Preparation and Reactions of Carbamate-Modified Polyethylene

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Synopsis

The reaction of azidoformates with low-density polyethylene melts gives rise to carbamate-modified polymers. The reaction is accompanied by crosslinking especially at high concentration of azide. The polymer-bound carbamate group is relatively unreactive, but may be thermally decomposed to give isocyanate-modified polyethylene.

INTRODUCTION

The functionalization of relatively inert polymers has been of considerable interest to a wide variety of researchers.[1-3] Our interest has focused on the modification of low-density polyethylene (LDPE), particularly by methods which could be used to modify the polymer as a melt. In addition to free radical methods,[4] the reactions of certain nitrenes and carbenes seemed attractive in achieving this end.

The reactions of nitrenes with hydrocarbons in solution have been well studied.[5a] To a first approximation, it appears reasonable to suppose that a specific nitrene will behave similarly in solution or in a hydrocarbon polymer melt. In the absence of any facile intramolecular rearrangement, the nitrene will bond to the polymer by addition to a carbon–carbon double bond or insertion into a carbon–hydrogen bond. A detailed study of the reactivity of phenylnitrene in fluid solution and in several polymer matrices showed that the basic chemistry of the nitrene is unchanged in going from solution to polymer matrix.[6] The major effect of the polymer matrix is to change the distribution, not the nature, of the reaction products.

Carboalkoxynitrenes are good candidates for the modification of LDPE.[7,8] The nitrene precursors, azidoformates, are readily available from the corresponding chloroformates. Moreover, their decomposition occurs at a sufficiently high temperature to allow for thorough mixing in the polymer melt. Decomposition of the azidoformates is clean, yielding nitrogen and the nitrene. Curtius-type rearrangements of azidoformates were not observed.[5]

Grafting reactions of carboalkoxynitrenes to PE were conducted in a small, steel mixing bowl using a Brabender mixer. Torque and temperature of the low-density PE melt were monitored continuously. Decomposition of the azidoformate, which had been added dropwise to the melt, was accompanied by a slight torque increase and gas evolution. The colorless material produced was analyzed before and after purification for carbamate absorbance (by infrared spectra) and nitrogen content to determine the extent of grafting.

Unstabilized polyethylene (Cities Service; density 0.920) was used as the

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substrate for these experiments. Infrared (IR) analyses[9] indicated a low level of unsaturation, 0.823 double bonds per 1000 carbon atoms. The number of methyl groups per 1000 carbon atoms was 24.9.

EXPERIMENTAL

General

Nitrogen analyses were performed using the Kjeldahl technique. Infrared spectra were obtained using a Perkin–Elmer 457 grating infrared spectrophotometer. Gas chromatographic mass spectral (GCMS) analyses were performed using a Varian Mat 111 system; gas chromatography was done using a 1/4-in. × 10-ft Pyrex column, packed with 3% OV-17 on gas chromosorb-Q.

Procedure for Melt Grafting

The reactions were run in a 50-ml electrically heated mixing bowl (Haake) equipped with roller blades using an instrumented Brabender mixer. The torque and temperature of the reaction were constantly monitored. In a normal run, the bowl was preheated to 115–120°C and charged with 42-g low-density PE. After equilibration of the melt (~5 min), the appropriate amount of azide (2.1–6.3 g) was added dropwise and mixed for 2–5 min. The melt was then heated to 130–175°C. Heating was continued until the torque, which initially rose, began to decrease (5–10 min). Blade speed was 40 rpm in all cases.

The modified polymers were purified by precipitation from a solution of hot toluene, xylene, or chlorobenzene by slow addition of the solution to methanol, ethanol, or chloroform. The samples were pressed into films for IR analysis on a heated Carver press (5000 psi, 120–150°C).

In the case of methylazidoformate, a control experiment showed that the by-product, methylcarbamate, was not retained in the melt under the reaction conditions. Similar results were seen when phenylcarbamate and benzoxazolidinone, by-products of the grafting of phenylazidoformate, were added to a PE melt. Both materials were removed after initial precipitation of the polymer.

Nitrogen analyses were performed on precipitated polymers. Repeated precipitation and analysis showed no change in the wt % nitrogen within experimental error. Unmodified PE showed less than 0.005% nitrogen.

IR spectra. All samples are pressed films: 120–150°C, 5000 lb/in.[2]. Absorbances due to PE are omitted. PE–NHCOOCH$_3$ (Fig. 2); 3455, 3370, 1740, 1505, 1085 cm^{-1}. PE–NHCOOn-C$_{18}$H$_{37}$; 3450, 3360, 1730, 1500, 1080 cm^{-1}. PE–NHCOϕ (Fig. 3); 3445, 3360, 1755, 1200 cm^{-1}. PE–NHCOOt-Bu; 3455, 3370, 1725, 1490, 1170 cm^{-1}.
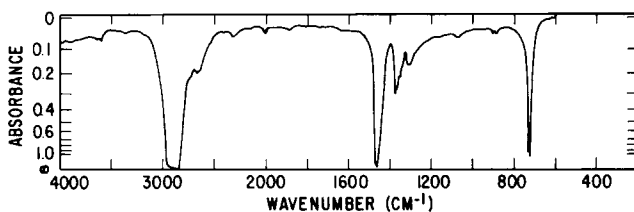

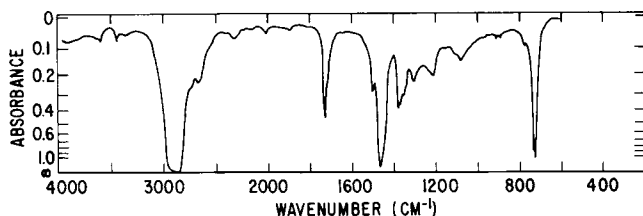Fig. 1. Low-density polyethylene.

Fig. 2. Methylcarbamate-modified polyethylene.

Preparation of Azidoformates

Methyl, n-octadecyl, and phenyl azidoformates were prepared from the corresponding chloroformates as described in the literature.[10,11] t-Butylazidoformate was prepared by nitrosation of t-butylcarbazate.[12]

Thermal Decomposition of Carbamate-Modified PE

Decomposition of the modified polymers was conducted in several different ways, all giving equivalent results. Preliminary experiments were conducted by heating a sample of polymer in a Carver press and examining the IR spectrum of the product. In other experiments, a sample of modified polymer was heated in a glass tube to 300°C under a stream of nitrogen. Volatile products were absorbed on a Tenax absorbent column and analyzed by GCMS. Decompositions were also conducted on polymer melts in the mixing bowl, and in refluxing phenyl cyclohexane solution (240°C) under a blanket of nitrogen.

Samples of precipitated 1.7% phenylcarbamate-modified PE were heated in a Carver press (~5000 psi) for 5 min at 200, 250, and 300°C. No reaction was observed at 200°C, but by 250°C an isocyanate absorbance was clearly visible. At 300°C, the carbamate absorbance was almost gone and a strong isocyanate band was present. GCMS analysis showed the major volatile product of this decomposition to be phenol.

A 5-g sample of 1.7% phenylcarbamate-modified PE was dissolved in 250-ml phenylcyclohexane and refluxed under nitrogen. The progress of the reaction was monitored by IR. After 20 min, a sample taken from solution, precipitated by methanol and pressed into a film, showed a slight isocyanate absorbance. Isocyanate and carbonyl bands of approximately equal intensity were observed after 40 min. After 80 min of heating, only a slight carbonyl absorbance remained.

Addition of 1.0 g cetyl alcohol to an isocyanate-modified polymer solution in toluene followed by 10 min continued heating gave a material whose IR spectrum was almost identical to that of n-octadecylcarbamate-modified PE.
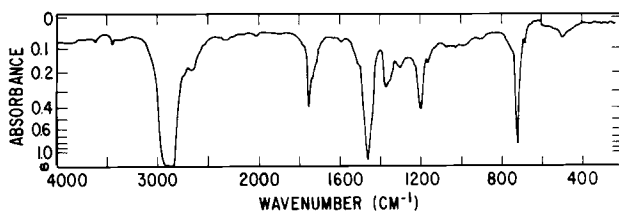

Fig. 3. Phenylcarbamate-modified polyethylene.

A solution of phenylcarbamate-modified PE refluxed in chlorobenzene (132°C) overnight showed no isocyanate formation. This solution of the polymer was also unreactive in the presence of n-dodecylamine (1.0 g heated for 1 hr). Similarly, heating a toluene solution of phenylcarbamate-modified PE for 1 hr in the presence of a large excess of n-butyl isocyanate resulted in no change. IR spectra: PE–NHCOOnC$_{15}$H$_{31}$; 3450, 3360, 1730, 1500, 1080 cm^{-1}. PE– NCO (Fig. 4): 2260 cm^{-1}.

The IR spectra of n-octadecylcarbamate-modified PE heated for 15 min at 300°C showed isocyanate and carbonyl absorbances of comparable intensity. Analysis of the volatile products by GCMS showed n-octadecanol as the major product. Identity of this product was confirmed by IR analysis.

Methylcarbamate-modified PE showed behavior similar to the n-octadecyl material. Heating in a Carver press for 5 min at 300°C gave partial conversion to the isocyanate.

Decomposition of 1.2% t-butylcarbamate-modified PE in a mixing bowl (5 min, 225°C) or heated press (5 min, 300°C) gave similar results. The carbonyl absorbance of the starting material eventually vanished, leaving essentially a spectrum of PE with small carbonyl peaks at 1720 and 1690 cm^{-1}. Volatile products of decomposition were identified as carbon dioxide, isobutylene, and t-butanol by comparison of the mass spectrum with those of authentic samples.

A sample of t-butyl carbamate PE decomposed in refluxing phenyl cyclohexane (3 hr under N$_2$) gave a product whose IR spectrum was similar to that observed in the other decompositions: a spectrum of PE with slight carbonyl absorbance at 1720 and 1690 cm^{-1}.

Nitrogen analyses of this product showed a slight drop from 1440 to 1230 ppm. The product was assumed to be an amine-modified PE. Reaction of a toluene solution of this product with n-butyl isocyanate gave a product whose IR spectrum indicated formation of a urea-modified PE. Nitrogen content of the polymer increased from 1230 to 1590 ppm. If the reaction of polymer-bound amine and isocyanate in solution is assumed to be 100% efficient, then 65% of the nitrogen on the unreacted polymer (PE–amine) is present as amine. The remaining nitrogen is probably present as urea crosslinks. IR spectra: PE–NHCONHn-C$_4$H$_9$; 3360, 1720, 1640, 1505, 1070, 810 cm.$^{-1}$.

Reaction of Dimethyldiazomalonate with PE

Dimethyldiazomalonate (2.1 g), prepared as described elsewhere,[13] was added to a PE melt (42 g) in a mixing bowl (120°C). Conditions were as previously mentioned. Temperature was increased to 185°C and, after 10 min, no torque
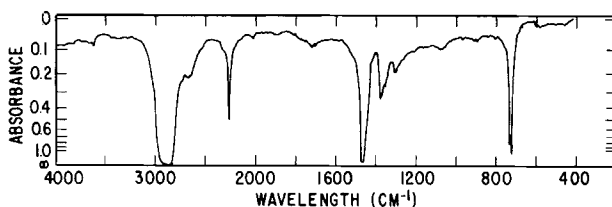

Fig. 4. Isocyanate-modified polyethylene.

increase was observed. The slightly yellow-colored polymer was precipitated from toluene. IR analysis showed the product to be consistent with the formation of a malonate modified PE. IR spectra: PE–CH(COOCH$_3$)$_2$; 1750, 1735, 1250, 1150 cm^{-1} (see ref. 14).

Reaction of Sulfonyl Azides with PE

Benzenesulfonyl azide and p-carboxybenzenesulfonyl azide were prepared as described in the literature.[13] Both of these materials were reacted with PE melts as previously indicated. In both cases, after heating to 170°C for 5 min, no torque increase was observed. The polymers did show some discoloration which persisted even after two precipitations from toluene. Nitrogen analysis and IR spectra did not change substantially after initial purification. The extent of grafting using benzenesulfonyl azide was 42% resulting in 2.0% sulfonamide-modified PE; values for the p-carboxybenzenesulfonyl azide were also 42 and and 2.0%, respectively. IR spectra: PE–NHSO$_2$–C$_6$H$_5$; 3390, 3270, 1160, 1090, 750, 685, 590 cm^{-1}. PE–NHSO$_2$–C$_6$H$_4$–COOH; 3160, 1700, 1600, 1170, 660 cm^{-1}.

Percent Gel Determination

Percent gel values for various modified polymers shown in Table I were determined by placing a sample of the crude material (100–250 mg) between two nickel screens (200×200 mesh) and extracting in a Soxhlet for 24 hr with toluene. Reaction of the isocyanate-modified polymers during extraction, leading to increased crosslinking, cannot be ruled out. The polymer showed IR absorbances indicative of isocyanate groups after extraction.

RESULTS

The reaction of carbomethoxynitrene in the LDPE melt proceeded as expected.[10] IR spectra of the modified polymer (Fig. 2) were consistent with the presence of a polymer-bound carbamate group formed via C—H insertion.
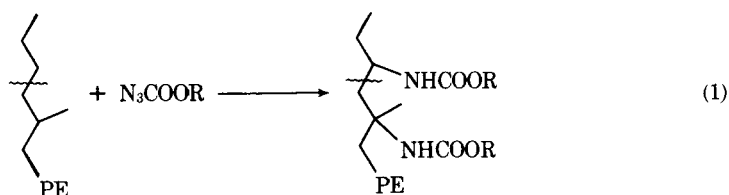

$$+ \ N_3COOR \longrightarrow \tag{1}$$

TABLE I
Relative Amounts of Crosslinking Accompanying Grafting

Polymer	% Gel[a]
5% Phenylcarbamate–PE	36
5% n-Octadecylcarbamate–PE	35
5% t-Butylcarbamate–PE	31
10% n-Octadecylcarbamate–PE	53
PE–NCO (from phenylcarbamate)	68
PE–NCO (from t-butylcarbamate)	74
5% Benzene sulfonamide–PE	0
5% Dimethylmalonate–PE	0

[a] All samples could easily be pressed into thin films before extraction.

Based on the results of competition experiments done in hydrocarbon solution[5] the preferred site of carboalkoxynitrene insertion on the polymer should be the tertiary C—H bonds, although insertion into methylene C—H bonds should also occur. Attempts to explore the nature of the carbamate attachment to the polymer by nuclear magnetic resonance (NMR) spectroscopy failed to yield any useful data.

Addition of the nitrene to the few sites of unsaturation of the polymer is probable, but the observation of the N—H stretch at 3450 cm^{-1} in the IR spectrum confirms C—H insertion as the major reaction pathway.

Repeated purification of the modified polymers by precipitation from hot toluene by slow addition of the polymer solution to methanol did not change the nitrogen analysis or the IR spectrum substantially after the first precipitation (Table I). Under similar conditions, the carbomethoxynitrene abstraction product, methylcarbamate, was not retained in the polymer.

The efficiency of carbomethoxynitrene grafting to LDPE was poor (7%). This is the result of a relatively high volatility of methylazidoformate. The nitrene precursor boiled out of the melt before decomposition (130°C). In order to improve the efficiency of the grafting reaction, the decomposition of azidoformates of lower volatility than the methyl compound was explored.

n-Octadecylazidoformate[11] was reacted in a LDPE melt in the manner previously described. Owing to the lower volatility of the n-octadecylazidoformate, grafting to the polymer was more efficient. However, the yield of the grafted carbamate (55%, based on nitrogen analysis) was still not as high as desired. The IR spectrum of the crude product showed several carbonyl absorbances. Purification of the polymer caused the disappearance of all but one of these bands. The final IR spectrum was consistent with an n-alkylcarbamate-modified LDPE. The "extra" carbonyl absorbances present in the spectrum of the crude product probably arise from the products of intramolecular cyclization 4-n-hexadecyl-2-oxazolidinone and abstraction n-octadecylcarbamate. These compounds, known to be by-products in the decomposition of n-octadecylazidoformate in cyclohexane, were not isolated in this instance.[11] The competition between addition to the polymer and intramolecular cyclization, along with the formation of unbound carbamate (vide infra), account for the modest yield of grafting.

Similar addition of the nitrenes derived from phenyl azidoformate[15] and t-butyl azidoformate[16] to LDPE melts was also successful in preparing carbamate-modified PEs. In both cases, the yield of grafting to the polymer was modest (41 and 31%); again, intramolecular cyclization competes with addition to the polymer. Literature references indicate that the major side products arise via intramolecular cyclizations yielding benzoxazolidinone and 4,4-dimethyl-2-oxazolidinone, respectively. The grafting of carbophenoxynitrene, generated from the decomposition of phenylazidoformate, was investigated in some detail. Gas chromatographic mass spectral (GCMS) analysis of the material extracted from the crude polymer confirmed the presence of benzoxazolidinone, and phenylcarbamate. Control experiments showed that the two expected by-products, phenylcarbamate and benzoxazolidinone, could easily be removed from the polymer after addition to the melt, either simultaneously or separately.

Grafting of carboalkoxynitrenes to polyethylene is usually accompanied by a torque increase and, at concentrations of azidoformate >10%, the polymer is highly crosslinked. The relative amounts of crosslinking accompanying the

grafting of carboalkoxynitrene to PE is reflected in the percent gel (Table I). The crosslinking probably arises from the formation of radical sites on the polymer backbone by the triplet nitrene:
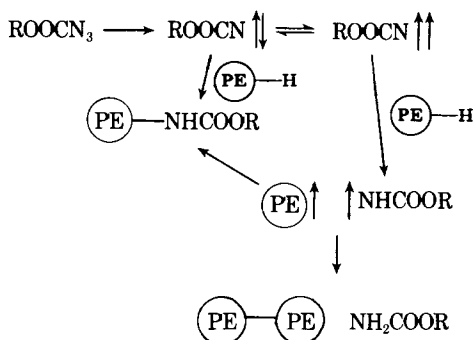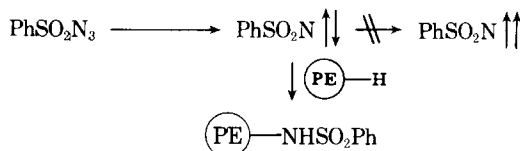

Scheme I

Decomposition of the azidoformate gives rise to a singlet nitrene which reacts by direct insertion into a C—H bond yielding intramolecular cyclization products or carbamate-modified polyethylene. In the case of carboalkoxynitrenes, the triplet state is known to be thermally accessible from the singlet[5a]; therefore, conversion to the triplet competes with direct insertion. The triplet nitrene can also react with the polymer but by an abstraction–recombination mechanism. A triplet nitrene abstracts a hydrogen from the polymer, forming a radical pair in which the electron spins are aligned. In order for this radical pair to form a chemical bond, a spin-flip must occur. However, escape from the initially formed radical pair can also occur; this leaves a radical site on the polymer which eventually leads to crosslinking. The carbamate radical forms an unsubstituted carbamate.

As a consequence of the facile singlet–triplet equilibrium in carboalkoxynitrenes, crosslinking of the polymer and formation of abstraction products, i.e., primary carbamates, is unavoidable. Highly functionalized polyethylenes (>10%) which are not severely crosslinked cannot be prepared using carboalkoxynitrenes in the manner described.

In order to explore this hypothesis further, the reaction of a nitrene which reacts only as a singlet was explored. Thermally generated sulfonyl nitrenes have been well studied and are known to react as singlets.[5b] The reaction of benzenesulfonyl nitrene with LDPE resulted in the formation of a sulfonamide-modified LDPE. Suitable control experiments showed that the sulfonamide was bonded to the polymer. The yield of grafting was 42%. Grafting to the polymer occurred with no torque increase and no crosslinking. The low yield of polymer-bound sulfonamide may be the result of nitrene addition to unreacted azide or further reaction of the polymer-bound sulfonamide. Sulfonylnitrene-modified PE was brown, whereas carboalkoxynitrene-modified PE was colorless.

The sulfonylnitrene is formed from the azide by thermal decomposition as a singlet. The triplet nitrene is thermally inaccessible under the reaction con-
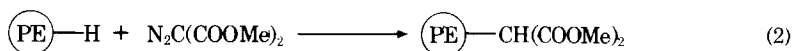
ditions.

$$\text{PhSO}_2\text{N}_3 \longrightarrow \text{PhSO}_2\text{N} \uparrow\downarrow \nrightarrow \text{PhSO}_2\text{N} \uparrow\uparrow$$

$$\downarrow \text{(PE)}-\text{H}$$

$$\text{(PE)}-\text{NHSO}_2\text{Ph}$$

Scheme II

Functionalization of the polymer takes place by a concerted insertion of the singlet nitrene; radical pair formation does not occur. There is no crosslinking of the polymer. Several reports of hydrocarbon polymer modification by sulfonyl nitrenes are in agreement with this observation.[17-19]

The reaction of dimethyldiazomalonate with a LDPE melt is also consistent with Scheme II. The bis-carbomethoxycarbene, formed from the thermolysis of the diazo compound in the polymer melt, adds to the polymer forming a dimethylmalonate-modified PE. The carbene is formed as a singlet and the triplet state is not thermally accessible.[20] Addition to the polymer takes place by a concerted mechanism; radical pair formation does not take place and consequently no crosslinking of the polyethylene is observed:

$$\text{(PE)}-\text{H} + \text{N}_2\text{C}(\text{COOMe})_2 \longrightarrow \text{(PE)}-\text{CH}(\text{COOMe})_2 \qquad (2)$$

It is interesting to note that the efficiency of grafting of the nitrene derived from n-octadecylazidoformate is independent of the initial concentration of azide (Table II). Under the reaction conditions, the nitrene gives the same extent of grafting regardless of azidoformate concentration.

In an attempt to produce a more chemically reactive material than the carbamate-modified PE, the thermal behavior of the modified polymer was investigated. The preparation of isocyanates from the pyrolysis of carbamates is well known,[21,22,23] and it appeared that the decomposition of a carbamate group bound to PE would give rise to a polymer-bound isocyanate:

$$\text{(PE)}-\text{NHCOOR} \xrightarrow{\Delta} \text{ROH} \uparrow + \text{(PE)}-\text{NCO} \qquad (3)$$
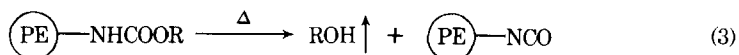
Other reactions are, of course, also possible, depending on the specific nature of the carbamate. Secondary reactions of the isocyanate group could also be anticipated.

A sample of 1.7% phenyl carbamate-modified PE was heated in a modified Carver press for 5 min at 300°C. IR analysis of the polymer showed the disappearance of carbamate absorbances and the formation of a new band at 2260 cm^{-1} indicative of an isocyanate (Fig. 4). Similar results were obtained when the phenyl carbamate-modified polymer was decomposed as a melt in a mixing bowl or by refluxing in a phenyl cyclohexane solution. In no case was decomposition seen below 235°C even with prolonged heating. This temperature is considerably

TABLE II
Grafting of Carboalkoxynitrenes to Polyethylene

R	Precipitation	Percent azidoformate added	Efficiency of grafting %	Percent carbamate on PE[a]
CH$_3$	1×	5	12	0.4
	1×	10	7	0.5
	2×	10	7	0.5
	1×	15	10	1.1
	2×	15	10	1.1
n-C$_{18}$H$_{37}$	1×	5	56	2.6
	2×	5	54	2.6
	3×	5	55	2.6
	1×	10	56	5.1
	2×	10	54	4.9
	3×	10	53	4.9
	1×[b]	15	53	8.0
t-Bu	1×	5	32	1.3
	2×	5	30	1.2
φ	1×	5	42	1.7
	2×	5	39	1.6
	3×	5	41	1.7

[a] % By weight.
[b] Sample was severely crosslinked.

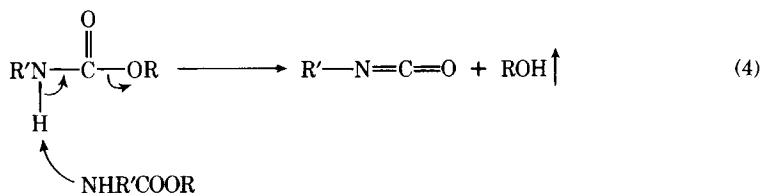higher than the 180°C decomposition temperature reported for n-alkylaryl-carbamates.[21]

In order to confirm the nature of the decomposition as shown in eq. (3), the volatile products of the thermolysis were analyzed by GCMS. The single major product was phenol, consistent with the expected elimination. Nitrogen analysis of the polymer indicates that most of the carbamate groups on the starting material remain bonded to the polymer as isocyanates. Cleavage of the carbamate from the polymer did not occur.

The isocyanate-modified polymer has a slight yellow color and, judging by percent gel values, is more crosslinked than the starting material. The polymer could, however, be easily pressed into thin films. Increased crosslinking could be the result of partial isocyanate dimer or trimer formation. Control experiments showed no crosslinking of a PE sample subjected to identical conditions. A thin film of the isocyanate-modified polymer showed no reaction after overnight exposure to ambient moisture.

A derivative of the isocyanate-modified polymer was prepared by reacting a phenyl cyclohexane solution of the polymer with an excess of cetyl alcohol. The IR spectrum of the product was indistinguishable from that of n-octadecylcarbamate-modified PE. The intensity of the carbonyl stretch was comparable to that of the starting material. A polymer-bound urea formed by the reaction of the isocyanate-modified PE solution with n-dodecylamine was also prepared.

The high-thermal stability of the polymer-bound phenyl carbamate compared to unbound phenyl carbamates is unexpected. Attachment of the carbamate to the polymer appears to inhibit elimination of phenol, perhaps by isolating the

carbamates from each other and preventing base assistance in the elimination:

$$R'N\!-\!\overset{\overset{\displaystyle O}{\|}}{C}\!-\!OR \longrightarrow R'\!-\!N\!=\!C\!=\!O + ROH\uparrow \qquad (4)$$

$$\underset{\overset{\displaystyle |}{H}}{} \qquad NHR'COOR$$

n-Octadecyl carbamate-modified PE reacted in a similar manner to the phenyl carbamate-modified material. Decomposition at 300°C led to the formation of an isocyanate-modified PE in addition to n-octadecanol and some CO_2. A small, residual carbamate absorbance was also present in the IR spectrum. Control experiments showed no decomposition after heating for 10 min at 250°C. The alkylcarbamate-modified PE is more stable than unbound alkylcarbamates or the polymer-bound phenyl carbamate. n-Alkylcarbamates are generally more stable than phenylcarbamates.[21]

Methyl carbamate-modified PE showed reactivity almost identical to that of the n-octadecyl material. Some isocyanate formation was observed after 5 min heating at 300°C. Volatile products were not analyzed.

The decomposition of t-butyl carbamate-modified PE was more complex than the aryl or n-alkyl cases. The GCMS analysis of the volatile products of pyrolysis (300°C, N_2) showed the presence of t-butanol, isobutylene, and CO_2. IR analysis of the polymer showed neither isocyanate nor carbamate absorbance; only bands arising from PE were observed. Similar results were obtained by decomposing a sample of modified polymer in a Haake mixing bowl (225°C) or by refluxing the modified polymer in a solution of phenyl cyclohexane. Analyses of all these samples showed only slight loss of nitrogen after carbamate decomposition. As observed in the decomposition of carbamate-modified PE, the t-butyl carbamate-modified material showed considerable stability compared to the unbound compounds.

Several possibilities are consistent with the results of the decomposition of t-butyl carbamate-modified PE. One explanation is that isobutylene is formed from t-butanol under the pyrolysis conditions, and the observation of CO_2 is fortuitous. This implies that only loss of alcohol to form the polymer-bound isocyanate occurs. However, if this is the case, the isocyanate, which was shown to be stable in the other cases, would be observed as the product. · The most plausible explanation of the results is that the first two, and possibly all three, reactions noted in scheme III are occurring simultaneously.
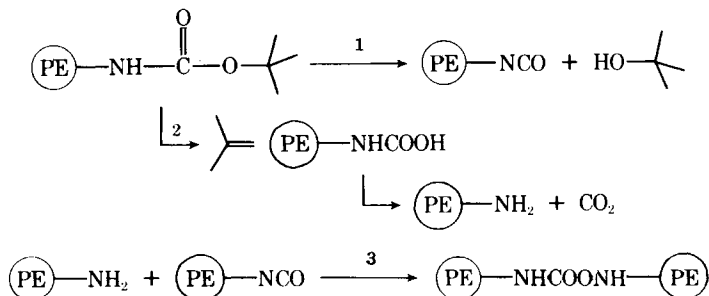
Scheme III

These results are in general agreement with those obtained for the thermolysis of N-t-alkoxycarbonyl-protected amino acids and peptides.[24]

The major reaction of the bound carbamate gives an amine-modified PE, carbon dioxide, and isobutylene via a cyclic mechanism. Isocyanate formation is a minor pathway. The isocyanate is consumed by amine groups on the polymer crosslinking the polymer by urea formation. Neither the small amount of urea nor the free amine is observed in the IR spectrum.

In order to assess the amine concentration on the modified polymer, the sample was reacted in solution with an excess of n-butyl isocyanate. Any free amine would react with the added isocyanate to form polymer-bound n-butyl urea. The urea crosslinks already present would be unreactive. The difference in the nitrogen analysis between the pyrolyzed t-butyl carbamate-modified PE and the material reacted with n-butyl isocyanate would be proportional to the amine concentration on the polymer. (Reaction of the polymer-bound amine groups with n-butyl isocyanate in solution is assumed to be quantitative.)

The IR spectrum of the material formed by the reaction of n-butyl isocyanate with the product of the pyrolysis of t-butyl carbamate-modified PE indicated formation of a urea-modified PE. Nitrogen content of the product of this reaction was 65% of the value expected if all the t-butyl carbamate groups were converted to amino groups. Based on this analysis, the formation of bound isocyanate and capture by bound amine (to form urea crosslinks) account for 35% of the t-butyl carbamate groups on the original polymer. Thus, the decomposition of the t-butyl carbamate-modified PE initially gives an 83:17 mixture of bound amine and bound isocyanate groups. Capture of the bound isocyanate leaves approximately 65% of the nitrogen present in the t-butyl carbamate PE as free amine.

In conclusion, it appears that isocyanate-modified polyethylenes may be prepared in the melt using the intermediacy of carbamate-modified materials produced by the reaction of carboalkoxynitrenes. The isocyanate-modified polymer undergoes reactions typical of that functional group.

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