

Alkyne Creation in Aliphatic Polymers: Influence of Side Groups

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In this article, we focus on the influence of side groups on terminal alkyne creation, in aliphatic polymers submitted to swift heavy ions, under vacuum. Terminal alkyne creation was compared in polyethylene and in substituted polymers. We selected two classes of side groups: alkyl groups, which differed in their length (polypropylene and polybutene) and allyl groups, which were linear (EPDMh) or cyclic (EPDMn). Irradiated samples were analyzed using Fourier transform IR spectroscopy, in the transmission mode, at room temperature. Alkynes are created when the electronic stopping power, $(dE/dx)_e$, exceeds a threshold value. This threshold value was moderately influenced by the presence of an alkyl side chain but was clearly reduced in the presence of C=C bonds on the side chain. Nevertheless, in all-saturated polymers, below the $(dE/dx)_e$ threshold, terminal alkyne formation is observed after a latent dose, rather independently of the side-chain length and directly related to the formation of radiation-induced double bonds prior to alkyne formation. Under S ion irradiation, the radiation chemical yield G_0 value obtained in EPDMh was 4 times the value of G_0 in PE. This effect is understandable only if important energy transfers, from the backbone to C=C double bonds, are considered.

I. Introduction

Swift heavy ions (SHI) deposit their energy mainly through electronic processes (ionization–excitation) occurring close to the ion path, in a track core of a few nanometers.^{1,2} The huge amount of energy locally deposited by SHI within the track core induces specific damage processes, very different from those occurring under classical low-ionizing irradiation conditions (γ -rays and electron beams). The high density of ionizations triggers these specific damage mechanisms, which involve complex molecular rearrangements and collective motions of atoms.

Recently, an important effort has been devoted to a better understanding in the behavior of solids with high electronic excited states. In this field, a rather coherent comprehension of the SHI effects has been reached in a few polymers^{3,4–12} at least. Nevertheless, some specific features still need clarification.

In most insulators, the damage induced by an individual ion, the latent track, is easily etchable, giving rise to a cylindrical pore. Presently, there is a clear regain of interest on polymer track etching for nanomaterial manufacturing, especially by replica techniques.^{13–19} To optimize nanopore formation and thus to enlarge applications, a good comprehension of the damage creation is required. Therefore, it is important to determine how the damage process is influenced by the polymer composition, the beam parameters (dose, ion velocity, electronic stopping power $(dE/dx)_e$), and irradiation conditions (temperature, vacuum, or air).

In polymers submitted to SHI under vacuum, defects such as crosslinking, isolated or conjugated double bonds, cumulated double bonds (allenes), and triple bonds (alkynes) are created. Both alkynes and allenes are specific to SHI irradiations and require a large energy deposition in very short time to be

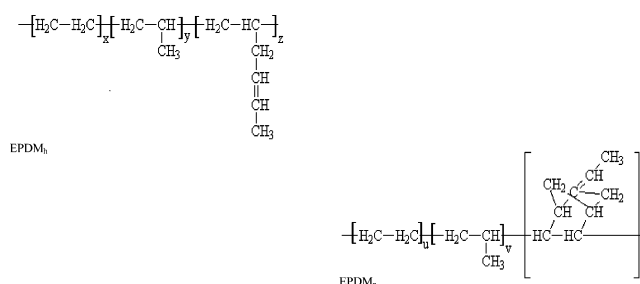


Figure 1. Molecular formula of EPDMh and EPDMn repeating units. The values x , y , z , u , v , and w (molar contents) are given in the text.

formed.⁴ We focus here on alkyne creation and specifically on R–C≡CH groups (monosubstituted acetylene, called hereafter terminal alkyne) remaining in the polymer film. These alkynes are created only above a $(dE/dx)_e$ threshold between 4 and 6 MeVcm²/mg in PE.²⁰ Swift heavy ions also induce the creation of small molecules, mostly unsaturated, that diffuse out of the polymer film, thus inducing a significant gas release. Among them, the most important is acetylene.^{6,21} We do not follow these volatile species here.

We also studied the role of irradiation temperature. We recently published results on 8 K irradiations on polyethylene (O and S ion irradiations)²² and ethylene–propylene–hexadiene copolymers (C ion irradiations).²³ For PE, we showed that terminal alkyne formation is sensitive to the irradiation temperature,²² and the yield is 2.6 times higher at 8 K than at room temperature (RT). For EPDMh,²⁴ the same behavior is observed and the corresponding ratio is 2. Thus, the terminal alkyne formation process is slow enough to allow radical migration out of the track core. The resulting decrease in the radical concentration at RT reduces the alkynes creation yield.

The aim of this paper was to analyze the influence of pre-existing side groups on alkyne creation. These side groups are different linear alkanes and linear or cyclic alkenes. We therefore looked at the influence of both side-chain length and double

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TABLE 1: Characteristics of the Polymer Films and Ion Beams^a

polymer	ion beam E_i (MeV/amu)	C 5.96 ^b 10.13 ^c	Ne 7.2	S 10 ^b 11.2 ^c	Kr 8.6
PE $d = 0.95$	e (μm)	37.5	27.6	38	44.4
	$(dE/dx)_e$ (MeV $\text{mg}^{-1} \text{cm}^2$)	2.84	6.33	11.9	49.1
	dose range (MGy)	0–60	0–1.7	0–22.5	0–15.7
PP $d = 0.85$	e (μm)	43.6	26.3	36	34.7
	$(dE/dx)_e$ (MeV $\text{mg}^{-1} \text{cm}^2$)	2.80	6.28	11.84	48.3
	dose range (MGy)	0–60	0–1.7	0–24.6	0–12.4
PB $d = 0.91$	e (μm)	21.5		30	40.2
	$(dE/dx)_e$ (MeV $\text{mg}^{-1} \text{cm}^2$)	2.75		11.76	48.1
	dose range (MGy)	0–60		0–24.5	0–15
EPDMh $d = 0.87$	e (μm)	76.2	56.0	30.2	
	$(dE/dx)_e$ (MeV $\text{mg}^{-1} \text{cm}^2$)	1.86	6.61	10.81	
	dose range (MGy)	0–0.6	0–1.7	0–12.5	
EPDMn $d = 0.88$	e (μm)		56.7		
	$(dE/dx)_e$ (MeV $\text{mg}^{-1} \text{cm}^2$)		6.62		
	dose range (MGy)		0–1.7		

^a All irradiations were performed at the GANIL facility. The notation E_i stands for the beam energy entering the polymer film. EPDM irradiations were performed under vacuum. For the polyolefins, S and Kr irradiations were performed under He atmosphere (1 bar), and C and Ne irradiations were carried out under vacuum. The electronic stopping power, $(dE/dx)_e$, is the mean value over the sample thickness; e is the film thickness; and d is the polymer density. ^b For S and C irradiations, this is for PE, PP, and PB. ^c For S and C irradiations, this is for EPDMh.

bond existence on terminal alkyne creation. We carried out this study using, on one hand, different polyolefins (polyethylene (PE), polypropylene (PP), and polybutene (PB)), named hereafter polyolefins or all-saturated polymers and, on the other hand, ethylene–propylene–diene terpolymers (EPDM) with either a 1–4 hexadiene linear chain (EPDMh) or an ethylidene norbornene cycle (EPDMn).

II. Experimental

All the polymers studied were semicrystalline, with a crystalline ratio varying from one polymer to another. PE is 60% crystalline. The crystalline ratio in PP, calculated using an empirical formula proposed by Berticat,²⁵ is 65%. Polybutene can exist in three crystalline forms. We used form I (hexagonal structure), thermodynamically stable at room temperature.

Although EPDMs are frequently considered as amorphous, they contain a small part of crystallinity, around 15–20% as quantified by Fourier transform IR spectroscopy (FTIR). However, the very low melting point (≈ 47 °C for EPDMn) suggests a very small crystallite size.

Dienes in EPDM are 1,4 hexadiene and 5-ethylidene-2-norbornene, respectively, for EPDMh and EPDMn. The EPDMh molar contents, obtained by ¹³C solid-state NMR spectroscopy,^{26,27} were of 84% ethylene, 13.8% propylene, and 2.2% 1–4 hexadiene. In EPDMn, molar contents were of 77.9% ethylene, 21.4% propylene, and 0.7% ethylidene norbornene. The EPDM molecular structures are presented in Figure 1.

We performed irradiations, either under vacuum or helium gas flux, at RT, using the medium energy line (SME) at the GANIL accelerator (Caen, France). Both irradiation conditions and film characteristics are gathered in Table 1. Irradiated films were analyzed by FTIR performed in the transmission mode with a 2 cm^{-1} resolution. Spectra were recorded *in situ*, after

each irradiation dose step. A specific cell allowed us to perform irradiations and record FTIR spectra without removing the sample from the cell. Thus, contact with air was avoided, and post-irradiation oxidative degradation was prevented.

III. Data Analysis

As a matter of fact, the evolution of the double or triple bond concentration with dose generally follows a kinetics determined by zero-order formation and first-order destruction: $dc/dD = G_0 - kc$, where c is the considered unsaturated group concentration, G_0 is the creation yield at initial dose, and k is the destruction constant. Relation between the concentration and the irradiation dose is then $c = c_\infty - (c_\infty - c_0) \exp(-kD)$. Here, c_0 and c_∞ are the initial and saturation concentrations, respectively, and $c_\infty = G_0/k$.

When $c_0 = 0$ (no native unsaturated group), c follows the classical mathematical form $c = c_\infty(1 - \exp(-kD))$ that, in the limit of low doses, reduces to $c = G_0D$. Thus, the initial slope of the evolution of the defect concentration as a function of the absorbed dose corresponds to the radiation chemical yield G_0 .

In the absence of any specific indication, G_0 is calculated at zero dose as described hereafter. Depending on the polymer and irradiation conditions, evolution of the defect concentration with dose, in the dose range studied, can be linear or present a tendency toward saturation. Consequently, to calculate the initial slope and hence the yield, experimental data are fitted either with a linear equation or with an exponential function $c = c_\infty(1 - \exp(-kD))$. However, when a latent dose exists, we do not calculate the radiation chemical yield at initial dose; instead, we calculate it after the latent dose, using the same method as before.

In the case of pre-existing defects, the concentration evolves as $c = c_0 + k(c_\infty - c_0)D$ or equivalently as $c = c_0 - (c_0/c_\infty - 1)G_0D$. Then, if $c_0 > c_\infty$, the defect concentration decreases under irradiation with a slope equal to $(c_0/c_\infty - 1)G_0$. If $c_0 \gg c_\infty$, the slope is c_0k .

IV. Results

Terminal alkyne creation was followed through the increase of the vibration band at 3313 cm^{-1} , in the FTIR spectrum (Figure 2), corresponding to the $\equiv\text{C}-\text{H}$ stretching mode in monosubstituted acetylene. A molar extinction coefficient, ϵ , of 160 $\text{L mol}^{-1} \text{cm}^{-1}$, obtained for 1-butyne in hexane,²⁸ was used for quantification.

A. Polyolefins: Side-Chain Length Effect. As shown in Figure 3, whatever the polymer considered, terminal alkyne creation increased when going from C to Kr ion irradiation, that is, when $(dE/dx)_e$ increased. Terminal alkyne evolution under Ne ion irradiation is not reported because it remained undetectable in the dose range studied (0–1.6 MGy). Clearly, for the three polyolefins, C and Ne ion irradiations induced a $(dE/dx)_e$ lower than the threshold value for alkynes creation.²⁰ We confirm here the absence of alkynes creation during irradiation with those ions at low doses.

1. Below the $(dE/dx)_e$ Threshold Value. Figure 3a shows terminal alkyne concentration evolution during C ion irradiations up to very high doses. Whatever the polymer, the initial radiation chemical yield (G_0) was null. In fact, terminal alkynes were created only after a latent dose, D_{lt} , slightly dependent on the side-chain length. The D_{lt} value was around 10 MGy for PE and PB and 15 MGy for PP. Taking into account the fact that absorption bands in IRTF spectra were very small and consequently that errors, due to noise and baseline estimation, were not negligible, the quoted difference in D_{lt} may be within the

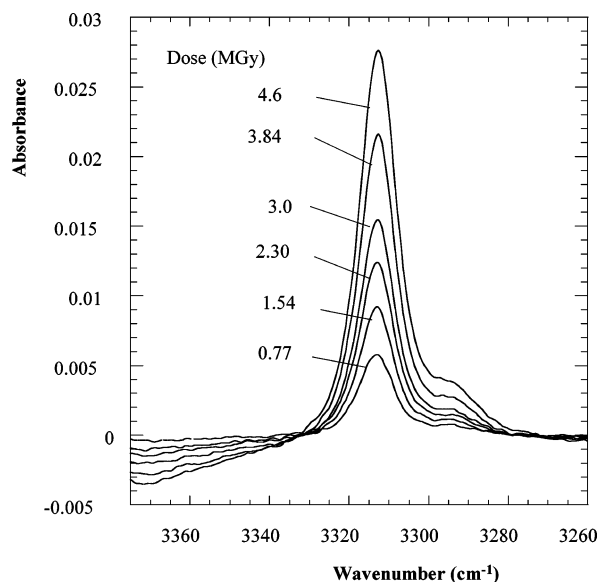


Figure 2. Polyethylene FTIR transmission spectra under Kr irradiation in the region of the $\equiv\text{C}-\text{H}$ stretching vibration of terminal alkyne groups. Evolution with irradiation dose is shown. The film thickness is $44.4\ \mu\text{m}$.

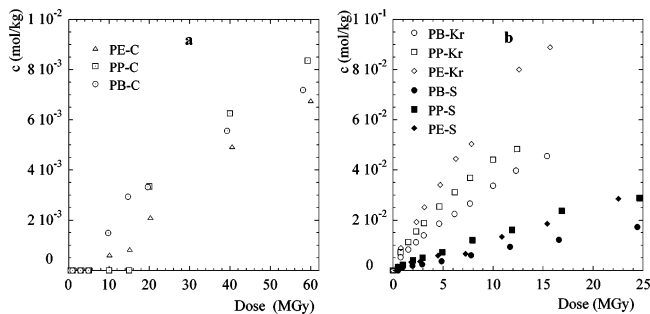


Figure 3. Side-group length effect on the formation of terminal alkynes in polyethylene (PE), polypropylene (PP), and polybutene (PB). (a) C irradiation. (b) S and Kr irradiations. Concentrations, c , are in moles of alkyne per kg of polymer.

TABLE 2: Initial Radiation Chemical Yield (G_0) of Terminal Alkyne Creation^a

polymer	G_0 (10^{-7} mol/J)			
	C	Ne	S	Kr
PE	0 1.3×10^{-3} ^b	0	1.2×10^{-2}	7.9×10^{-2}
PP	0 1.9×10^{-3} ^b	0	1.7×10^{-2}	7.0×10^{-2}
PB	0 1.3×10^{-3} ^b	0	8.5×10^{-3}	4.5×10^{-2}
EPDM _h	0 1.24×10^{-2} ^c	3.7×10^{-2}	4.6×10^{-2}	
EPDM _n		1.6×10^{-2}		

^a In polyolefins, Ne irradiations have not been carried up to doses high enough to measure alkyne formation. ^b Corresponds to a yield measured above the latent dose D_{lt} . PE, PB, and PP with $D_{\text{lt}} \approx 10$ MGy. ^c Corresponds to a yield measured above the latent dose D_{lt} . EPDMh with $D_{\text{lt}} \approx 0.1$ MGy.

error bars. To evaluate the side-chain influence on terminal alkyne creation above D_{lt} , we have calculated a mean radiation chemical yield in the $D_{\text{lt}}-60$ MGy dose range. As it appears in Table 2, the side-chain length did not influence so much the alkynes formation yield, the yields for PP being slightly higher than the yields for PE and PB. Finally, Figure 3a shows a rather linear evolution of alkyne concentration with absorbed dose in all polyolefins.

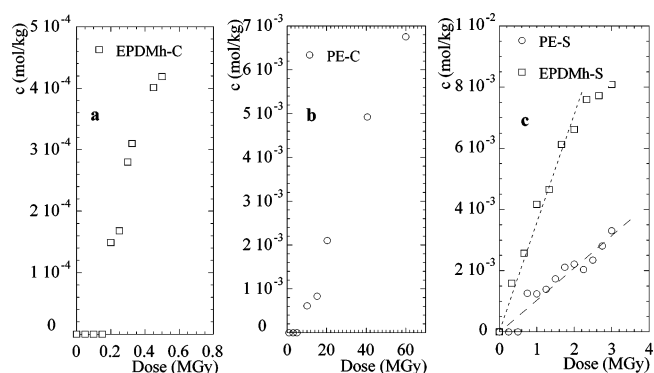


Figure 4. Role of native or radiation-induced $\text{C}=\text{C}$ double bonds in terminal alkyne creation. (a) EPDMh irradiated under C ions. (b) PE under C ions. (c) PE and EPDMh under S ions. Concentrations, c , are in moles of alkyne per kg of polymer.

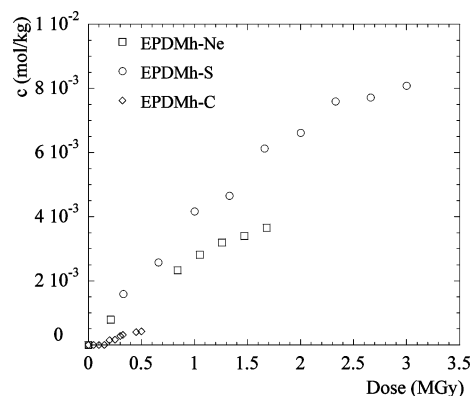


Figure 5. $(dE/dx)_e$ effect on terminal alkyne creation in EPDMh; Ne, S, and C ion irradiations. Concentrations, c , are in moles of alkyne per kg of polymer.

2. Above the $(dE/dx)_e$ Threshold Value. In PE, PP, and PB, above the $(dE/dx)_e$ threshold value, the side-chain length influence became more visible (Figure 3b). For S irradiation, terminal alkyne concentrations in PE and PP were very similar (although somewhat different) and perceptibly lower in PB. This influence was more important for Kr ion irradiations where terminal alkyne creation was more important in PE than in PP, which had higher terminal alkyne yield than PB ($\text{PE} > \text{PP} > \text{PB}$). The side-chain length influence on terminal alkyne creation radiation chemical yields at initial dose, G_0 , is shown in Table 2. When going from PE to PB, the yield decreased by a factor of 1.8.

B. EPDM: Influence of Pre-existing Double Bonds. The influence of pre-existing double bonds is presented in Figures 4–6. In Figure 4, the PE and EPDMh behaviors, for two values of $(dE/dx)_e$ (C and S irradiations), are compared. In Figure 5, we present the role of $(dE/dx)_e$ on terminal alkyne creation in EPDMh. In Figure 6, comparison between EPDMn and EPDMh gives a clear indication on the influence of side group nature (cyclic or not). All G_0 values are reported in Table 2.

1. The $(dE/dx)_e$ Threshold Value. The Ne ion irradiations of EPDMh and EPDMn induced terminal alkyne creation without any D_{lt} , and for the same beam in polyolefins, the D_{lt} was, at least, of 1.6 MGy. C ion irradiations of EPDMh induced a clear creation of terminal alkyne. The data of Figure 4a seem to indicate the presence of a small latent dose ($D_{\text{lt}} \approx 0.1$ MGy) in EPDMh. This eventual latent dose was 2 orders of magnitude smaller than the one observed in polyolefins for C ion irradiations (Figure 3a). It is not clear if this minute D_{lt} was real or came from analysis uncertainties due to very small signals

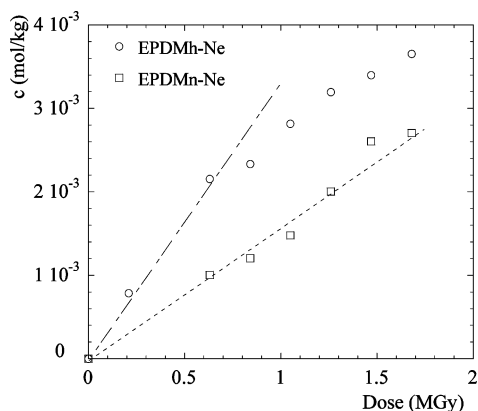


Figure 6. Influence of the nature of the unsaturated side group in terminal alkyne creation: EPDM_h and EPDM_n under Ne ion irradiation. Concentrations, C , are in moles of alkyne per kg of polymer. Dotted lines are guides for the eye.

of alkyne groups. We consequently believe that $(dE/dx)_e$ of C and Ne ion beams, in EPDM_h, were above the threshold value.

2. Terminal Alkyne Creation Yields. Data on the role of $(dE/dx)_e$ on the terminal alkyne creation radiation chemical yield (Figure 5) are only available for EPDM_h. Table 2 reports the G_0 values (measured in the 0.1–0.5 MGy range for C ion irradiations). The G_0 increase was significant when going from C to Ne (a factor of 3), but this increase was relatively small when going from Ne to S irradiation (24%), probably indicating a tendency toward saturation. Data required to compare, at the same $(dE/dx)_e$, G_0 in EPDM_h and polyolefins are available for the S ion irradiations. The effect of pre-existing double bonds was very significant: the yield in EPDM_h was 4 times higher than the one in polyolefins (Table 2).

The comparison of the terminal alkyne creation yield between both EPDMs was carried out for Ne ion irradiations (Figure 6). The radiation chemical creation yield at initial dose in EPDM_h was higher than the one in EPDM_n.

C. Alkene Creation and Destruction. Because we are trying to assess the influence of double bonds (either pre-existing or radiation-induced) on terminal alkyne creation, it appears useful, for clarity, to present here data on the SHI-induced alkene creation in the polymers studied here.

In polyolefins submitted to irradiations, IR spectroscopy helped to identify three unsaturated groups: trans-vinylene ($-R-CH=CH-R'-$), vinylidene ($-R-C(=CH_2)-R'-$), and vinyl ($-R-CH=CH_2$) groups. Other species such as *cis*-vinylene or trisubstituted alkenes (usually found near 690 and 820 cm^{-1} , respectively) could *a priori* be induced but were not visible in the FTIR spectra. The radiation chemical yields for the different alkenes groups obtained in polyolefins at different $(dE/dx)_e$ are presented in Table 3. As shown in Table 3, the corresponding creation yields of these three chemical groups depend on the polymer and on the $(dE/dx)_e$. At low $(dE/dx)_e$, the predominant form of C=C bonds was transvinylene in PE, vinylidene in PP, and vinyl in PB. The simplest interpretation of this result is to consider that the favored modifications are always those formed without inducing a main-chain C–C bond scission. Thus, this implies that in PB and PP vinyl and vinylidene groups, respectively, are mainly located in the side chain: ($-R-CH(-CH=CH_2)-R'-$) in PB and ($-R-C(=CH_2)-R'-$) in PP. However, we have to mention that in PP a competing process for the creation of vinyl groups might be a β -scission of the ($-R-C^\bullet(CH_3)-R'-$) radical giving the vinylidene ($-R-C(=CH_2)-CH_3$). For the three polymers, increasing $(dE/dx)_e$ diminished the difference between the yields

TABLE 3: Radiation Chemical Yields at Initial Dose, G_0 , for Several Alkenes in PE, PP, and PB Submitted to Different Ion Beams^a

C=C groups	ion beam	G_0 (10^{-7} mol/J)		
		PE	PP	PB
transvinylene	C	8.6×10^{-1}	1.6×10^{-1}	1.3×10^{-1}
967 cm^{-1}	S	1.07	1.6×10^{-1}	2.6×10^{-1}
ϵ ($1 \text{ mol}^{-1}cm^{-1}$): 169	Kr	1.22	1.9×10^{-1}	2.7×10^{-1}
vinylidene	C	3×10^{-3}	3.3×10^{-1}	1.4×10^{-2}
889 cm^{-1}	S	6×10^{-3}	3.1×10^{-1}	4×10^{-2}
ϵ ($1 \text{ mol}^{-1}cm^{-1}$): 160	Kr	3.5×10^{-2}	1.8×10^{-1}	1.6×10^{-2}
vinyl	C	5.4×10^{-2}	4×10^{-2}	2.6×10^{-1}
909 cm^{-1}	S	2×10^{-1}	1.2×10^{-1}	3.4×10^{-1}
ϵ ($1 \text{ mol}^{-1}cm^{-1}$): 153	Kr	3.3×10^{-1}	2.3×10^{-1}	2.4×10^{-1}
C=C	C	8.5×10^{-2}	1.23	3.1×10^{-1}
1640 cm^{-1}	S	2.9×10^{-1}	1.21	4.6×10^{-1}
ϵ ($1 \text{ mol}^{-1}cm^{-1}$): 28	Kr	5.5×10^{-1}	1.51	4.2×10^{-1}
total alkene	C	9.5×10^{-1}	1.39	4.4×10^{-1}
$G(1640 \text{ cm}^{-1} + 967 \text{ cm}^{-1})$	S	1.36	1.37	6.9×10^{-1}
	Kr	1.77	1.7	7.2×10^{-1}

^a The wave number of the selected IR vibration band and their corresponding molar extinction coefficient considered for quantification are quoted in the table. For estimating the total alkene yield, because transvinylene groups (967 cm^{-1}), due to their symmetry, do not contribute to the stretching mode of C=C bonds, we added the yields obtained using the bands at 967 cm^{-1} and 1640 cm^{-1} .

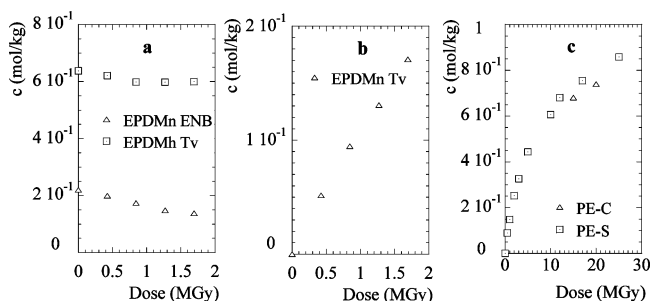


Figure 7. Evolution of the alkene concentrations with dose in different polymers. The alkenes measured are (i) transvinylene groups (Tv) in PE, EPDM_n, and EPDM_h and (ii) the trisubstituted alkene of the ethylidene norbornene (ENB) side group in EPDM_n. (a) EPDM_n and EPDM_h under Ne ion irradiations. (b) EPDM_n under Ne ion irradiations. (c) Transvinylene groups created in PE under C and S irradiations. Concentrations, c , are in moles of alkenes per kg of polymer.

of those different alkenes groups. This is consistent with the expected increase of chain scissions with increased $(dE/dx)_e$.

As an example, Figure 7c shows the evolution with dose of the stretching band at 967 cm^{-1} of C=C groups of the transvinylene type in PE. A wide range of dose is plotted. This band monitors the concentration of transvinylene and shows a clear tendency toward saturation, at very high doses. In EPDM_h, the transvinylene band at 966 cm^{-1} decreased under irradiation, indicating that $c_0 > c_\infty$ (Figure 7a). Transvinylene groups are globally destroyed in EPDM_h. One can easily imagine that the transvinylene initially present in the polymer side chain is consumed and partially replaced by other types of transvinylene groups, certainly located in the polymer backbone. In EPDM_h, vinylidene and vinyl are also created (not shown here). In EPDM_n, the ethylidene norbornene C=C bonds were consumed (Figure 7a), indicating again that $c_0 > c_\infty$. Moreover, transvinylene (Figure 7b), vinyl, and vinylidene groups (not shown here) were created, likely in the polymer backbone. As shown in Figure 7a, in EPDM_n ethylidene groups were more consumed (35% of the initial content), whereas in EPDM_h transvinylene concentration was only reduced by 10%. As shown in Section III, evolution with dose depends on both the ratio between

creation and destruction and on the initial content of unsaturated groups. In EPDMn, the destruction of the side-group unsaturations had to compete with the creation of trisubstituted alkenes in the main chain. The creation of trisubstituted alkenes in the main chain seems difficult in the PE segments but possible in the PP ones. The strong decrease of the trisubstituted alkenes band of the ethylidene norbornene moiety indicates that the ratio between destruction and creation is higher for this chemical group than for the hexadiene group. However, the dose range we have explored (up to 1.5 MGy) is too small to make definitive conclusions, and moreover, the simple model of a zero-order creation and first-order destruction surely suffers some limitation because a chemical group in a side chain or in the main chain may have different IR characteristics. The detailed study of the dose evolution of the unsaturated bonds in EPDM is beyond the scope of this work. We show this evolution here only to make understandable the influence of pre-existing double bonds on the terminal alkyne creation.

Finally, irradiations at low-temperature bring interesting results on EPDMh. The double bond concentration decreases with dose only at RT;²³ at 8 K an increase is observed. This indicates that at RT radicals and/or excitations are efficiently trapped on the hexadiene moiety inducing the alkene content decrease.

V. Discussion

Polyolefins and EPDM did not only differ by the presence of native unsaturated groups. Polyolefins were semicrystalline, and the EPDMs were almost amorphous. This could introduce a bias: for instance, ascribing the role of double bonds to crystallinity or *vice versa*. However, as alkynes are created near or into the track core, that is known to be amorphous,²⁹ crystallinity is considered ineffective on terminal alkyne creation yields in the polymers studied. Thus, crystallinity effect should not be discussed here.

For clarity purposes, and as the differences in the behavior of the two EPDM are irrelevant for the data understanding, we chose to focus on EPDMh results.

Alkyne creation is only triggered when unusual density of excited-ionized species is reached. Consequently, atypical formation mechanisms, necessarily involving multi-radicals (neutral or eventually charged) processes, must take place. However, considering the classical features of low ionizing radiation chemistry could tentatively help for analyzing the influence of side groups. Classically, the sensitivity of an organic material under ionizing radiation is determined either by the presence of weak bonds or by the occurrence of energy transfers. Both effects are considered. Our results showed very different behaviors between polyolefins and EPDM. We will first focus on polyolefins and hence on the influence of the polymer chemical structure, including the existence of a side chain on the polymer backbone and this side-chain length. Second, we will analyze the influence of double bonds, initially present in the polymer or created under irradiation.

A. The Role of the Chemical Structure in Polyolefins. The most striking result on polyolefins is the poor sensitivity of the terminal alkyne formation process on the polymer chemical structure. The presence of the weak points that are tertiary carbons in the polymer backbone might support higher terminal alkyne yields in PP and PB with respect to PE, but that is not what we observed. Starting from alkyl chains, terminal alkyne formation requires heavy dehydrogenation. In polyolefins without side groups or when this side group is made of less than two carbon atoms, dehydrogenation should simultaneously

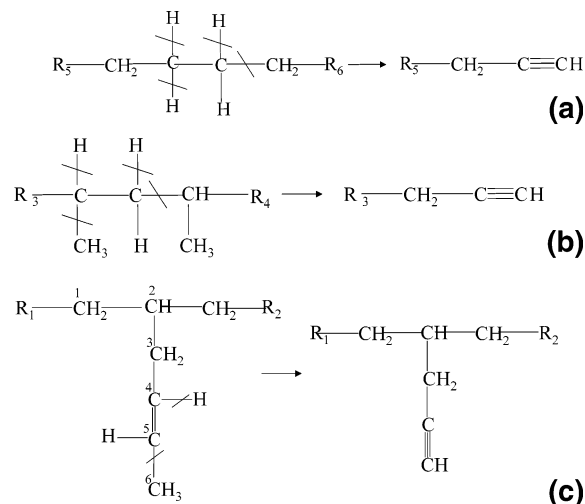


Figure 8. Oversimplified reaction schemes leading to terminal alkyne formation starting from PE (Figure 8a), PP (Figure 8b), and EPDMh (Figure 8c) under swift heavy ion irradiations.

occur with a backbone C—C bond scission (Figure 8a, b). Considering classical radiation chemistry, C—H bond scission has a higher yield than backbone C—C bond scission. Nevertheless, this backbone C—C bond scission could be favored by specific features such as tertiary carbons known to be weak points for main-chain scission under ionizing radiations. The weakness of bonds involving tertiary carbons is related to a higher stability of tertiary C centered radicals with the occurrence of β -scission. Tertiary carbons did not favor terminal alkyne creation in polymers containing side chains (PP and PB). Consequently, we showed that, under the energy deposition conditions leading to the formation of alkynes, the classical radiation chemistry mechanisms were overwhelmed by multi-radical processes.

Alternatively, terminal alkynes can be created on PB side chains only by dehydrogenation. *A priori*, this process favors terminal alkyne creation in PB. Yet experiments showed the opposite (Table 2): creation yields were slightly lower in PB compared with PE and PP. This result can be accounted for by results on gas emission achieved on the same polymers under similar irradiation conditions to I.^{6,21} In PB, high $(dE/dx)_e$ irradiations induced the side-group departure, thereby giving unsaturated two carbon molecules, mainly composed of acetylene, which diffuses out of the film. Thus, because this side group is labile, terminal alkynes remaining in the PB film do not come exclusively from side groups; they are also found in the polymer backbone and require a backbone C—C bond scission.

B. Influence of Double Bonds. 1. EPDM: Influence of Pre-existing Double Bonds. Under S ion irradiation, the terminal alkyne creation radiation chemical yield value in EPDMh is 4 times the one obtained in PE. This enhancement of radiation chemical yield in EPDMh is explained by the presence of native double bonds in EPDMh. The contribution of these C=C bonds can be considered in two ways. The first way is by considering the polymer chemical structure. The second way is by considering energy and species transfers.

Considering the polymer chemical structure, oversimplified ideas for alkyne creation (need of dehydrogenation and eventually of a C—C bond breaking), and assuming that alkynes are located in the 1–4 hexadiene moiety, the situation in EPDMh should be the following: (a) less dehydrogenation is needed because we are starting with a double bond (Figure 8c), and (b) one C—C bond scission is required if alkynes are located in

the C₄ position (Figure 8c), inducing the formation of a mobile methyl radical. The scission of the bond between C₅ and C₆ is easier than the scission of a backbone C–C bond. Both facts push toward having $G(\text{EPDMh}) > G(\text{PE})$.

What is surprising is that a small number of double bonds induced such a high increase in terminal alkyne radiation chemical yield. To analyze this effect, we designed a simple two-phase model with the EPDM main chain having the PE yield and the side-group moiety having a higher one. In EPDMh, because $G_{\text{EPDMh}}/G_{\text{PE}} \approx 4$, one deduces that 75% of alkynes must be created in the close vicinity of side-group double bonds. The effective terminal alkyne yield connected to the creation near the side group, G_{hexa} , is given by the relation $G_{\text{hexa}} = (G_{\text{EPDM}} - G_{\text{PE}})f_{\text{hexa}}^{-1} - G_{\text{PE}}$ where f_{hexa} is the hexadiene mass fraction ($f_{\text{hexa}} = 0.056$ in EPDMh). In fact, we showed that the concentration of native bonds decreased during irradiation (Figure 7). We have neglected this f_{hexa} decrease because it only slightly changed G_{hexa} . Thus, in EPDMh submitted to S ion irradiations, $G_{\text{hexa}} = 6.1 \times 10^{-8}$ mol/J. This value is as high as the yields of the most easily formed defects in polyolefins (Table 3). Consequently, G_{hexa} appears excessive for a modification as complex as alkyne creation. The ratio $G_{\text{hexa}}/G_{\text{PE}}$ is 48.8 and appears to be too high to be entirely explained by primary radiation effects (ionization–excitation). Actually, the first ionization energies of alkene molecules are only 20% lower than those of the corresponding alkane molecules. Probabilities to induce primary ionizations–excitations in the main chain or in the side group are thus similar.

The high G_{hexa} values can only be understood if excitations or radicals, created in EPDMh ethylene and propylene moieties, are efficiently transferred to the hexadiene moiety improving terminal alkyne formation. Even if the hexadiene moiety content represents only a few percent of the polymer, the distance of the energy transfer is still small. The distance between two C=C double bonds, $d_{\text{h-h}}$, is given by $d_{\text{h-h}} = (N_A f_{\text{hexa}} \rho / M_{\text{hexa}})^{-1/3}$, where N_A is the Avogadro number, ρ is the volumic mass of the polymer, and M_{hexa} is the molar mass of the hexadiene moiety. In the EPDMh used, we found a $d_{\text{h-h}}$ of 1.4 nm. This value considers inter- and intrachain distances. If the energy transfers occur intrachain, the mean distance between two C=C groups on the hexadiene moiety is 9.3 nm.

The roles of the migration of reactive species and of energy transfers were tentatively discriminated by considering irradiations at 8 K. At such a low temperature, long-range radical transfers are almost nonexistent. Only very short-range species transfer and energy transfer likely exist. For S irradiations,²⁴ G_{hexa} and $G_{\text{hexa}}/G_{\text{PE}}$ are, respectively, 1.0×10^{-7} mol/J and 30. These values are still exceptionally high and point out that the main mechanism is an energy transfer ending in the C=C environment and not a long-range migration of reactive species.

To explain these efficient energy transfers, one could invoke the role of double bonds on radical stabilization, which is due to the higher electronic density of C=C double bonds compared to single bonds. At 8 K, in polymers containing exclusively C–C single bonds, radicals formed are alkyl radicals that recombine readily. In polymers containing C=C double bonds, due to their great stability, radicals that are more likely formed are allyl radicals. Because of their great stability, due to the nonlocalization of electrons on a given carbon atom, allyl radicals are less involved in cross- or self-recombination than alkyl radicals are. This results in the increase of radical density necessary for alkynes to be formed.

The EPDMn samples were only submitted to Ne ions. Under these conditions, the effective radiation chemical yields con-

nected to the side group are very similar in EPDMh and EPDMn: $G_{\text{hexa}} = 6.6 \times 10^{-8}$ mol/J and $G_{\text{norb}} = 6.7 \times 10^{-8}$ mol/J ($f_{\text{norb}} = 0.024$). Consequently, the linear or cyclic nature of the side group and the nature of the double bond (di- or trisubstituted) has no perceptible influence on terminal alkyne creation. The chemical structure has little influence, and the alkyne radiation chemical yield is governed by energy transfer to the ethylidene norbornene moiety.

2. Comparison between Native and Irradiation-Induced Double Bonds. The presence of pre-existing double bonds decreased the $(dE/dx)_e$ threshold value for alkyne creation. Proof of this is given when considering initial yield in the low $(dE/dx)_e$ regime. In this regime, terminal alkynes were not created in polyolefins (C ion irradiation) but were observed in EPDMh (C and Ne ion irradiations). Naturally, irradiations with ions lighter than C are required to determine the $(dE/dx)_e$ threshold for EPDMh. However, irradiations performed with 1 MeV electrons (not shown here) up to 10 MGy did not reveal any alkyne formation in EPDMh. This leads to the conclusion that, in polymers with pre-existing double bonds, the terminal alkyne formation process involves both the energy and radical trapping on C=C double bonds and the huge ionization–excitation density characteristic of high $(dE/dx)_e$ irradiations.

In polyolefins, the role of irradiation-induced double bonds on terminal alkyne creation is better viewed when considering irradiation under C ions. A latent dose, D_{lt} , existed in the creation of terminal alkyne in polyolefins. In this section, unlike the previous sections, the comparisons are based on D_{lt} values and on the radiation chemical yield G calculated above D_{lt} but not based on G_0 , the radiation chemical yield at initial dose.

Qualitatively, the existence of the latent dose observed in polyolefins under C ion irradiations is understood. Alkenes are created under irradiation in polyolefins, and irradiation of EPDMh has demonstrated that double bonds decreased the $(dE/dx)_e$ threshold for alkynes formation, making it smaller than the $(dE/dx)_e$ induced by carbon ions in PE or PP. Therefore, the creation of double bonds in concentrations as high as the concentration of pre-existent alkenes in EPDMh led to the decrease of the threshold value and enabled terminal alkyne formation in polyolefins.

Quantitative analysis of the effect of the radiation-induced alkenes on D_{lt} in polyolefins is more difficult. Terminal alkyne yields in polyolefins (measured above D_{lt}) were typically 1 order of magnitude smaller than the yield in EPDMh. This occurred even though the concentration of radiation-induced alkenes in polyolefins and the concentration of pre-existing alkenes in EPDMh (0.68 mol/kg) were of the same order of magnitude. At around 10 MGy, which was the typical latent dose, radiation-induced alkene concentrations were 0.7 mol/kg in PE, 0.6 mol/kg in PP, and 0.4 mol/kg in PB. In polyolefins, it seems like if there were a competition between, on one side, energy transfers to radiation-induced unsaturated bonds enhancing terminal alkyne formation and, on the other side, energy trapping on radiation-induced modifications such as chain ends and crosslinks, that did not help the alkyne formation. Doses around 10 MGy surely highly modify polyolefins. The scission or crosslinking yields in polymers under ion irradiations are not accurately known. Nevertheless, for a rough estimation, one can use chain scission $G(\text{S})$ or crosslinking $G(\text{X})$ yields under electron or γ irradiations. In PB,³⁰ $G(\text{S}) = 3.2 \times 10^{-7}$ mol/J and $G(\text{X}) = 1.0 \times 10^{-7}$ mol/J, whereas in PE^{31,32} $G(\text{X}) = 1.7 \times 10^{-7}$ mol/J and $G(\text{S}) = 0.3 \times 10^{-7}$ mol/J. Taking for the amount of modified polymer (ΔC) the crude relation $\Delta C = GD$, it appears that, at 10 MGy, ΔC is as high as a few mol/kg. Consequently, at D_{lt} ,

polyolefins were deeply changed, and this can be enough for weakening energy transfers to radiation-induced unsaturated bonds.

VI. Conclusion

The study of homo- and copolymers with saturated or unsaturated side groups allowed a better understanding of terminal alkyne creation under SHI irradiations.

The terminal alkyne creation radiation chemical yield was poorly sensitive to the presence of short-length side groups (methyl or ethyl). The presence of tertiary carbons, known in classical radiation chemistry to favor chain scission, did not enhance formation of terminal alkynes remaining in the polymer, in PP and PB.

The presence of pre-existent C=C double bonds in both EPDMh and EPDMn had a major influence on terminal alkyne creation in these polymers. The $(dE/dx)_e$ threshold value for alkyne creation was decreased without being annihilated. Moreover, terminal alkyne creation yields were significantly enhanced. These two effects cannot be understood without considering an important energy transfer from the main chain to unsaturated C=C bonds located in the side chain. The higher stability of allyl radicals also certainly played an important role. The effect of radiation-induced alkenes in the polyolefins, on terminal alkyne creation, was less pronounced. However, a clear reduction of the $(dE/dx)_e$ threshold value was observed for C ion irradiations, at high doses.

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