Polyolefin functionalization by carbene insertion for polymer blends

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The insertion of controlled amounts of polar ester groups with well defined structure into polyolefin backbones has been accomplished by reacting different polymers with ethyl-(or chloroethyl-)diazoacetate at high temperature (≈ 210°C). The reaction temperature allowed the polymers to keep in the molten state and complete decomposition of the diazocompound with the formation of carbenic species ($:CH–COOC_2H_5$ or $:CH–COOC_2H_4Cl$). The functionalization reaction has been shown to proceed with a one-step mechanism in which the carbene species reacts in the singlet state. Further studies performed with ethylene–propylene copolymers (EPR) allowed optimization of the reaction conditions in order to obtain a rapid and complete decomposition of ethyldiazoacetate and the required (5–10%) low degree of functionalization. Higher degree of functionalization (≈ 10%) is obtained by successive reactions with additional diazoester on the previously functionalized polymer. Infra-red spectra of the functionalized EPR in different solvents indicate that the absorption maxima frequency of the carbonyl band depends on solvent polarity and structure connected to intermolecular interactions of hydrogen-bonding type involving the ester groups of the functionalized polymer and acidic hydrogen present in the solvent.

(Keywords: diazocompounds; carbene intermediate; polyolefins; polyethylene; ethylene/propylene copolymer; polyolefin functionalization; blends)

INTRODUCTION

There has been great interest in recent years in attempts to extend applications of functionalization reactions to polyolefins, due to the convenient mechanical, chemical and environmental properties of such materials. Such goals can be approached by introducing controlled amounts of functional groups into the saturated hydrocarbon backbone of the pristine paraffine structure. As well known from traditional organic chemistry however, saturated hydrocarbons are reactive only under very specific conditions and in a very limited number of reactions. Among these reactions, the most used for polyolefins are free radical reactions which, in principle, offer a lot of possibilities due to the large number of functional substrates, in general unsaturated, which can be used in combination with radical initiators, such as peroxides or hydroperoxides. Free radical based reactions suffer however, several disadvantages, the principal ones being low specificity, degradation and crosslinking of the macromolecules and polymerization reactions of the functional low molecular weight substrate.

This paper describes the polymer modification reaction (*Scheme 1*) allowing polyolefin functionalization with well defined groups and avoiding the side reactions mentioned above.

Scheme 1

R = H or CH_3
R' = CH_2-CH_3 or CH_2-CH_2Cl

This process, based on carbene insertion to C–H bonds, is described with reference to the reaction mechanism and structure of the functional groups attached to the macromolecules, taking into account the influence of reaction conditions on the degree of functionalization. Evidence of molecular interactions of the groups introduced on the polyolefin chain with polar low molecular weight molecules is obtained by infra-red spectroscopy.

EXPERIMENTAL

Materials

Polymers were purified according to the following procedures: atactic polypropylene (aPP) (Montedison PRA-Omopolimero, Brindisi, Italy) was previously extracted with boiling acetone and the insoluble residue extracted with boiling toluene. Only the toluene-soluble fraction was used (78 wt% with respect to the starting quantity). Isotactic polypropylene (iPP), (Montedison HEP-99) was employed without further purification. Ethylene–propylene rubber (EPR) (Montedison PRA, Ferrara, Italy) was previously extracted with boiling acetone and the insoluble residue extracted with boiling diethyl ether. This last ether-soluble fraction was used (59 wt% with respect to the starting quantity). High density polyethylene (HDPE) and Polyisobutene (PiBu) were commercial products and were used without further purification.

Ethyl-3-butylheptanoate and ethyl-3-pentylundecanoate were synthesized according to the procedure described in reference 12.

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Functionalization reactions

Functionalization of polymers was performed according to the following procedure, operating under a nitrogen atmosphere. EPR (1 g) together with 0.15 g of ethyldiazoacetate (EDA) were poured (monomeric unit/EDA ratio = 20 mol/mol) into a glassy, four-necked reactor equipped with a mechanical stirrer, a dropping funnel and a reflux condenser. The reaction mixture, vigorously stirred, was immersed in a silicone oil bath maintained at 210°C. The reaction was carried out for 30 min and then stopped, and room temperature restored. The recovered polymer was extracted with acetone for a long period in a 'Kumagawa extractor'; 1.04 g of a solid residue and 0.14 g of a dried acetone-soluble product were collected. The solid insoluble residue was dissolved in chloroform, filtered on a 10-cm alumina column ($\phi = 1$ cm), eluted with chloroform and then collected, after solvent distillation under reduced pressure, to give 0.93 g of product.

RESULTS AND DISCUSSION

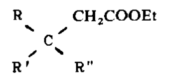
Insertion of carbene species generated by diazocompound decomposition into saturated hydrocarbons has been studied only in a limited number of cases. The few examples available in the literature are concerned with studies on photoinduced[1,2] or thermal[2,3] decomposition of diazocompounds in order to functionalize hydrocarbons, or analogous studies concerning metal-catalysed modifications of paraffins[2,4–6], or polymer surfaces[7,8]. In addition, the regiospecific insertion of different carbenes generated by photochemical decomposition of diazocompounds into C–H bonds in an α position to the methyl carbon in linear paraffins has been reported when using carbene-generating species bearing an electron-withdrawing group[9].

The application of such a reaction to polyolefins leads to the clean insertion of functional groups into the macromolecular backbone[10,11]. In preliminary experiments we used EDA and chloroethyldiazoacetate (ClEDA) as functionalizing agents with different polymers as substrates[10,11]. The high potentiality of the method was demonstrated by obtaining, in all cases, the insertion of the functional groups into macromolecular chains, in low but significant yields (0.5–1.5 mol %).

The relevant results obtained with iPP, aPP, EPR, PiBu and HDPE are reported in *Table 1*. The presence of the functional groups in the polymer was inferred by infra-red spectroscopy, due to the carboxylic stretching band at 1740 cm^{-1}, and the C–Cl stretching band at 658 cm^{-1} shown by the reacted polymers. The degree of functionalization was determined in several cases by elemental analysis (for chloro-containing products) or by infra-red spectroscopy.

The striking similarities of the ^{13}C nuclear magnetic resonance spectrum of a sample of HDPE functionalized with EDA and the analogous spectra of two model compounds, ethyl-3-pentylundecanoate (a) and ethyl-3-butylheptanoate (b) (see *Scheme 2*) indicate that the structure of the inserted functional groups is in full agreement with the structure predictable on the basis of the mechanism shown in *Scheme 1*. This structural demonstration is described in detail in a preliminary communication[12].

Scheme 2



a) $R = R' = C_4H_9$, $R'' = H$

b) $R = C_5H_{11}$, $R' = C_8H_{17}$, $R = H$

Table 1 Functionalization of polyolefins by thermal decomposition of diazoesters[a]

Polyolefin[b]	Diazoester[c]	Vibrational band at[d] 1740 cm^{-1}	658 cm^{-1}	Degree of functionalization[e]
iPP	EDA	+	−	–
iPP	ClEDA	+	+	1.5[f]
HDPE	EDA	+	−	0.4[g]
HDPE	ClEDA	+	+	1.0[f]
EPR	EDA	+	−	1.1[g]
EPR	ClEDA	+	+	1.3[f]
PiBu	EDA	+	−	–
PiBu	ClEDA	+	+	0.6[f]
aPP	EDA	+	−	–
aPP	ClEDA	+	−	–

[a] All reactions were performed at 210°C, under nitrogen, on molten polymers and for 30 min. Polyolefin structural unity/EDA ratio = 20 mol/mol

[b] iPP = isotactic polypropylene; HDPE = high density polyethylene; EPR = ethylene–propylene rubber; PiBu = polyisobutylene; aPP = atactic polypropylene

[c] EDA = ethyldiazoacetate; ClEDA = chloroethyldiazoacetate

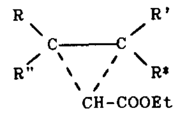
[d] + (or −) indicates the presence (or the absence) of the respective band

[e] Moles of ester for hundred residues

[f] Evaluated by elemental analysis

[g] Evaluated by infra-red spectroscopy

Scheme 3



In order to establish if the insertion reaction proceeds with a 'one-step' mechanism in which the generated carbene reacts in the singlet state, forming a cyclic intermediate as that shown in *Scheme 3*, the reaction between EDA and *trans*-stilbene was performed. From the crude products, *trans*-2,3-diphenylcyclopropancarboxylic acid was isolated as the only addition product. This result supports the proposed 'one-step' mechanism. Indeed the carbene in the triplet state would show low selectivity as a radical species; thus a mixture of two products (*cis*- and *trans*-isomers of the recovered acid) would be obtained, due to possibility of rotation around the PhCH–CHPh bond in the transition state. The isolation of the *trans*-isomer as a single product shows, unequivocally, that the addition reaction is stereospecific and this feature indicates the singlet character of the carbene[13,14].

We have devoted successive studies to the reaction of n-hexadecane with EDA in order to determine the best conditions for rapid and complete decomposition of the diazoester. The completion of the reaction was detected by infra-red analysis of the reaction mixture, by looking at the intensities of three diagnostic bands, at 2110 cm^{-1} due to the N=N stretching in EDA, at 1740 cm^{-1} attributable to the C=O stretching in the inserted functional groups, and at 1720 cm^{-1}, corresponding to the stretching C=O frequency in the unreacted EDA.

By operating at a temperature lower than 210°C, such as 190–200°C or at 210°C for 20 min, infra-red analysis of the mixture revealed the presence of functional groups on the n-hexadecane but also of unreacted EDA. On the contrary, by operating at 210°C for 30 min the total decomposition of EDA takes place, as revealed by the disappearance of the bands at 2110 and 1720 cm^{-1} in the infra-red spectra of the reaction mixture. The mixture containing eight esters obtained from the reaction between EDA and n-hexadecane was examined by gas chromatography/mass spectroscopy technique and we observed that the molecular weight of these esters was 312 for all the compounds. This value is in perfect agreement with the one we could expect from the insertion reaction on n-hexadecane, and the number of esters obtained is predictable taking into account the number of possible sites of insertion on the saturated hydrocarbon and the inability of the carbene to distinguish different carbon atoms on the hydrocarbon chain. This result indicates that the carbene reaction is not selective as far as type of C–H bond is concerned as previously reported in the literature[15], operating under milder conditions and for a longer time.

On the basis of these results, all successive reactions between EDA and EPR were performed at 210°C, and the effect of parameters such as reaction time and reagent ratio (*R*) on the degree of functionalization was evaluated.

The results obtained varying only reaction time, with constant *R* ratio are summarized in *Table 2*. The degree of functionalization of each sample was determined by infra-red spectroscopy, by comparing the optical densities ratio of the bands at 1740 cm^{-1} (–COOEt) and 1460 cm^{-1} ($-CH_2-$ groups in the polymer backbone), with those of EPR/poly(ethyl acrylate) mixtures of known composition.

As shown by the listed data, almost 20 min are necessary to obtain a constant degree of functionalization; longer reaction times do not give any substantial improvement.

Results obtained varying the *R* ratio are listed in *Table 3*; these data indicate that the degree of functionalization remains relatively constant during every reaction, but decreasing the *R* ratio is accompanied by the progressive increase in weight of the acetone-soluble products due to the concurring formation of low molecular weight fragments by thermal degradation.

Table 2 Evaluation of the degree of functionalization and the amount of acetone-soluble products obtained by reacting EPR with EDA, with different reaction times[a]

Time (min)	Acetone-soluble fraction (g)	Acetone-insoluble crude fraction (g)	Acetone-insoluble fraction recovered from alumina (g)[b]	Degree of functionalization wt% (mol%)
10	0.10	1.04	0.93	0.0 (0.0)
15	0.10	0.99	0.93	1.8 (0.8)
20	0.09	0.93	0.71	2.3 (1.0)
25	0.08	0.90	0.89	2.3 (1.0)
30	0.08	0.88	0.83	2.3 (1.0)
60	0.08	0.91	0.90	2.3 (1.0)
90	0.09	0.96	0.90	2.3 (1.0)

[a] Monomeric residues/EDA molar ratio = 20

[b] The acetone-insoluble crude product was dissolved in chloroform and passed through a 10-cm alumina column ($\phi = 1$ cm), eluting with chloroform

Table 3 Evaluation of the degree of functionalization and amounts of acetone-soluble products obtained by reacting EPR with EDA at different *R* ratios[a,b]

R[a]	Acetone-soluble fraction (g)	Acetone-insoluble crude fraction (g)	Acetone-insoluble fraction recovered from alumina (g)[c]	Degree of functionalization W5% (mol%)
α	0.03	0.63	–	0 (0)
60	0.04	0.96	0.88	< 1 (< 0.61)
50	0.08	0.87	0.72	1.5 (0.67)
40	0.06	0.93	0.79	1–1.5 (0.61–0.67)
30	0.08	0.83	0.63	1–1.5 (0.61–0.67)
20	0.12	0.90	0.88	1.6 (0.72)

[a] *R* = monomeric residues/EDA molar ratio

[b] All reactions were allowed to continue for 30 min

[c] The acetone-insoluble crude product was dissolved in chloroform and passed through a 10-cm alumina column ($\phi = 1$ cm), eluting with chloroform

Table 4 Evaluation of the degree of functionalization obtained performing successive additions of EDA to EPR[a,b]

Acetone-soluble fraction (g)	Acetone-insoluble crude fraction (g)	Acetone-insoluble fraction recovered from methanol (g)[c]	Degree of functionalization Wt% (mol%)
0.75	8.17	8.00	3.0 (1.6)
0.80	8.36	7.70	4.0 (2.0)
0.56	7.52	7.31	6.0 (2.8)

[a] During every reaction, the *R* ratio was constant and equal to 20; in successive reactions it was calculated neglecting the introduced amount of functional groups

[b] All reactions were allowed to continue for 30 min

[c] The acetone-insoluble crude product was dissolved in chloroform and precipitated in methanol

In order to improve the degree of functionalization, the previously functionalized polymer was submitted to successive reactions. After three reactions with addition of fresh EDA without isolating the product, a total degree of functionalization of about 5 wt% (2.3 mol%) with respect to the recovered product was achieved. During all these steps *R* was constant and equal to 20. In a second experiment the reacted polymer was isolated, and the degree of functionalization was determined each time.

This second procedure allows slight (*Table 4*) improvement in the functionalization degree of EPR, to a final 6 wt% (2.8 mol%). Also in these reactions *R* was constant (*R* = 20), with respect to the starting polymer.

MOLECULAR INTERACTIONS OF MODIFIED POLYMERS WITH POLAR MOLECULES

From this set of data, it seems that the introduction of a 'predetermined' amount of functional groups in polyolefin chains could give rise to new possibilities for applications of polyolefins as coating materials or components in blends. Indeed polyolefins, once modified by radical reactions, give evidence of interactions with functional polymers as demonstrated from recent studies[16,17] of their blends with PVC.

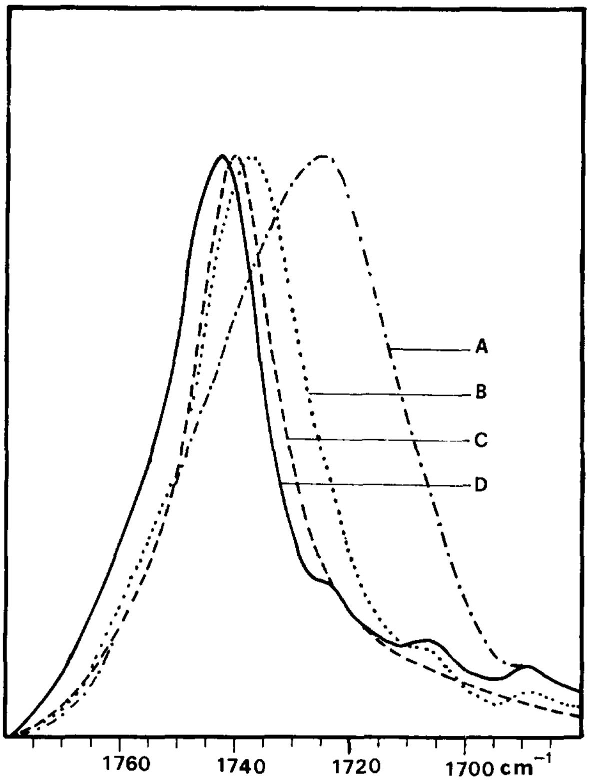


Figure 1 C=O stretching band as determined by Fourier transform infra-red spectroscopy (Perkin Elmer Mod. 1760-X) on functionalized EPR sample (–COOEt 2.8 mol%). A, $CHCl_3$ solution; B, CCl_4 solution; C, neat polymer; D, heptane solution

In this context, it appeared interesting to analyse the behaviour of the functionalized polyolefins in solution in order to show possible interactions between the ester units on the macromolecular chains and the functional groups of the different solvents. The observed modifications of the position and/or shape of some vibrational bands can be thought of as a consequence of weak interactions among functional groups (or heteroatoms) located on the polymer and on the solvent molecule[16,18,19] thus allowing the prediction of polymer–polymer miscibility.

The Fourier transform infra-red spectra in the carbonyl stretching region for the functionalized polymer (FEP) examined in different solvents is reported in *Figure 1*. The maximum of the absorption shows a shift towards lower frequencies when passing from n-heptane (1743 cm^{-1}) to chloroform (1725 cm^{-1}), the value for the bulk polymer being in an intermediate position (1740 cm^{-1}) but much closer to the n-heptane solution.

n-Heptane behaves as an inert solvent in which polymeric chains are characterized by the lack of inter- and intramolecular interactions. The large variation of the carbonyl band for the polymer in $CHCl_3$ solution compared with the same absorption in n-heptane solution or in the bulk may be associated with the presence of intermolecular interactions of hydrogen-bonding type involving the ester groups of the functionalized polymer and the hydrogen of $CHCl_3$. However, the intermediate shift of the band position in CCl_4 solutions suggests that dipole–dipole interactions atoms have to be also considered.

On the basis of these results, a study concerning intermolecular interactions in blends of carbene modified polyolefins with PVC and other polar polymers is in progress[20].

REFERENCES

1 Wang, B., Zheng, G. and Wang, H. *Scientia Sinica B* 1982, **25**, 925
2 Von, E., Doering, W. and Knox, L. H. *J. Am. Chem. Soc.* 1956, **78**, 4947
3 Smith, L. I. and Tawney, P. O. *J. Chem. Soc.* 1934, 2167
4 Demonceau, A., Noels, A. F., Hubert, A. J. and Teyssie, P. *J. Chem. Soc., Chem. Commun.* 1981, 688; 2nd IUPAC Symposium on Organometallic Chemistry Directed Toward Organic Synthesis, Dijon, 1983, Abstracts, 184; *Bull. Soc. Chim. Belg.* 1984, **93**, 945
5 Callot, H. J. and Metz, F. *Tetrahedron Lett.* 1982, **23**, 4321
6 Sarkany, A. *J. Chem. Soc., Faraday Trans.* 1986, **82**, 103
7 Morgan, A. W. and Swenson, J. S. US Patent 3,376,278; *Chem. Abstr.* 1968, **68**, 105746 e
8 Ranby, B., Gao, M. Z., Hult, A. and Zhang, P. Y. *ACS Symp. Ser.* No. 364, 1988, p. 168
9 Von E. Doering, W. and Knox, L. H. *J. Am. Chem. Soc.* 1961, **83**, 1989
10 Aglietto, M., Ruggeri, G., Ciardelli, F. and Segre, A. L., 8th Congress of Industrial Chemistry Division of Italian Chemical Society, Trento, 1986, Abstracts, p. 80
11 Skell, P. S., Aglietto, M., Ruggeri, G., Speranza, S. and Ciardelli, F. Italian Patent, 1985, No. 48950A/85
12 Aglietto, M., Bertani, R., Ruggeri, G., Fiordiponti, M. and Segre, A. L. *Macromolecules* in press
13 Skell, P. S. *Tetrahedron* 1985, **41**, 1427
14 Marchand, A. P. and MacBrockway, N. *Chem. Rev.* 1974, **74**, 431
15 Forbes, A. D. and Wood, J. *J. Chem. Soc. B* 1971, 646
16 Benedetti, E., D'Alessio, A., Aglietto, M., Ruggeri, G., Vergamini, P. and Ciardelli, F. *Polym. Eng. Sci.* 1986, **26**, 9
17 Benedetti, E., Posar, F., D'Alessio, A., Vergamini, P., Aglietto, M., Ruggeri, G. and Ciardelli, F. *Br. Polym. J.* 1985, **17**, 34
18 Coleman, M. M., Zarian, J., Varnell, D. F. and Painter, P. C. *J. Polym. Sci., Polym. Lett. Edn.* 1977, **15**, 745
19 Lu, F. J., Benedetti, E. and Hsu, S. L. *Macromolecules* 1983, **16**, 1525
20 Aglietto, M., Ruggeri, G., Galleschi, F., D'Alessio, A., Benedetti, E. and Ciardelli, F. 'Bononiachem 88', 16th Congress of Italian Chemical Society, Bologna, 9–14 October 1988, Abstracts, p. 270