), cyclohexane (spectroquality MCB), isooctane (Gold Label Aldrich 99%), and chloroform (spectroquality MCB) were used as received. Naphthalene (Aldrich) was sodium fused and then a gradient sublimation was performed. 2-Ethylnaphthalene (Aldrich 99+%) was used as received while 4-methylbiphenyl (Aldrich 98%) was recrystallized several times from methanol and then chromatographed on alumina using hexane as the eluent.

The laser flash photolysis unit was the same as that used previously[7] at the Center for Fast Kinetics Research, University of Texas at Austin. A Q-switched Quantel 481-Nd:YAG laser (λ 266 nm, 70 mJ, 11-ns pulse width) was used as the excitation source. The laser beam is circular (8–10 mm in diameter) and the intensity profile is approximately Gaussian. Optical alignment for this experiment was a cross beam arrangement in which the excitation beam is 90° to the monitoring beam provided by a 150-W xenon lamp that was powered by a PRA Model 303 lamp supply. The monitoring beam could also be pulsed by a PRA Model 305 pulser which produces a more intense interrogation light source with essentially constant intensity for up to 20 μs. A cylindrical lens is used to direct most of the laser light into an image parallel to the direction of the monitoring beam. The monitoring beam sampled the first millimeter of the side of the cuvette toward the laser beam. The path length of the cuvettes used in these experiments was 1 cm. Solutions used in the intensity dependence studies and triplet quantum yield measurement had optical densities of 0.5 at the laser wavelength while for the transient spectra the optical density was 1.5 at λ_{ex}. Naphthalene in cyclohexane[9] was used as the standard in the measurement of the triplet quantum yield and also as the relative actinometer in determining the average photon flux over the path length of the cuvette using the relation derived by Bensasson et al.[10] It should be stressed that our calculated values for the laser intensity are averaged over the spatial inhomogeneity of the laser beam across the path length of the cuvette.

Signals for the absorption experiments were captured with a Biomation 8100 transient recorder while for the emission experiments a Tektronix 7912 digitizer was used. The signal traces were then transferred to a PDP 11/70 computer where the data were stored and processed. Time-resolved absorption spectra were obtained by assembling decay curves at every 5 or 10 nm. The integrated fluorescence values (I_F) were obtained by integrating the area underneath the decay curve of the emission taken from the same optical alignment as the absorption with the monitoring beam turned off.

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0024-9297/84/2217-2116$01.50/0