Dose Dependence of the Charge Carrier Mobility and Decay Kinetics in Radiation Polymerized Diacetylenes

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ABSTRACT: Single crystals of the diacetylene derivatives ETCD, 4BCMU, IPUDO, and DCH were polymerized by repeated irradiation with single pulses of 3 MeV electrons. The conductivity induced by these pulses was determined as a function of the accumulated dose. At low doses the transient radiation-induced conductivity increases due to the production of polymer chains, on which the charge carriers are highly mobile. For low accumulated radiation dose the charge carrier mobility is found to be of the order of 1 $cm^2/(V\ s)$. For higher accumulated dose the lifetime of the charge carriers toward trapping as well as their mobility decrease. For accumulated radiation doses that are conventionally used to produce polydiacetylenes, the charge carrier mobility has decreased by approximately 1 order of magnitude.

Introduction

Most polymers are amorphous solids, and where crystallinity exists, it is usually over small regions of space of a few microns or less. Polydiacetylenes, however, are distinct from most polymers in that they can be produced as large single crystals by solid-state polymerization of the crystalline monomer.[1,2] The initiation of the diacetylene polymerization involves the formation of a diradical or dicarbene. Such a radical can react with an adjacent monomer to form a covalent bond. This polymerization reaction proceeds until halted by a defect or internal stress in the lattice. The polymerization of monomer crystals can be initiated by heat[1,3−9] and by high-energy radiation.[1,9−15] Thin layers of polydiacetylenes can also be produced by polymerization of the diacetylene monomer using UV light.[16−21]

Polymerization of diacetylene crystals by high-energy radiation is usually carried out using γ-rays from a ^{60}Co source with typically an accumulated dose between 10^5 and 10^6 Gy. Although such a dose can lead to complete conversion of the monomer to polymer, it is not known to what extent the polymer chains are degraded by the radiation. The aim of the present work is to study the effect of accumulated radiation dose on the mobility and the decay of the charge carriers in polymerized single crystals of the diacetylene derivatives ETCD, 4BCMU, IPUDO, and DCH. High-energy (3 MeV) electron pulses with a dose of typically 2 Gy per pulse are used, which makes it possible to study the radiation-induced conductivity after small increments of the accumulated radiation dose. Polymerization with high-energy electrons is similar to that with a ^{60}Co source, since the γ-rays produce high-energy electrons in the sample mainly by Compton scattering. To be able to study the mobility and the decay of the charge carriers on polymer chains diluted in a monomer matrix, a time-resolved ac conductivity technique is required. A suitable method that meets this requirement is the pulse-radiolysis time-resolved microwave conductivity (PR-TRMC) technique, which has been applied previously by Van der Laan et al.,[22,23] who observed that charge transport in nBCMU diacetylenes is rather sensitive to radiation-induced defects.

Experimental Section

Materials Four diacetylene monomers are investigated in this paper (for their molecular structure see Figure 1). The synthesis of the different diacetylene derivatives is briefly described below.

ETCD; Bis(ethylurethane)-5,7-dodecadiyne-1,12-diol. The ETCD monomer was synthesized by Hay coupling of monoacetylenes as described elsewhere.[24] Single crystals of the monomer were grown from ethyl acetate solution by slow cooling. The single crystals had a rectangular shape and a pale purple color, indicating a few percent of monomer conversion.

4BCMU; 5,7-Dodecadiyne-1,12-bis(n-butoxycarbonylmethylurethane). The monomer was synthesized by reaction of an isocyanate with a diacetylene diol. The detailed procedure for synthesis of the monomer has been described elsewhere.[25] The monomer was recrystallized twice from acetone−hexane mixtures after which a crystalline powder was obtained. The monomer crystals of 4BCMU were pale blue in color, indicating that polymerization has occurred to a certain extent. However, the conversion of monomer into polymer was only a few percent.[25]

IPUDO; Bis(isopropylurethane)-5,7-dodecadiyne-1,12-diol. The IPUDO monomer samples were prepared by a reaction of 5,7-dodecadiyne-1,12-diol with isopropylisocyanate using triethylamine and dibutyltin di(2-ethylhexanoate) as catalysts.[26] Single crystals were grown from a solution in ethyl acetate. The single crystals were rectangular and colorless, which indicated that the extent of polymerization was negligible.

DCH; 2,4-Hexadiyne-1,6-bis(carbazolyl). The DCH monomer was prepared following the general method of Yee and Chance.[10] However, the precursor 3-(9-carbazolyl)-1-propyne

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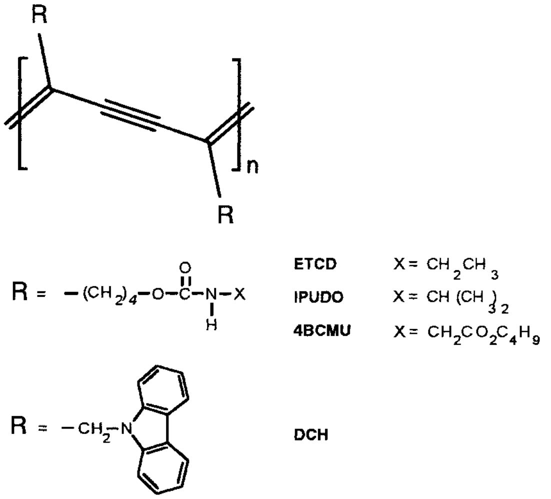

Figure 1. Molecular structure of diacetylene and the pendent group of the monomers investigated.

was prepared using butyllithium as reagent for ease of purifying the product. Fine needlelike crystals were grown by rapid cooling of a hot acetone solution, while larger, chunky crystals were grown by very slow evaporation of an acetone solution. Their very pale color indicated only a small (<1%) initial polymer content.

Radiation-Induced Polymerization. The samples were irradiated in a microwave cell, which consisted of a 14 mm length of rectangular, 7.1 × 3.55 mm^2, copper waveguide closed at one end with a metal plate and flanged at the other end. Both 4BCMU and DCH were available in sufficient amounts (ca. 200 mg) to fill the microwave cell over a length of ca. 10 mm. The available amounts of ETCD and IPUDO (ca. 30 mg) were too small to fill the microwave cell, and therefore a Perspex block of 20 × 7.1 × 3.5 mm^3, with a small cavity of 2 × 6 × 3 mm^3 (length × width × depth) was used to contain the sample. The filled Perspex block was inserted into the microwave cell.

The microwave cell containing the monomer sample was irradiated using 4 A pulses of 3 MeV electrons from the Van de Graaff accelerator. The integrated beam charge per pulse was monitored. The energy deposition is close to uniform throughout the sample and equal to 1.09 Gy per nanocoulomb beam charge (1 Gy = 1 J/kg), measured using thin film radiochromic dosimeters (Far West Technology Nr. 92).[27] Hence, the dose rate is 4 × 10^9 Gy s^{-1} during the pulse. To reach a total accumulated dose of 10 kGy, a series of pulses of 0.5 ns were used. To obtain higher accumulated doses, a series of 2 or 5 ns pulses were applied.

In the case of 4BCMU the monomer-to-polymer conversion could be determined by removing a few milligrams of the material from the microwave cell after reaching certain levels of accumulated dose. The polymer of 4BCMU was dissolved in chloroform, and the absorption of the polymer at 468 nm was measured using a Uvikon 940 UV/vis spectrophotometer. At this wavelength the extinction coefficient of the polymer in chloroform was taken to be 17 500 dm^3 mol^{-1} cm^{-1}.[11] This procedure was not possible for ETCD, IPUDO, and DCH, since the corresponding polymers are insoluble.

Radiation-Induced Conductivity. During the polymerization with a series of electron pulses, intermittent measurements of the conductivity induced by a single electron pulse were carried out. The transient change in conductivity due to such a single electron pulse was monitored by measuring the change in the microwave power reflected by the sample using the time-resolved microwave conductivity (TRMC) technique.[28−31] In the present experiment microwaves in the Ka band (26.5−38 GHz) were used. For small changes the relative change in absorbed microwave power $\Delta P/P$ is proportional to the change in conductivity of the sample, $\Delta\sigma$. The quantitative relation between the microwave loss and $\Delta\sigma$ was determined using computational and data fitting procedures described previously.[28] To obtain radiation-induced conductivity changes in the range 10^{-4} and 10^{-3} S/m, electron pulses with a duration from 0.5 to 20 ns had to be used. To prevent spurious conductivity signals due to electrons produced in the irradiated air inside the waveguide, the waveguide was flushed with sulfur hexafluoride.

Changes in the output of the microwave detector diode were monitored using either a Tektronix TDS680B digital oscilloscope or a Sony/Tektronix RTD 710 digitizer. Using the former, the time response is approximately 1 ns. The latter has a rise time of 5 ns but is capable of registering the data using a pseudo-logarithmic time base.[32] This allowed recording of transient data from 10 ns to 5 ms using a single electron pulse.

Relation between radiation-induced conductivity and charge carrier mobility The radiation-induced conductivity is proportional to the product of the sum of the mobilities of the (positive and negative) charge carriers, $\Sigma\mu$ (m^2/(V s)), and the number of mobile electron−hole pairs present per unit volume. Assuming that only those charge carriers that are produced in the polymer regions are mobile the radiation-induced conductivity induced is given by

$$\Delta\sigma = eN_{\mathrm{pol}}\sum\mu \tag{1}$$

where N_{pol} is the concentration of charge carriers in the polymer regions and e is the elementary charge (1.6 × 10^{-19} C).

The initial concentration of charge carriers in the polymer regions is

$$N_{\mathrm{pol}} = \frac{D_{\mathrm{v}}}{E_{\mathrm{p}}} X \tag{2}$$

in which D_{v} is the dose per unit volume deposited in the sample, E_{p} is the average energy to form an electron−hole pair, and X is the fraction of monomers that have been converted to polymer. For polydiacetylenes, E_{p} is estimated to be approximately 20 eV.[33] Note that D_{v} (J m^{-3}) is the dose per unit volume, which is applied to obtain a single radiation-induced conductivity transient. To relate the dose per unit mass, D (Gy), as obtained from dosimetry measurements using thin film radio chromic dosimeters to the dose per unit volume, knowledge of the density of the sample is needed. Assuming the densities of a monomer sample to be equal to that of a polymer sample, the densities were taken to be ρ(poly-ETCD) = 1.16 g/cm^3,[34] ρ(poly-4BCMU) = 1.22 g/cm^3,[35] ρ(poly-IPUDO) = 1.16 g/cm^3,[26] and ρ(poly-DCH) = 1.30 g/cm^3.[36] (Note that the BCMU results in this work differ from the results published earlier[22,23] in the sense that in the earlier work the density was assumed to be unity.)

Results and Discussion

Dose Dependence of Radiation-Induced Conductivity. In Figure 2 dose-normalized conductivity transients induced by a single 3 MeV electron pulse are shown for samples of ETCD, 4BCMU, IPUDO, and DCH. The transients were normalized to the dose per unit volume deposited by each pulse and were monitored after accumulated radiation doses (per unit mass) as indicated. The conductivity increases with accumulated dose, which is due to conversion of monomers into polymers. Clearly, the mobility of charge carriers in a monomer region is much smaller than on a polymer chain.

The conductivity shows a fast increase on a short time scale due to the production of charge carriers during the pulse and the 1 ns time resolution of the TRMC technique. For low accumulated dose the conductivity increases slightly after the pulse, which is most clearly visible in the transient obtained in ETCD after irradia-

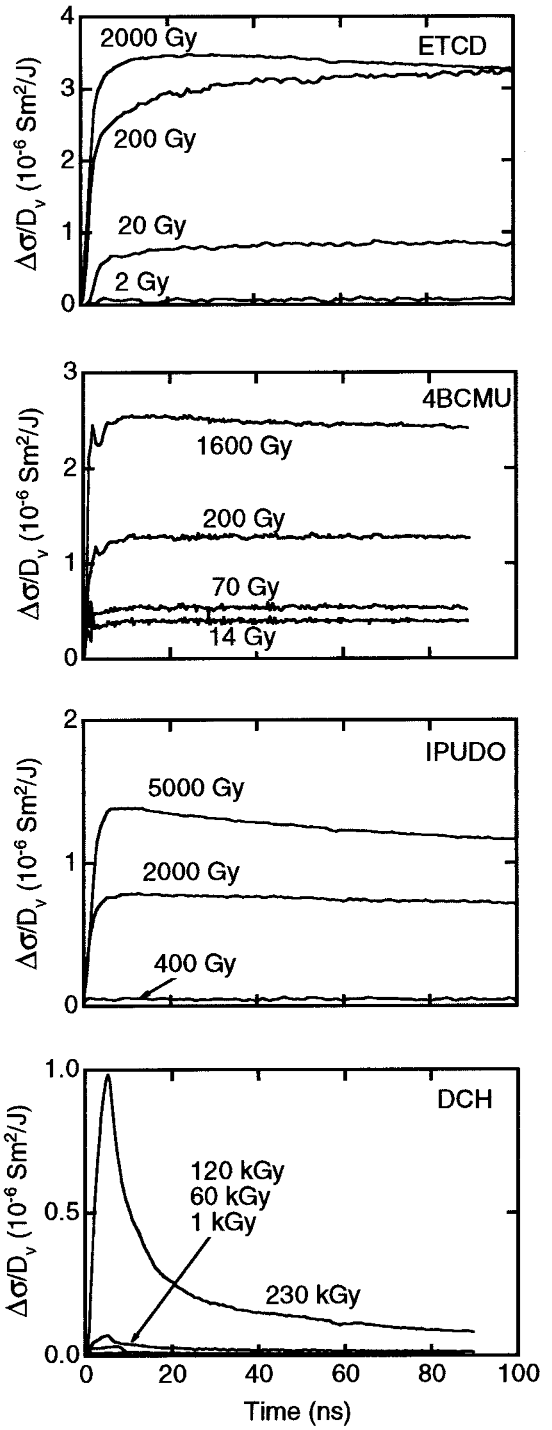

Figure 2. Dose-normalized radiation-induced conductivity transients induced by 0.5 ns pulses in ETCD, 4BCMU, and IPUDO for accumulated doses indicated. The results for DCH were obtained using 5 or 20 ns pulses.

tion with an accumulated dose of 200 Gy. This could be due to motion of charge carriers from monomer regions, where the mobility is low, to polymer chains on which the mobility is much higher. This effect decreases with accumulated dose since for high doses most of the monomers have become polymerized.

The dose-normalized conductivity in ETCD, 4BCMU, IPUDO, and DCH, directly after a high-energy electron pulse, is presented as a function of accumulated dose in Figure 3. It can be seen that the conductivity in ETCD, 4BCMU, and IPUDO immediately increases with the accumulated dose, while in DCH conductivity is observed only after an accumulated dose of ~10^5 Gy. In the dose range between 10^5 and 3×10^5 Gy the conductivity in DCH exhibits a rapid increase. Such autocatalytic behavior has been observed previously for the thermal and radiation-induced polymerization of DCH[9,10,37] and for the thermal polymerization of TS.[3,6,9,38] DCH is distinct from the urethane-substituted derivatives in the sense that the DCH monomer does not exhibit an ideal crystal packing conformation required for solid-state polymerization. It was demonstrated by Enkelmann[37] that in the early stage of polymerization only very short chains are formed. At a conversion of approximately 25% the crystals were found to undergo a phase transition as is evidenced by a sudden change of the lattice parameters. The autocatalytic behavior is observed for a dose of ca. 2×10^5 Gy, which agrees with other studies.[9,10,37]

The data in Figure 3 show that the accumulated dose at which the conductivity is maximum increases in the order ETCD, 4BCMU, IPUDO, and DCH. The decrease of the conductivity at higher accumulated doses can be attributed to a decrease of the charge carrier mobility due to degradation of the polymer chains by radiation induced defects as will be discussed below.

Dose Dependence of the Conductivity Decay Kinetics. In Figure 4 the radiation-induced conductivity transients obtained for ETCD, 4BCMU, IPUDO, and DCH are shown for different values of the accumulated dose. To compare the decay kinetics, the transients have been vertically scaled to coincide at short times. At higher accumulated dose the decay of the conductivity becomes faster. The faster decay is most likely due to the introduction of defects by radiation, since high-energy radiation can induce chemical changes in the side chains of the polymer[11,39] or scission of the polymer backbones.[13] These radiation-induced defects may act as trapping sites at which the charge carriers can become localized. The conductivity in DCH decays much faster than in the three urethane-substituted samples. The average polymer chain length of poly-DCH is significantly shorter than that of the urethane-substituted polydiacetylenes.[37,40] Thus, the faster decay in poly-DCH could possibly be due to faster trapping of electrons on polymer chain ends. In addition, an ionized carbazole could cross-link with an adjacent chain,[41] making interchain transport more likely, which in turn could lead to a faster encounter of a trap by a charge carrier.

In Figure 5 the time at which the conductivity has decreased to half of the value at the end of the pulse is shown as a function of accumulated dose. This half-life decreases considerably with accumulated dose. Of the three urethane-substituted diacetylenes, 4BCMU exhibits the longest half-life. This could be due to the fact that this compound has the longest pendent group and hence the longest distance between the polymer chains, which leads to the slowest rate of interchain charge recombination.

For accumulated radiation doses between 10^5 and 10^6 Gy, which are typically used to produce polydiacetylenes, the half-life of the conductivity in the urethane-substituted polydiacetylenes has decreased by several orders of magnitude compared to the half-life at low accumulated dose.

In DCH the half-life for accumulated doses below 10^5 Gy is only about 20 ns. In this dose range the radiation-induced conductivity is at least 2 orders of magnitude

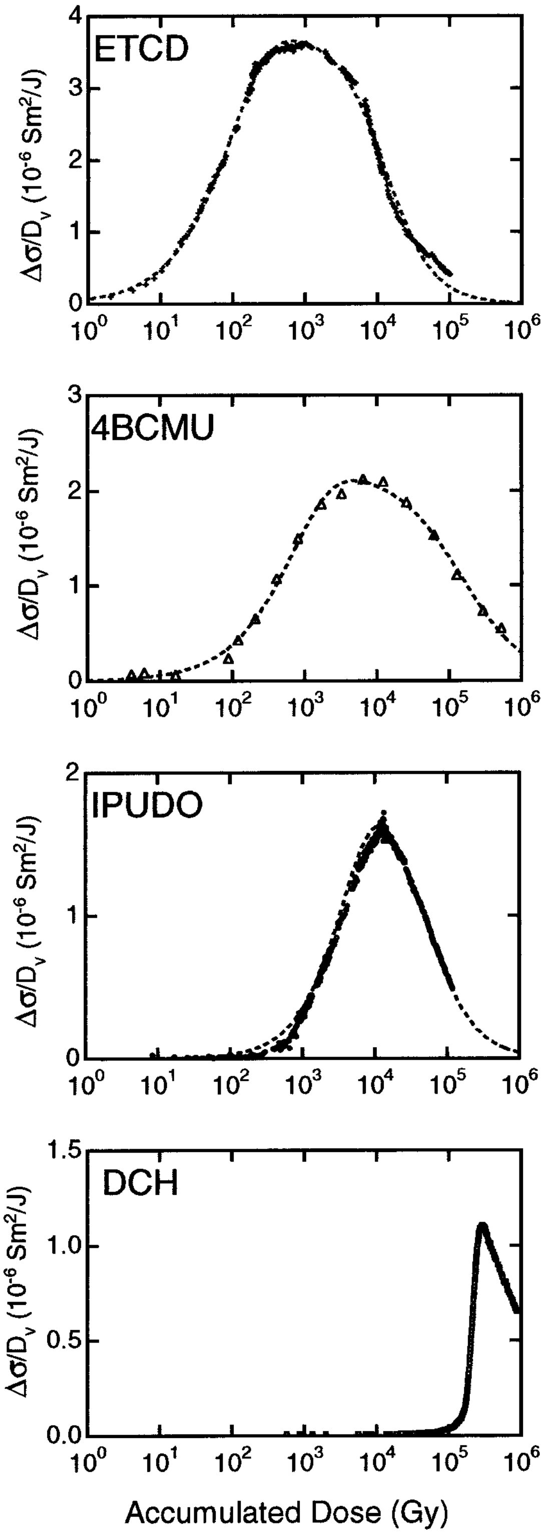

Figure 3. Dose-normalized conductivity for ETCD, 4BCMU, IPUDO, and DCH as a function of accumulated dose. The dashed lines through the data points are the result of fitting eq 6 to the experimental data.

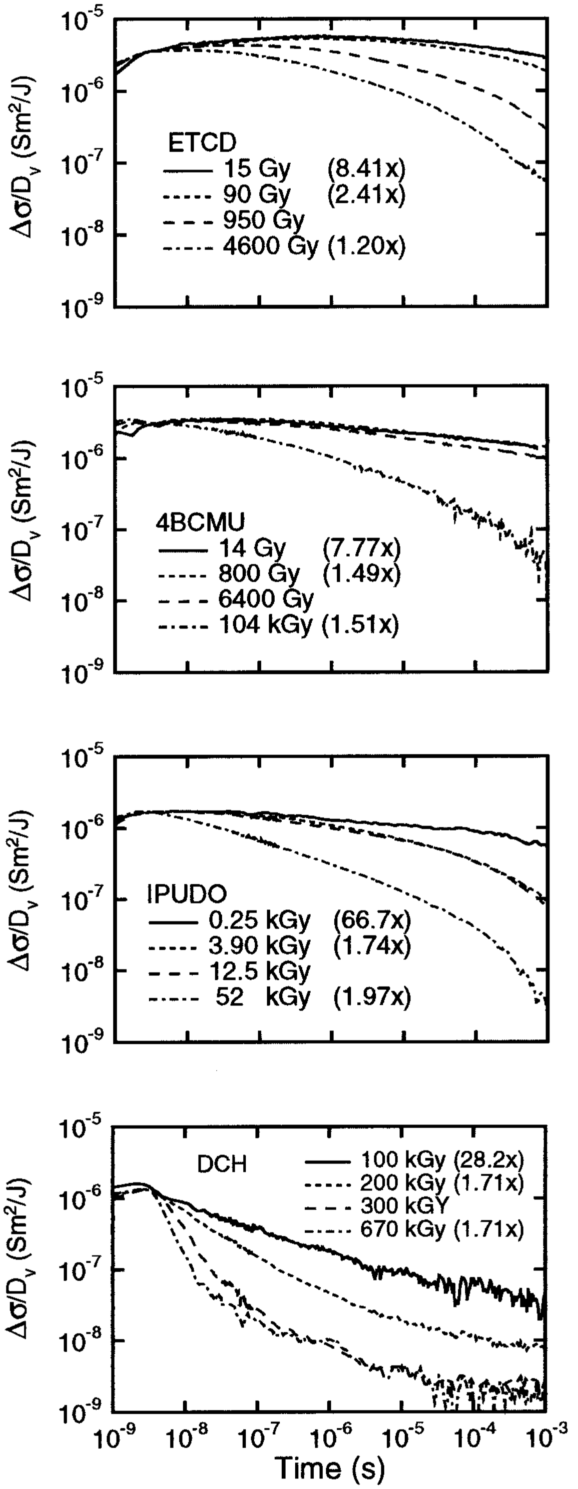

Figure 4. Effect of accumulated dose on the decay of the conductivity. To facilitate comparison of the decay kinetics, the conductivity transients were scaled with the factors between brackets. For ETCD, 4BCMU, and IPUDO 0.5 ns pulses were used, and the results for DCH were obtained using 5 or 20 ns pulses.

smaller than the maximum conductivity attained (see Figure 3). The low conductivity at low doses in DCH could be due to the charge transport on relatively short chains[37,40] or due to motion of holes along the carbazole stacks. At an accumulated dose near 10^5 Gy, where the conductivity starts to increase due to charge transport along the polymer chains (see Figure 3), the half-life of the conductivity decreases. This decrease is probably due to trapping of charge carriers in deep traps resulting from radiation damage.

Monomer-to-Polymer Conversion in 4BCMU. Since poly4BCMU can be dissolved in chloroform, the monomer conversion (*X*) could be determined as a function of the accumulated dose, as described in the Experimental Section. The results are shown in Figure 6. As can be seen from the inset, the conversion

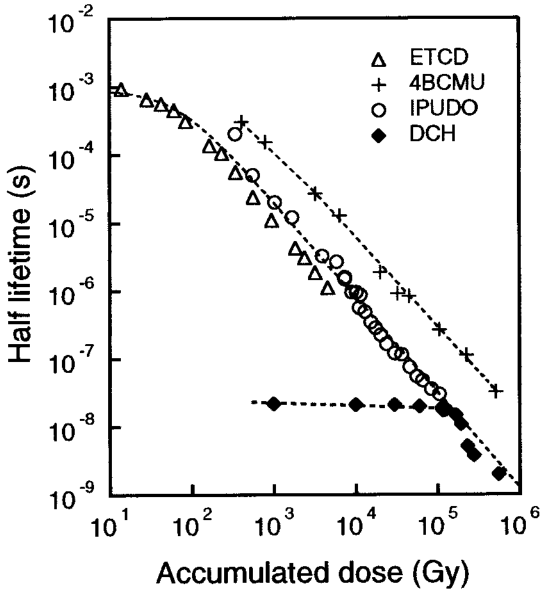

Figure 5. First half-lives of the conductivity as a function of accumulated dose in ETCD, 4BCMU, IPUDO, and DCH. The dashed lines are a guide to the eye.

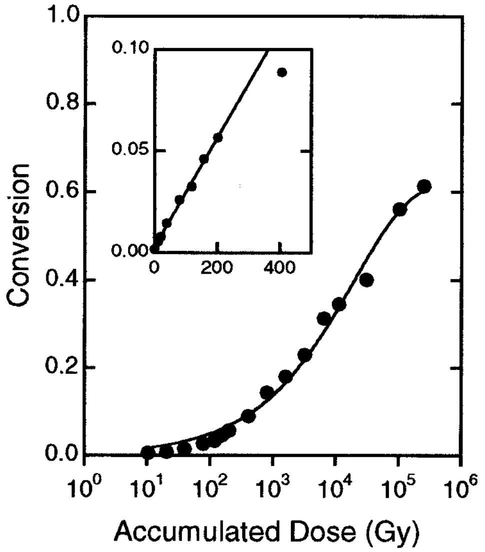

Figure 6. Monomer-to-polymer conversion for a 4BCMU sample as a function of the total accumulated dose. The inset shows the conversion for low accumulated dose on a linear scale. The drawn line represents a fit of the Avrami equation to the experimental data.

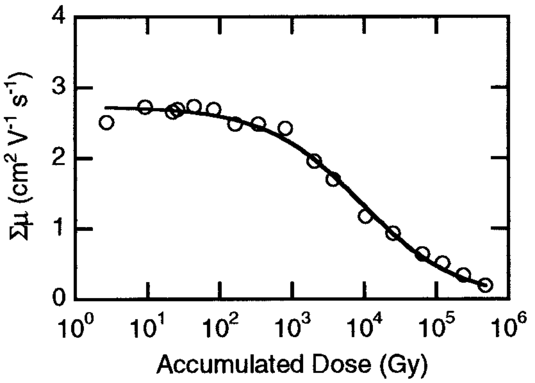

Figure 7. Sum of the mobilities of the charge carriers in the 4BCMU polymer regions as a function of the accumulated dose. The line represents a fit of eq 5 to the experimental data.

increases linearly for low accumulated dose; i.e., the conversion per unit dose (X/D) is constant. At higher accumulated dose, as can be seen in Figure 6, the conversion efficiency decreases. The efficiency decreases with the degree of polymerization since the polymer chains already formed can block the polymerization of new chains.[42]

It has been suggested by Bloor[43] that the conversion can be described by the general Avrami equation

$$X = X_{\max}[1 - \exp(-kD^n)] \qquad (3)$$

in which $X_{\max}$ is the maximum conversion and k and n are empirical constants. The good fit of eq 3 to the experimental data in Figure 6 shows that the present conversion data for 4BCMU can be described quite well by the Avrami equation. The optimal values of the fitting parameters were found to be $X_{\max} = 0.65$, $k = 0.01$ Gy$^{-0.5}$, and $n = 0.5$. The conversion maximum is considerably lower than the value of 0.92 reported by Patel[25] for an accumulated dose of 500 kGy. Note that in the present study the dose rate during the high-energy electron pulse is 4×10^9 Gy s^{-1}, which is 9 orders of magnitude larger than in the work of Patel, who used a ^{60}Co source.

Dose Dependence of the Charge Carrier Mobility. It can be seen in Figure 3 that the conductivity in 4BCMU decreases at accumulated doses exceeding 10^4 Gy, while the monomer-to-polymer conversion, X, still increases (see Figure 6). This indicates that the mobility of charge carriers on the polymer backbones decreases with accumulated dose. The decrease of the mobility with accumulated radiation dose could be due to increasing structural disorder. For instance in ETCD and IPUDO mechanical strains come about because of mismatch between the monomer lattice and the growing polymer chains.[44]

According to eqs 1 and 2, the sum of the charge carrier mobilities as a function of the accumulated dose, $\sum\mu(D)$, is

$$\sum\mu(D) = \frac{E_p}{e}\left[\frac{\Delta\sigma(D)}{D_v}\right]\frac{1}{[X(D)]} \qquad (4)$$

The sum of the charge carrier mobilities in 4BCMU was obtained using eq 4 with the dose normalized conductivity values, $[\Delta\sigma(D)/D_v]$, from Figure 3 and the conversion values, $[X(D)]$, from Figure 6. The results are shown as open circles in Figure 7. With the PR-TRMC technique it is only possible to measure the sum of the electron and hole mobilities and not the individual contributions. However, using a time-of-flight method, Fischer[45] has found that the major charge carrier in polydiacetylenes is the electron.

The mobility of the charge carriers is approximately 2.7 cm^2 V^{-1} s^{-1} for accumulated doses below 200 Gy and decreases at higher doses. For doses between 10^5 and 10^6 Gy, which are conventionally used to produce polydiacetylenes, the mobility has decreased by an order of magnitude. The line in Figure 7 was calculated using the empirical expression

$$\sum\mu(D) = \frac{\sum\mu(0)}{1 + (\beta D)^{\alpha}} \qquad (5)$$

The parameters used were $\sum\mu(0) = 2.7$ cm^2 V^{-1} s^{-1}, $\beta =$

1.1×10^{-4} Gy^{-1}, and $\alpha = 0.65$. Note that $\sum\mu(0)$ corresponds to the charge carrier mobility on nondegraded polymer backbones diluted in a monomer matrix.

The value obtained for $\sum\mu(0)$ is dependent on the assumption that only the charge carriers that are produced in the polymer regions will contribute to the conductivity. It could be possible, however, that charge carriers that are produced in the monomer regions in the vicinity of a polymer may migrate slowly to the polymer and thus may contribute to the transient conductivity. Such an effect could also explain the slow 10−25% increase of the conductivity after the pulse, which is observed at low accumulated dose in 4BCMU and ETCD, respectively (see Figure 2). Such an eventual correction would reduce the value of $\sum\mu(0)$.

It is also possible that the assumption that only the charge carriers that are produced in the polymer regions will contribute to the conductivity yields a too high value for the number of charge carriers, since no correction has been made for the eventual loss of mobile charge carriers due to charge recombination and/or trapping during to the pulse. Such a correction will increase the value of $\sum\mu(0)$.

From the present work it is not possible to give an accurate estimate of the uncertainty in the value of $\sum\mu(0)$, the charge carrier mobility on the nondegraded polymer backbones which are diluted in the monomer matrix. The value of $\sum\mu(0) = 2.7$ cm^2 V^{-1} s^{-1} as determined for 4BCMU in this work is comparable to the values found in polydiacetylene single crystals from time-of-flight measurements.[46−53]

Since ETCD, IPUDO, and DCH are insoluble, the polymer fraction could not be determined by the method used for 4BCMU. Assuming that the polymerization of these compounds can also be described by the general Avrami equation, eq 3, and that the charge carrier mobility depends on the accumulated dose in a manner similar to 4BCMU, eq 5, the dose-normalized conductivity data of Figure 3 can be described by

$$\frac{\Delta\sigma(D)}{D_{\rm v}} = \frac{X_{\max}\sum\mu(0)}{1 + (\beta D)^{\alpha}}\frac{e}{E_{\rm p}}[1 - \exp(-kD^{n})] \qquad (6)$$

Equation 6 could be fitted to the dose-normalized conductivity in DCH (see Figure 3). The optimal values of the fitting parameters were found to be $X_{\max}\sum\mu(0) = 0.4$ cm^2 V^{-1} s^{-1}, $\beta = 1.65 \times 10^{-6}$ Gy$^{-1.2}$, $\alpha = 1.2$, $k = 2.3 \times 10^{-28}$ Gy^{-5}, and $n = 5$.

The experimental data of ETCD and IPUDO could also be reproduced by eq 6; however, the uncertainty in the values of the fitting parameters was large. Since the molecular structure of ETCD and IPUDO is comparable to that of 4BCMU, it is assumed that the distortion of the polymer backbones by high-energy radiation is comparable. The latter would lead to a comparable reduction of the charge carrier mobility as a function of the accumulated dose. Therefore, the values of α and β for ETCD and IPUDO were fixed to those found for 4BCMU. The results of fitting the remaining parameters in eq 6 to the experimental data for ETCD and IPUDO are presented in Figure 3 by the dashed lines. These fits yielded a value close to 1 cm^2 V^{-1} s^{-1} for the product $X_{\max}\sum\mu(0)$ for both ETCD and IPUDO. It has been reported by Sandman et al.[54] that the maximum monomer conversion in both ETCD and IPUDO single crystals is close to 1. Using this value of $X_{\max}$ results in a charge carrier mobility for both compounds close to 1 cm^2 V^{-1} s^{-1}. For the parameters k and n in eq 6, values of 0.02 Gy$^{-0.75}$ and 0.75 were found for ETCD, while values of 2.8×10^{-5} Gy$^{-1.2}$ and 1.2 were obtained for IPUDO.

Conclusions

In this work ETCD, 4BCMU, IPUDO, and DCH diacetylenes were polymerized using high-energy (3 MeV) electrons. The radiation-induced conductivity after a single electron pulse was monitored as a function of the accumulated dose. The radiation-induced polymerization was found to be very different for these compounds. While the polymerization in the urethane-substituted diacetylenes (ETCD, 4BCMU, and IPUDO) immediately starts at low accumulated dose, the polymerization of DCH shows a threshold behavior. At high accumulated dose the radiation-induced conductivity decreases for all diacetylenes investigated. This is attributed to the introduction of defect sites by high-energy radiation, which reduces both the mobility and the lifetime of the charge carriers. An important result is that the reduction of the mobility and the lifetime starts at an accumulated dose, which is substantially lower than those used conventially for the production of polydiacetylene crystals.

Assuming that the extent of polymerization can be described by the general Avrami equation, it is found that the charge carrier mobility decreases with accumulated dose. For low accumulated dose, the charge carrier mobility on the polydiacetylene backbone is of the order of 1 cm^2 V^{-1} s^{-1}. For a dose between 10^5 and 10^6 Gy the mobility of the charge carriers in ETCD, 4BCMU, and IPUDO is about 1 order of magnitude lower than at low accumulated dose. Although such doses are required to reach the maximum monomer to polymer conversion, the present results indicate the conductive paths for charge transport have become far from optimal.

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