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Linear Energy Transfer Effects in the Radiolysis of Polymers. 1. Main-Chain Degradation of Poly(methyl methacrylate)

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ABSTRACT: Thin foils of poly(methyl methacrylate) about 84 μm (10 mg/cm^2) thick, in most cases stacks of 10–15 foils, were irradiated with 45-MeV $^{4}_{2}He^{2+}$, 240-MeV $^{20}_{10}Ne^{7+}$, and 90-MeV $^{16}_{8}O^{4+}$ particles in vacuo at room temperature. Molecular weight distributions were measured with the aid of gel permeation chromatography. It was found that the radiation chemical yield of main-chain scission, $G(S)$, depends on the linear energy transfer (stopping power) dE/dx (given in brackets) as follows: $G(S) = 0.3 \pm 0.1$ [57.7 eV/Å ($^{16}_{8}O^{4+}$) and 47.6 eV/Å ($^{20}_{10}Ne^{7+}$)], $G(S) = 0.8 \pm 0.1$ [1.99 eV/Å ($^{4}_{2}He^{2+}$)], and $G(S) = 1.5 \pm 0.2$ [0.02 eV/Å (^{60}Co γ-rays)]. $G(S)$ was independent of the particle path x over the investigated range of x, corresponding to an energy loss of up to about 80% of the initial energy. The homogeneous irradiations of poly(methyl methacrylate) carried out in this work caused (apparently) random main-chain scission.

Introduction

This paper is the first in a series of publications devoted to the effects of linear energy transfer (LET) on the radiolysis of solid polymers. This subject has been occasionally studied during recent decades[1] and there is an urgent need for exact quantitative data, which will allow the interpretation of the effects observed so far. It is known, for instance, that the 100-eV yield for main-chain scission, $G(S)$, in poly(methyl methacrylate) (PMMA) decreases with increasing LET. Zverev et al.[2] reported $G(S) = 0.03$ for irradiation of PMMA with 28-MeV α-particles (LET: ca. 3 eV/Å) and $G(S) = 0.46$ for irradiation with ^{60}Co γ-rays (LET: 0.02 eV/Å). In more recent studies by Egusa et al.[3] PMMA was subjected to the mixed radiation of fast neutrons and γ-rays produced in a nuclear reactor. The following scission yields were reported: $G(S) = 1.0$ for fast neutrons (LET: ca. 3.7 eV/Å) and $G(S) = 1.54$ for ^{60}Co γ-rays. In that paper[3] it was pointed out that if the polymer was subjected to high LET radiation, the inhomogeneous energy deposition caused nonrandom main-chain degradation. This was inferred from the dependence of the ratio $\bar{M}_w/\bar{M}_n$ on the absorbed dose. $\bar{M}_w/\bar{M}_n$ increased, and after passing through a maximum, decreased with increasing absorbed dose in the case of neutron irradiation. γ-Irradiation, on the other hand, induced random degradation with $\bar{M}_w/\bar{M}_n$ decreasing steadily and approaching the expected value of 2.

The present paper also concerns the influence of inhomogeneous energy distribution on main-chain rupture. In order to inspect quantitatively the radiation damage caused by α-particles along their tracks in the polymer, a package of thin polymer foils was irradiated with 45-MeV α-particles, the beam being vertically incident on the foils. The thickness of the foils was chosen so that the total range of the particles was subdivided into 10–14 sections. Molecular weight determinations via GPC of the single polymer foils subsequent to irradiation provided the desired information concerning the function $G(S) = f(x)$, where x denotes the path length of the α-particles.

It should be pointed out that the LET, also called stopping power, expressed by dE/dx, depends on the kinetic energy of the particles traversing the polymer. As is shown for PMMA in Figure 1, dE/dx increases with increasing energy E and passes through a maximum at a relatively low value of E. In the case of 45-MeV α-particles traversing PMMA, this maximum is at $E = 1$ MeV. Because the particles are steadily losing energy on their way, the LET is not constant but varies as indicated by the curve in Figure 1. In other words, if a stack of thin polymer sheets of equal thickness were placed in the beam of heavy particles, the energy deposited per sheet would differ. If the foils were thin enough, $G(S) = f(dE/dx)$ could be evaluated in addition to $G(S) = f(x)$.

As will be reported below in detail, $G(S)$ was found to be independent of x in the case of irradiation of PMMA with 45-MeV α-particles as far as energy losses of up to about 80% are concerned. Due to the fact that the foil thickness could not be reduced arbitrarily, radiation effects generated at the end of the tracks could not be elucidated. It could be clearly shown, on the other hand, that $G(S)$ depended significantly on dE/dx and that main-chain scission occurred apparently at random if the polymer foils were irradiated homogeneously.

Experimental Section

(a) Preparation of Polymer Foils. The poly(methyl methacrylate) (PMMA) was a commercial product (Esschem). It was subjected to a rough fractionation from a 1% solution in acetone with methanol ($\bar{M}_w = 1.27 \times 10^6$, $\bar{M}_n = 0.51 \times 10^6$). The polymer foils were prepared by casting chlorobenzene solutions (10 wt %) on glass plates which were floating on mercury in order to guarantee a constant thickness. After evaporation of the solvent the plates were dipped into water, where the foils separated. Finally, the foils were heated for 30 min at 150 °C. Platelets of 0.6-cm diameter were made with a punching machine.

(b) Determination of the Molecular Weight Distribution. Molecular weight distributions (MWD) were determined by gel permeation chromatography with an apparatus from Waters with a set of five μ-Styragel columns (10^3-, 10^4-, 10^4-, 10^5-, and 10^6-Å porosities) and tetrahydrofuran as solvent. Calibration was performed with a series of PMMA fractions of narrow MWD provided by Röhm GmbH. The calibration curve is shown in Figure 2. For the evaluation of MWDs a Gaussian quadrature approximation method, using linear programing, as proposed by Tung,[4] was applied.

(c) Irradiation of Polymer Foils. A sample holder containing 12 bars in a circular arrangement was used. Each bar contained six tubular openings (diameter 0.6 cm), into which stacks of polymer platelets (ca. 3 mg each) were inserted. The sample holder

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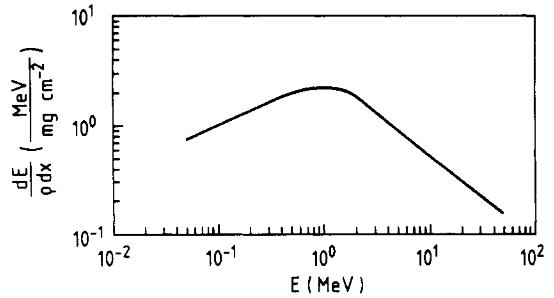

Figure 1. Stopping power of poly(methyl methacrylate) vs. the kinetic energy of α-particles. dE/dx was calculated according to Bragg's rule on the basis of tabulated literature data.[6,7]

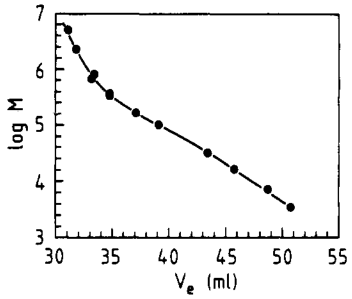

Figure 2. GPC calibration curve for PMMA in tetrahydrofuran. Molecular weight as a function of the elution volume.

could be rotated and lifted inside a vacuum chamber, into which the heavy-particle beam generated by the accelerator VICKSI (Van de Graaff Isochron Cyclotron Kombination für Schwere Ionen) was directed. Details about VICKSI were described earlier.[5] Prior to irradiation the pressure in the vacuum chamber was lowered to about 2 × 10^{-6} mbar. Irradiations were carried out with the following particles: 45-MeV $^4_2He^{2+}$, 240-MeV $^{20}_{10}Ne^{7+}$, and 90-MeV $^{16}_8O^{4+}$.

In order to avoid the polymer foils being significantly heated during irradiation, all experiments had to be carried out at beam currents $i \le 1$ nA. Actually, the estimated temperature increase was less than 20 °C.

(d) Determination of the Exposure Dose. In order to guarantee homogeneous irradiation of the polymer foils, the particle beam was scanned over the circular openings in the sample holder containing the polymer platelets (0.28 cm^2) with the aid of a wobble magnet (horizontal frequency 500 Hz, vertical frequency 23 Hz). The scanned area was about 1.2 × 1.2 cm. Prior to hitting the target the beam had to pass a rectangular collimator having an aperture of 0.8 × 0.8 cm. Thus a certain fraction of the beam was stopped by the collimator, a fact used to continuously control the beam current during irradiation by measuring i_{coll}. In order to measure the exposure dose D_{exp} (particles/cm^2), Faraday cup was placed occasionally in front of the polymer target (for calibration). Upon reading both currents, i_{cup} and i_{coll}, D_{exp} was readily obtained according to

$$D_{exp} = 6.25 \times 10^{18}\left(\frac{i_{cup}}{i_{coll}}\right)\frac{i_{coll}t}{zF} \quad \text{(particles/cm}^2\text{)} \tag{1}$$

where i_{coll} is the current measured at the collimator (A), i_{cup} is the current measured at the cup (A), z is the charge state of the beam particles, i.e., the number of elementary charges per particle, F is the area of the aperture of the collimator (cm^2), and t is the time of irradiation (s). The factor 6.25 × 10^{18} designates the number of elementary charges corresponding to 1 A s. Whereas the ratio i_{cup}/i_{coll} was independently determined before and after irradiation, the total charge $i_{coll}t$ was measured with the aid of a frequency counter (Berthold) in conjunction with a current/frequency converter.

(e) Determination of the Stopping Power of PMMA. The stopping power of PMMA for heavy particles was calculated with the aid of tabulated values of dE/dx = $f(E)$ for the elements C, H, and O[6,7] according to Bragg's additivity rule:

$$\frac{dE}{dx} = \frac{1}{m}\sum_i N_iA_i(dE/dx)_i \tag{2}$$

where $m = \sum_i N_iA_i$ is the molecular weight of the irradiated compound consisting of N_i atoms per molecule of atomic weight A_i. In the case of PMMA, m = 100 corresponds to the molecular weight of the repeating unit ($C_5H_8O_2$). From eq 2 one obtains

$$\frac{dE}{dx} = 10^{-2}\left[60\left(\frac{dE}{dx}\right)_C + 8\left(\frac{dE}{dx}\right)_H + 32\left(\frac{dE}{dx}\right)_O\right] \tag{3}$$

Figure 1 shows a plot of dE/dx divided by ρ, the density of PMMA (1.19 g/cm^3), as a function of the particle energy. Our calculations took into account "electronic" stopping processes only. In the range of particle energies referred to in Figure 1, the portion of the total energy loss corresponding to nuclear collisions is rather small ($\le$1%).[8] It is, therefore, considered to be negligible in this work.

(f) Determination of the Absorbed Dose. The absorbed dose D_{abs} was calculated for each platelet separately. This was done by assuming an average value of the stopping power, with the aid of Figure 1, corresponding to the energy the particles possessed at the moment of entering the surface of the respective foil. The absorbed dose was then calculated according to

$$D_{abs} = \frac{D_{exp}\Delta EF}{w_{foil}} \quad \text{(eV/g)} \tag{4}$$

where D_{exp} is the exposure dose (particles/cm^2), ΔE is the energy lost by one particle upon traversing the foil (eV/particle), F is the area of foil, and w_{foil} is the weight of foil (g).

(g) Determination of the Scission Yield. The number of main-chain scissions per gram of polymer is $N_A(\bar{M}_{n,D}^{-1} - \bar{M}_{n,0}^{-1})$. Therefore, the number of main-chain scissions per 100 eV of absorbed energy, $G(S)$, is given by

$$G(S) = (\bar{M}_{n,D}^{-1} - \bar{M}_{n,0}^{-1})\frac{10^2N_A}{D_{abs}} \tag{5}$$

where N_A is Avogadro's number and $\bar{M}_{n,0}$ and $\bar{M}_{n,D}$ are the number-average molecular weights of the polymer before and after irradiation. $\bar{M}_n$ was calculated from the molecular weight distribution curves obtained by GPC measurements (vide ante). It should be pointed out that eq 5 is independent of the initial molecular weight distribution of the polymer.[9]

Results and Discussion

(a) LET Dependence of $G(S)$. Single PMMA platelets were irradiated with 45-MeV $^4_2He^{2+}$, 240-MeV $^{20}_{10}Ne^{7+}$, and 90-MeV $^{16}_8O^{4+}$ ions. Upon traversing one foil the particles lost between 5 and 10% of their energy. As the absorbed dose was increased, the number-average molecular weight decreased as expected on the basis of eq 5. It turned out that $G(S)$ = 0.8 ± 0.1 at dE/dx $\approx$ 2 eV/Å (45-MeV $^4_2He^{2+}$) and $G(S)$ = 0.3 ± 0.1 at dE/dx = 47.6 eV/Å (240-MeV $^{20}_{10}Ne^{7+}$) and 57.7 eV/Å (90-MeV $^{16}_8O^{4+}$). For irradiations of PMMA with ^{60}Co γ-rays (dE/dx = 0.02 eV/Å), $G(S)$ = 1.5 ± 0.2 was found in earlier studies.[3,10,11]

From these data it is concluded that $G(S)$ depends only relatively weakly on dE/dx. Actually, $G(S)$ decreased by a factor of 5 when dE/dx was increased by a factor of about 3000. The dependence of $G(S)$ on dE/dx is shown in Figure 3.

(b) Dependence of $G(S)$ on the Path Length of the Particles. These studies were carried out exclusively with $^4_2He^{2+}$ particles. Stacks of 12–14 foils were irradiated. Typical data obtained with a stack irradiated at an exposure dose of 2.6 × 10^{12} particles/cm^2 is presented in Table I.

If stacks of total thickness less than the range of the α-particles were irradiated, the change of both the number- and the weight-average molecular weight seemed to be the more pronounced the larger the number of the foil. (The beam entered the stack at foil one.) Typical results are

Table I
Irradiation of PMMA ($\bar{M}_{w,0} = 1.27 \times 10^6$, $\bar{M}_{n,0} = 5.08 \times 10^5$) with 45-MeV α-Particles in Vacuo at Room Temperature[a]

foil								
no.	wt, mg	thickness, mg/cm^2	dE/(ρ dx), (MeV cm^2)/mg	dE/dx, eV/Å	ΔE,[b] MeV	$\bar{M}_w$/$\bar{M}_n$	$10^6/\bar{M}_n$[c]	$G(S)$[d]
1	3.5	12.5	0.167	1.99	2.08	1.95	8.1	0.87
2	3.4	12.1	0.174	2.07	2.11	1.82	7.4	0.70
3	3.4	12.1	0.180	2.14	2.18	1.97	8.8	0.90
4	3.4	12.1	0.189	2.25	2.29	1.83	9.3	0.92
6	3.0	10.7	0.206	2.45	2.20	1.87	9.8	0.90
7	2.8	10.0	0.218	2.59	2.18	1.86	8.2	0.68
9	3.1	11.1	0.246	2.93	2.73	1.90	11.5	0.91
11	3.1	11.1	0.307	3.65	3.40	1.94	10.3	0.64
13	2.9	10.4	0.403	4.80	3.54	2.04	15.3	0.77
14	2.7	9.6	0.515	6.13	4.94	2.07	15.6	0.63

[a] $D_{exp} = 2.57 \times 10^{12}$ particles/cm^2. (The beam entered the stack at foil no. 1.) [b] Energy loss per particle upon passage through the foil. [c] Reciprocal number-average molecular weight. [d] Number of main-chain scissions per 100 eV absorbed by the polymer.

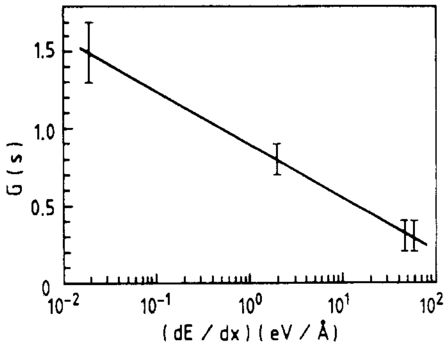

Figure 3. 100-eV yield for main-chain scission in PMMA as a function of the linear energy transfer.

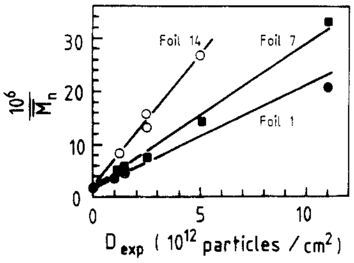

Figure 4. Dependence of the reciprocal number-average molecular weight on the exposure dose. Irradiation of PMMA with 45-MeV α-particles.

presented in Figure 4, where the reciprocal number-average molecular weight is plotted vs. the exposure dose. It turned out, however, that this finding reflects the fact that the energy absorbed per foil increased with increasing distance of the foil under consideration from the first foil. This can be seen from the last column in Table I. Actually, the same value of $G(S)$ was calculated (within the error limit) for all foils in one stack. This result shows that the radiation chemical yield is not measurably dependent on the path length x, in accordance with the rather weak dependence of $G(S)$ on dE/dx. Thus, the variation of $G(S)$ expected upon increasing x on the basis of the variation of $G(S)$ with dE/dx would be detectable only if $G(S)$ values were measured much more accurately than in the present work. If stacks of total thickness exceeding that of the range of 45-MeV α-particles in PMMA (ca. 180 mg/cm^2 corresponding to 1.5×10^3 μm) were irradiated, the last foils of the stack were not affected.

(c) Randomness of Main-Chain Scission. The results indicate that heavy-particle irradiation at moderate LET values induces apparently random main-chain scission in PMMA. The molecular weight distribution of the polymer samples used for the present work had an initial broadness corresponding to $(\bar{M}_{w,0}/\bar{M}_{n,0}) = 2.50$. Upon irradiation, the distribution became narrower with increasing absorbed dose: $\bar{M}_w/\bar{M}_n$ decreased and approached the value 2, in accordance with the theory of random main-chain scission. This finding does not exclude, however, that multiple electronic excitations and ionizations in neighboring repeating units induced main-chain scissions. However, these processes would not be detectable by GPC measurements, because this method cannot discriminate between main-chain ruptures induced by cleavage of several chemical bonds located close together in the chain and those induced by cleavage of a single bond only.

Conclusions

Irradiations of poly(methyl methacrylate) with heavy ions in vacuo at room temperature resulted in main-chain scission. The radiation chemical yield $G(S)$ decreased with increasing linear energy transfer (stopping power), dE/dx. The decrease was significant but not very pronounced, since upon increasing dE/dx by a factor of about 3000, $G(S)$ decreased only by a factor of 5. In accordance with this relatively weak LET effect on $G(S)$ is the finding that $G(S)$ was independent of the path length x. This behavior was found for irradiations with 45-MeV α-particles up to values of x corresponding to an energy loss of about 80% of the initial energy. The yield of main-chain scissions generated at the very ends of the tracks of the α-particles could not be determined.

Heavy-particle-induced main-chain degradation occurs apparently at random, provided the polymer sample is irradiated homogeneously, as in the present case where thin polymer foils were irradiated and the heavy particles lost only a small fraction of their kinetic energy during passage through the foil. Changes of molecular weight distributions indicating "nonrandom" main-chain degradation are expected when polymer samples would be inhomogeneously irradiated. In the present studies, this was avoided.

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Registry No. PMMA (homopolymer), 9011-14-7.

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Entrapment of Functionalized Ethylene Oligomers in Polyethylene

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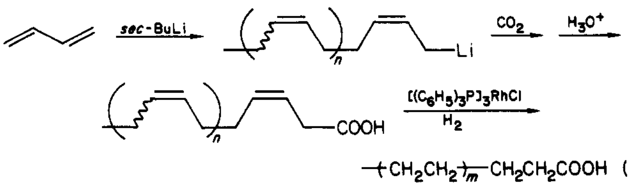
ABSTRACT: Functionalization of polyethylene by entrapment of functionalized ethylene oligomers in precipitates of polyethylene is described. The reactivity of the resulting entrapped functionalized ethylene oligomers toward various reagents and the degree of mobility of these entrapped ethylene oligomers 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



$-\!(CH_2CH_2)_m\!-CH_2CH_2COOH$ (1)

1

previously shown that anionic polymerization of butadiene followed by protonation of the intermediate anionic