

Trapping of Xenon Induced in Polymeric Films by UV and X-ray Irradiation

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ABSTRACT: X-ray and UV photons were used to store xenon atoms in polymeric films. The trapping was found to be stable at room temperature for Kapton and PVDC films. In Kapton, concentrations of xenon up to about 18.5 mg/cm³ were attained. The dependence of the rare gas concentration on the irradiation dose, film thickness, gas pressure, and on the polymers and gases nature was probed. The results are interpreted in terms of a simple three-step model: the xenon atoms are first physisorbed at the surface of the substrate and then diffuse into the bulk where they are finally trapped as a result of radiation chemistry effects of the UV or X-rays on the structure of the polymer.

Introduction

In a recent paper,¹ we presented a new technique that allows the storage of noble gases in polymeric films at ambient temperature. The trapping of the rare gases in the polymer was realized via X-ray irradiation of the gas and the polymer film. Two interpretations of the observed phenomenon were considered. The first involved cross-linking effects in the polymer as a result of the X-ray irradiation, whereas the second was based on the assumption that photoinduced chemisorption or persorption of xenon occurs in the polymeric substrate. In this paper, we present results of supplementary investigations which have allowed us to clarify some open questions raised in the preliminary study.

Absorption of photons in polymers^{2–5} creates excited-state analogues of the ground state from which photochemical reactions can occur. In radiation chemistry of polymers, two groups are usually considered. Polymers that cross-link under irradiation belong to the first group while those that degrade are members of the second one. In group I, polymers chains are linked together, leading to branched structures of higher molecular weight, until ultimately a tridimensional network is reached. On the other hand, polymers of group II degrade under irradiation to lower molecular weight products through a random-chain-scission process. Several polymers exhibit a behavior intermediate between that of polymers of group I and II.

In the various studies dealing with radiation effects in polymers, different types of radiation have been used. These include photons, high-energy electrons, and mixed radiation from nuclear reactors. In most cases, the same amounts of absorbed energy produce the same changes in polymer properties, irrespective of the type of radiation used.²

Initial tests have been performed with hard X-rays (up to 80 keV) by irradiating the polymeric samples with the bremsstrahlung of an X-ray tube.¹ This technique has two principal disadvantages. The first one resides in the long irradiation time needed to obtain a saturated sample (several days), whereas the second concerns the

cost of the “loading device” which requires high-power X-ray tube equipment.

For these reasons alternative methods were probed. Tests with low-energy electrons produced as a result of electric discharges in the noble gas¹ proved to be unsuccessful. Further attempts with UV radiation were found, however, to be very promising. The present paper is focused on the results obtained with the UV irradiation method. At first the technique employed for trapping the xenon in the polymeric substrates under UV irradiation and the method used to determine the quantity of trapped gas are described. The speed of the storage process is then discussed, and results concerning the dependence of the sorbed gas quantity on the thickness of the polymeric substrate, gas pressure, radiation type, and sorbent and sorbate nature are presented. In the last part, a crude model based on our findings is outlined.

Instrumentation and Experimental Methods

UV Irradiation Device. The UV trapping technique consists of enclosing the sorbent and the sorbate in a chamber transparent to UV radiation and irradiating it with an UV photon beam. The chamber has the form of a rectangular prism (38 × 62 × 36 mm³) with a 27 × 51 mm² window. The latter made of a polished spectroil 2000 quartz plate (4 mm thick) permits a quasi-total transmission of the UV radiation. The air contained in the chamber is pumped out and then replaced by the rare gas, at the chosen pressure, by means of a dedicated air-lock device. As shown in Figure 1, the experimental setup allows the simultaneous exposure of two different samples.

For the sample irradiation a 400 W Philips HPA400s lamp was employed. The emission spectrum of this double-ended medium-pressure metal halide radiator is centered on the UV-A region (315–400 nm). The distance between the lamp and the sample chamber was 16.5 cm. This distance represents a compromise between two effects: the time of irradiation needed to load a sample and the heating of the latter as a result of the irradiation, which has to be kept at a reasonably small value.

The UV radiation doses were monitored with a 0.8 × 0.8 mm² GaAsP photodiode located at a distance of 53 cm from the lamp (see Figure 1). A filter was mounted in front of the detector in order to cut the visible light above 400 nm. The electric charge integrated in the photodiode during the sample irradiation served to control the duration of the sample

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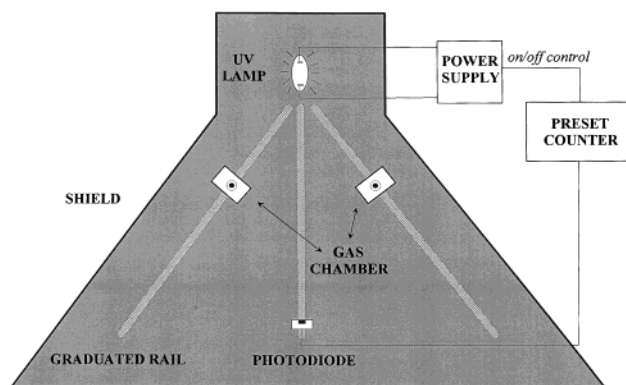


Figure 1. Schematic view of the UV irradiation device.

exposure. The effective irradiation times were also measured with the purpose of cross-checking the stability of the photodiode + UV lamp system.

Determination of the Relative Quantity of Sorbed Gas. The relative quantities of xenon sorbed in the different polymeric films were determined by the XRF (X-ray fluorescence) method. For the production of the xenon fluorescence X-ray lines a Coolidge X-ray tube with a gold anticathode and a 1 mm thick beryllium window was employed. The tube was operated at 45 kV and 10 mA. The distance between the tube and the sample was 5 cm. To diminish in the ADC spectrum the number of pileup events resulting from the coherent scattering of low-energy photons by the sample, a 5 mm thick Al absorber was placed between the sample and the detector. The sample and X-ray source were enclosed in a 2 cm thick stainless steel shielding.

The fluorescence X-rays of xenon were measured by means of a planar high-purity Ge detector having a thickness of 1 cm and an active area of 20 cm². To minimize the background originating from the scattering of the X-ray tube radiation in the stainless steel walls of the shielding chamber, a 3 cm long lead collimator, with a 30 mm high × 0.5 mm wide rectangular aperture, was installed in front of the detector. The angle between the sample surface and the sample-to-detector direction was 10° so that the whole width of the measured polymeric samples could be viewed by the detector despite the narrowness of the collimator aperture. With this setup we obtained counting rates of several thousands of counts per second, which were manageable for the detection electronics and high enough to acquire good statistics data in reasonably short acquisition times (typically 600 s).

The data acquisition was performed with a standard PC equipped with an ADC board (PCI-MIO-16E-4 from National Instruments, Inc.). A program based on the software package LabVIEW⁶ was developed to control the data acquisition. The same code was used for the data analysis which was performed with a least-squares-fitting method employing Gaussian profiles for the X-ray transitions and a fourth-order polynomial for the background. A typical fitted spectrum is shown for illustration in Figure 2 where one can distinguish the xenon $K\alpha_{1,2}$ (2p–1s), $K\beta_{1,3}$ (3p–1s), and $K\beta_2$ (4p–1s) transitions. The relative amount of xenon contained in a sample was determined by comparing the fitted intensity of the strongest 2p–1s doublet of that sample with the corresponding yield of a reference sample.

Determination of the Absolute Quantity of Sorbed Gas. The knowledge of the relative quantities of sorbed gas is sufficient to probe the dependence of the trapping process on several parameters such as the gas pressure or sample thickness. A deeper understanding of the storage mechanism requires, however, to know the absolute amount of gas contained in the sample. This absolute amount needs to be determined only for one sample because the quantity of sorbed xenon in any other foil can then be determined from this standard sample with the method discussed in the preceding section.

To determine the absolute quantity of stored gas or the equivalent "thickness" of the latter, we first tried to use the

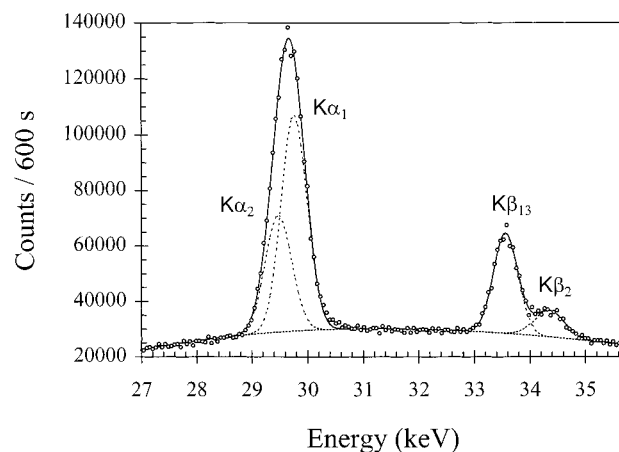


Figure 2. Xe $K\alpha,\beta$ X-ray spectrum measured with the Ge detector. The open circles correspond to the measurement, the dashed and dotted lines to the fitted transitions and background, respectively, and the solid line to the total fit.

simple gravimetric method which, unfortunately, revealed to be not sensitive enough. Another technique based on the observation of the K absorption edge of xenon failed, too. We have thus developed a new method which consists of comparing the experimental intensity of a strong and well-resolved fluorescence X-ray line emitted by the target of unknown thickness with the corresponding theoretical intensity obtained from simulation calculations. The target thickness which is used as a free parameter in the simulation is varied until the computed intensity fits the experimental one. The reliability of the method was checked with metallic Sn and Gd foils of known thicknesses. An agreement on the order of 4% was found for both foils.

This technique was then employed to determine the "thickness" of xenon absorbed in two 75 μm thick Kapton films which were used afterward as standard probes. The first sample was loaded using X-rays (64 h irradiation at 80 kV/30 mA, Xe pressure of 2 bar) and the second one by means of UV (28.5 h irradiation, 2 bar). Xe "thicknesses" of 49.8 ± 1.1 and 85.5 ± 1.9 $\mu\text{g}/\text{cm}^2$, respectively, were obtained for the two samples. These "thicknesses" correspond to xenon concentrations of 6.64 and 11.4 $\mu\text{g}/\text{cm}^3$.

Results and Discussion

Speed of Storage. The photoinduced storage of xenon in polymers is a very slow process. Several tens of hours is indeed needed to reach the saturation concentrations. This is illustrated in Figure 3, which shows the quantity of xenon captured in 25 and 75 μm thick Kapton films, immersed in a 2 bar xenon atmosphere, as a function of the irradiation time.

The experimental data reported in Figure 3 could be well reproduced with the following function:

$$Q(t) = Q_{\text{sat}}(1 - e^{-\alpha t}) \quad (1)$$

where $Q(t)$ and Q_{sat} are the quantity of sorbed gas at the time t and at saturation and α is a constant related to the speed of the storage process.

The time interval Δt needed to reach 90% of the saturation value can be deduced from the relation

$$\Delta t = \frac{\ln 10}{\alpha} \quad (2)$$

The parameters Q_{sat} and α were determined with a nonlinear least-squares-fitting method. The obtained values are presented in Table 1 together with the time intervals Δt .

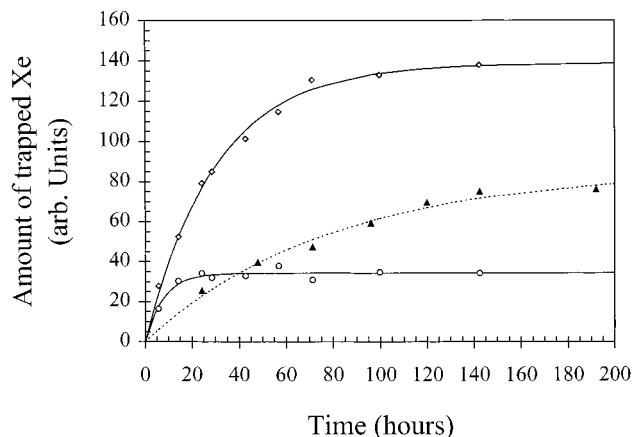


Figure 3. Variation of the quantity of trapped xenon as a function of the irradiation time. The open rhombs and open circles correspond to the values obtained with a 75 and 25 μm thick Kapton film irradiated with UV, respectively. The full triangles correspond to the 75 μm sample irradiated with X-rays.

Table 1. Values Q_{sat} and α Obtained from the Least-Squares Fit of the Data Presented in Figure 3; the Time Intervals Δt Needed To Reach 90% of the Saturation Values Were Calculated from Relation 2

sample thickness [μm]	storage technique	Q_{sat} [arb. units]	α [h^{-1}]	Δt [h]
24.2	UV	34.2	0.129	19
78.1	UV	139	0.033	69
78.1	X-ray	83	0.013	180

Trapping Probability. If λ represents the probability for one xenon atom to be trapped in the irradiated polymeric sample, the decrease of the number of available trapping sites during the time interval dt can be written as follows:

$$dN = -\lambda N(t) dt \quad (3)$$

where $N(t)$ stands for the number of trapping sites that are still unoccupied at the time t . $N(t)$ is then given by the solution of the differential equation (3):

$$N(t) = N_0 e^{-\lambda t} \quad (4)$$

with $N_0 = N(t=0)$.

The number of occupied trapping sites at the time t is thus

$$N^*(t) = N_0 - N(t) = N_0(1 - e^{-\lambda t}) \quad (5)$$

Relation 5 has exactly the same form as relation 1. This is not surprising since the number of occupied trapping sites $N^*(t)$ is just equivalent to the quantity $Q(t)$ of trapped xenon at the time t , and the number N_0 of unoccupied sites at the time $t = 0$ is equal to the maximal number of sites that can be occupied, i.e., to the quantity Q_{sat} of sorbed gas at saturation. The trapping probability λ should then be proportional to the storage velocity parameter α .

Bulk Contribution to the Sorption Process. To determine to which extent the polymer bulk contributes to the observed trapping, the quantities of xenon stored in different Kapton films which differed only in their thicknesses (nominal values of 8, 13, 25, 50, and 75 μm) were compared. The experiment was performed with the X-ray (irradiation at 80 kV/30 mA, xenon pressure of 2

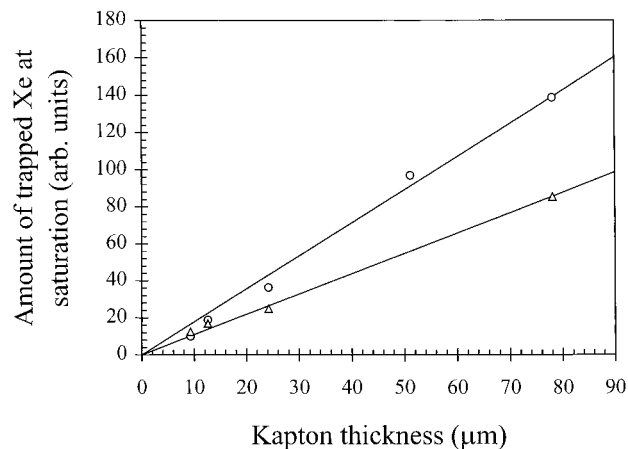


Figure 4. Amount of xenon trapped at saturation as a function of the sample thickness for UV (circles) and X-ray (triangles) irradiation.

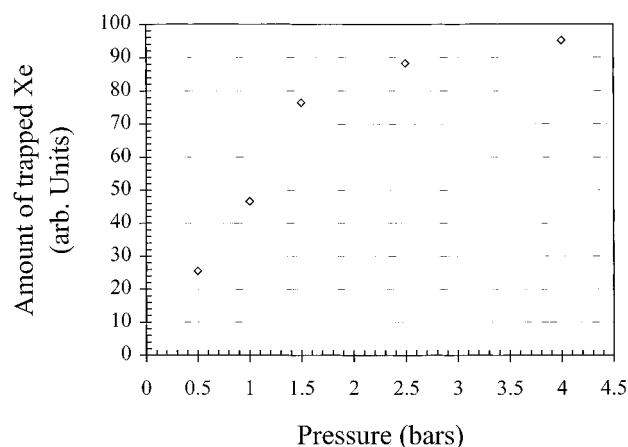


Figure 5. Quantity of xenon stored in a 75 μm thick Kapton film irradiated with UV and immersed in Xe atmospheres of different pressures.

bar) and UV sorption methods (xenon pressure of 2 bar). The results are presented in Figure 4 where one can see that the quantity of trapped xenon at saturation increases almost linearly with the film thickness for both UV and X-ray irradiation.

The large number of trapped xenon atoms and the evolution of the amount of xenon stored as a function of thickness permit us to exclude a capture limited to the surface of the sorbate. The xenon atoms must penetrate and diffuse into the polymeric substrate through the surface before being trapped.

Pressure Dependence. Polymers that are characterized by relatively open structures exhibit in general sizable gas permeabilities. The permeability is given by the product of the diffusivity and the solubility.⁷ In our case, the solubility governs the saturation value of the stored gas amount while the diffusivity is the determining factor for the speed of the loading process. At low pressure, i.e., below about 1 atm, the diffusivity and the solubility are independent of the gas pressure in the atmosphere surrounding the specimen.⁷ Consequently, the flow rate should vary linearly with the pressure. At high pressure, however, polymers frequently exhibit significant deviations from this model, even when the pressures are as low as a few atmospheres.

In Figure 5, the quantity of xenon sorbed in a 75 μm thick Kapton film irradiated for 24 h with UV is represented for different values of the gas pressure. The

Table 2. List of the Probed Polymers with Their Principal Characteristics; the Glass Transition Temperatures T_g Were Taken from Ref 22 Except That of Kapton Which Was Obtained from Ref 23

name	chemical formula	T_g [°C]	UV abs (%)	cross-link or degrade	radiation resistance
polyimide Kapton HN	$(-C_{22}H_{10}N_2O_5-)_n$	385	100	cross-linking	good
polyethylene low density (LPDE)	$(-CH_2CH_2-)_n$	-130	9	cross-linking	fair
polypropylene (PP)	$[-CH_2CH(CH_3)-]_n$	-17	9	cross-linking	fair
polyamide-nylon 6 (PA 6)	$[-NH(CH_2)_5CO-]_n$	40	20	cross-linking	fair
poly(ethylene terephthalate), (polyester, PET)	$(-OCH_2CH_2O_2CC_6H_4-4-CO-)_n$	74	25	cross-linking	good
poly(tetrafluoroethylene) (PTFE)	$(-CF_2CF_2-)_n$	-73	40	degrading	α, β, γ : poor UV: excellent
poly(vinylidene chloride) (PVDC)	$(-CH_2CCl_2-)_n$	-18	21	degrading	fair

amount of trapped xenon is found to increase with increasing pressure. Up to a value of about 1.5 bar, the variation seems to be nearly linear, whereas above, as predicted by theory, a significant deviation from that linear dependence is observed.

Comparison between the UV and X-ray Techniques. As shown in the preceding paragraphs, the UV and X-ray induced storage processes present several very similar features. We are thus inclined to believe that the trapping mechanism is essentially the same in the two methods. On the other hand, differences were found between the saturation concentrations and storage speeds corresponding to the two techniques. These differences may be accounted for by the different amount of energy left in the sample by the UV and X-ray radiations.

In the UV-A wavelength domain, the emission power of the lamp is 80 W, according to the manufacturer's specifications. The UV absorption by xenon was checked and found to be negligibly small so that in the standard setup (irradiation chamber at 16.5 cm from the source) the samples were exposed to radiation intensities of about 20 mW/cm². As the Kapton films employed in our measurements were found to be completely opaque to UV, the energy deposition could be determined. A value of about 70 J/cm² of Kapton and hour of irradiation was obtained. In addition, the fact that a full absorption of the radiation is observed even in the case of the thinnest sample (8 μ m) indicates that the whole UV energy is deposited in the few first micrometers of the Kapton film.

In the alternative method which consists of loading the samples with X-rays, a Coolidge-type Au anode X-ray tube operated at 80 kV and 30 mA was employed.¹ The efficiency of the tube was estimated with the empirical relation given in ref 8. A value of 0.88% was found from which an X-ray emission power of about 20 W was deduced. Considering the distance (4.5 cm) between the tube and the sample and the absorption of the bremsstrahlung in the gas and window of the irradiation chamber, one finds that in this case the samples were exposed to X-ray intensities of about 60 mW/cm² (for a Xe pressure of 2 bar). With X-rays, the energy left in the polymeric sample is homogeneously distributed in the whole volume and depends on the foil thickness. For the 75 μ m thick film, calculations based on the photoabsorption cross sections quoted by Storm and Israel,⁹ and the spectral intensity of the X-ray tube showed that the fraction of absorbed energy is only 0.3%. For the same irradiation time, the energy deposition is thus more than 100 times smaller than in the UV case.

As discussed above, the maximum quantity of Xe that can be stored is proportional to the film thickness. This observation seems reasonable for the X-ray method in which the trapping process takes place in the whole

volume of the sample since the energy deposition is uniformly distributed over the film thickness. In contrast to that, in the UV method, one would expect that above a certain thickness the saturated amount of sorbed Xe does not increase any more, the energy of the radiation being entirely left in a thin layer close to the front surface. We tentatively explain that apparent contradiction by the fact that in this case the photoinduced structure modification of the polymer occurring in the front layer of the sample constitutes a barrier which blocks in the bulk the Xe atoms which have diffused beforehand into the sample volume. As a result of the multiple reflections of the UV light on the metallic walls of the irradiation chamber, a similar barrier is created in the rear part of the foil, which prevents the gas to escape.

The temperatures of the samples exposed to the UV and X-ray radiation were measured. Values of 52 °C (UV) and 40 °C (X-rays) were found. As a consequence of the higher temperature of the sample in the UV method, the xenon diffusivity in Kapton is increased, which in turn results in an enhancement of the storage speed, i.e., of the constant α , as observed. Moreover, the temperature dependence of the diffusion phenomenon is the result of two processes: the increase in the thermal energy of the gaseous entities with temperature and the opening of the structure as the free volume increases and relaxation times decrease.¹⁰ As the increase of the free volume in the polymer leads to a higher solubility of the gas, the sample heating observed in the UV-induced storage may also explain the larger values obtained with this technique for the saturation concentrations.

Sorption Tests with Other Polymeric Films. To gain a deeper insight into the mechanisms involved in the storage process, the UV sorption technique was applied to several degrading or cross-linking type polymers. The films which were all 50 μ m thick (except PET: 13 μ m) were probed as obtained from the manufacturer (Goodfellow Cambridge limited, UK) without any pretreatment. Their principal characteristics are presented in Table 2. The percentages of UV absorption quoted in this table were measured with the GaAsP photodiode.

In these measurements, the polymeric samples were immersed in a 2 bar xenon atmosphere and then irradiated for 24 h with an UV lamp. To verify the permanent character of the storage, the amount of sorbed xenon was determined immediately after the irradiation and again 24 h later. For each sample, both results are presented graphically in Figure 6. We remark that in low-density polyethylene (LPDE) and polyamide-nylon 6 (PA6), no trace of xenon was detected, even in the first measurement, indicating thus that these two polymers are characterized by nearly zero

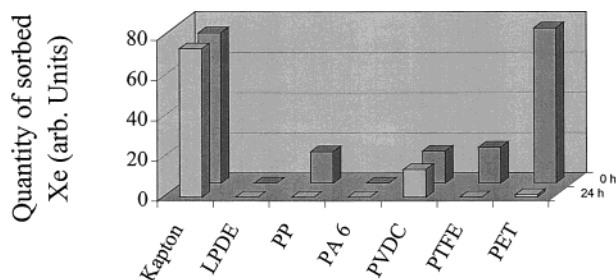


Figure 6. Quantities of xenon trapped in different polymers measured immediately after the UV irradiation and 24 h later.

permeabilities for xenon. In polypropylene (PP), poly(tetrafluoroethylene) (PTFE) and poly(ethylene terephthalate) films (PET), absorption occurs, but the stored gas desorbs rapidly. In particular, for the PP and PTFE films, a complete desorption was observed already after 20 min. To check whether the nonpermanent character of the trapping was related to the radiation type, both polymers were also loaded with the X-ray technique. A similar unstable trapping was observed. Figure 6 shows that a permanent trapping occurs only for Kapton polyimide and poly(vinylidene chloride) (PVDC). The ratio of the quantities of xenon sorbed in these two polymers is almost equal to the ratio of their UV absorption coefficients, i.e., of the energy deposited in each film. More intriguing is the fact that the two loadable polymers belong to two different groups, group I (cross-linking) for Kapton and group II (degrading) for PVDC.

In general, the results depicted in Figure 6 are difficult to interpret. Actually, no specific characteristic or property of the examined polymers was found that is necessary for a successful and permanent trapping of xenon, except that the film must present a sizable gas permeability and should be not fully transparent to the employed radiation. The most efficient gas trapping was found for Kapton which is characterized, as shown in Table 2, by the highest glass transition temperature ($T_g = 385\text{ }^\circ\text{C}$). As in addition most of the studied polymers with negligible storage capacity have T_g 's below or near room temperature, one would be tempted to associate successful trappings with polymers in the glassy state and unsuccessful ones with polymers in the rubbery state. This simple explanation, however, fails for PVDC which has a T_g as low as $-18\text{ }^\circ\text{C}$ but for which a permanent gas storage was observed and for PET which is characterized by a higher glass temperature ($74\text{ }^\circ\text{C}$) but for which the trapping was found to be unstable at room temperature.

In a control experiment a Kapton foil immersed in a 2 bar xenon atmosphere was heated to $52\text{ }^\circ\text{C}$ (the sample equilibrium temperature in the UV method), kept at this temperature for 24 h, and then cooled again to the room temperature ($23\text{ }^\circ\text{C}$). The XRF measurement performed immediately after the sample has reached room temperature showed that about the same quantity of xenon was sorbed in the foil as after a 24 h irradiation with UV. However, the trapping was found to be unstable, the amount of sorbed gas decreasing rapidly as a function of the time. A further experiment in which the Kapton film was irradiated with X-rays just after the thermal treatment showed that in this case no gas desorption is observed. This confirms the assumption that the sample heating resulting from the UV irradiation cannot account alone for the permanent character of the trapping.

Summary and Concluding Remarks

The investigations performed in the present work have shown that xenon can be stored in polymeric films exposed to UV or X-ray radiations and that the gas trapping is stable at room temperature, but only for a restricted number of polymers. It was further demonstrated that the quantity of sorbed gas tends to a saturation value proportional to the substrate thickness. The loading times needed to reach saturation were found to be in the order of days, the storage speed being proportional to the ratio of the gas pressure outside the sample to the thickness of the latter. As a result of the lower energy deposition characterizing the X-ray irradiation technique, the saturated amount of sorbed xenon and the speed of the storage process were found to be both smaller than in the UV irradiation method. The loading mechanism, however, seems to be the same in the two methods: the xenon atoms are first physisorbed at the polymer surface, then diffuse into the bulk as in a standard permeation process, and are finally trapped as a result of the structural modifications induced in the substrate by the UV or X-ray irradiation.

In this simple picture, the storage capability must also depend on the dimensions of the trapped atoms relative to the size of the polymer lattice. As a consequence, for a given polymer, one can expect that the trapping probability should increase with the atomic radius of the gas. As in addition the gas solubility in polymers, in contrast to inorganic materials, usually increases with increasing size of the dissolved entity,¹¹ one expects that the storage is more difficult to achieve for lower Z noble gases. This was confirmed by the results of measurements performed with Kapton films placed in krypton and argon atmospheres. For krypton (atomic radius $r = 2.00\text{ \AA}$), the trapping could be achieved but the obtained concentrations were found to be markedly smaller than in xenon ($r = 2.17\text{ \AA}$) and less stable, desorption occurring already at room temperature. For Ar ($r = 1.88\text{ \AA}$), all attempts to observe the X-ray emission of the sorbed atoms were unsuccessful, indicating that trapping does not occur at all or is unstable at ambient temperature.

In our previous paper¹ presenting preliminary results concerning the X-ray induced storage of xenon in Kapton, a second interpretation was proposed, in which chemisorption or persorption of the xenon atoms in the polymeric bulk was envisaged as a possible explanation of the observed phenomenon. In this alternative interpretation we assumed that the interactions between the noble gas atoms (in the ground state) and radical sites formed in Kapton by the X-ray irradiation could result in a weak chemical binding. The possibility for a chemical bond was based on two experimental results: the high value found for the thermal energy needed for desorbing xenon from the Kapton film (67 kJ/mol) and the energy shift of $1.04 \pm 0.48\text{ eV}$ observed for the 5p orbital of the sorbed xenon atoms.

The activation energy of 67 kJ/mol found in the previous study corresponds to the sum of the escape energy, diffusion energy, and heat of desorption¹² so that it is not possible to determine the exact contribution of the desorption process to this activation energy. No definitive conclusion can thus be drawn regarding the strength of the trapping potential. Moreover, inconsistent values concerning the magnitude of the activation energy of the physisorption and chemisorption processes are given in the literature. The heat of physisorption is

usually assumed to be less than 20–25 kJ/mol,^{13,14} but some references give values comprised between 30 and 60 kJ/mol.^{15,16} For these reasons, we believe that physisorption cannot be excluded a priori from the above-mentioned activation energy. In other words, the value of 67 kJ/mol alone is not sufficient to certify that chemisorption involving a chemical bond between the sorbent and the sorbate does really exist in the trapping process.

Although fluoride, oxide, and chloride krypton and xenon compounds have been successfully studied¹⁷ since 1962, it is well-known that the ability of the rare gases to combine with other atoms is very limited. To our knowledge, information concerning polymer–noble gas interactions does not exist in the literature. For xenon–metal interactions, for which similar energy shifts of the 5p orbital were observed, experimental and theoretical information is available, but contradictory interpretations are proposed. In general, it is concluded that perturbations from metals on the electronic configuration of inert gases can only occur via van der Waals dispersion forces.¹⁸ Several other studies^{19,20} claim that theoretical models that do not include bond-charge-transfer mechanisms cannot account for the measured heats of adsorption or for the observed energy shifts of the electronic orbitals. Finally, the shift of 1.04 ± 0.48 eV found in our previous study was determined from a comparison between the energies of the 5p–1s transitions in gaseous xenon and xenon sorbed in Kapton. As it can be assumed that in atoms as heavy as xenon core levels are not affected by chemical effects, the same energy shift should be observed in the 5p–2s transitions. A measurement of this transition was thus performed with a von Hamos bent crystal spectrometer,²¹ using first a gaseous xenon target and then a Kapton foil containing sorbed xenon. An energy shift of 0.19 ± 0.07 eV was obtained. Both results are thus not consistent within the quoted 1σ uncertainties. The explanation resides in the fact that only the statistical errors arising from the fit of the data were considered in these measurements. The true experimental uncertainties are therefore somewhat bigger than the given values. If we assume that the total errors are each about 2 times bigger than the quoted statistical uncertainties, then both measured energy shifts are almost consistent with zero, which makes questionable the chemical bond hypothesis.

To summarize, this study has demonstrated that the macroscopic features of the storage of xenon in polymers could be explained by a crude model based on simple considerations. The microscopic aspects of the trapping mechanism are, however, not fully understood. In view of our findings, we are inclined to believe that bond ruptures, bond rearrangements, and cross-linking of

unsaturated polymer chains caused by the photon irradiation and secondary electrons prevent the sorbed xenon atoms to escape. A more detailed and deeper understanding of the process needs further experimental and theoretical investigations. In particular, the question concerning the properties of the polymeric substrate required for a stable trapping at room temperature should be elucidated.

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