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Spectroscopic investigation of the photodegradation of polydiacetylene solutions†

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The degradation of chloroform solutions of *n*BCMU-polydiacetylenes [nBCMU$=$Bu^{n}O$_2$CCH$_2$NHCO$_2$(CH$_2$)$_n$], and related polymers with chiral urethane sidegroups, stored in Pyrex glassware under normal laboratory atmosphere and lighting was studied by the measurement of changes in the optical absorption spectrum. Both the magnitude and wavelength of the absorbance maximum decrease as the mean molecular weight is reduced by degradation. Measurements made on a reference sample stored in the dark showed that thermal degradation was negligible. Comparison with the spectra of a sample degraded by UV radiation ($\lambda < 300$ nm) shows that the degradation behaviour of white light exposed samples is distinctly different. While the precise temporal dependence of the degradation varies from polymer to polymer there is a discernible generic behaviour. This is also true for the shift in the energy of the absorption maximum when plotted against the decrease in absorption strength. A model based on the known dependence of the absorption maximum on polymer chain length is developed to describe the observed generic behaviour. Degradation by random scission followed by depolymerization is shown to be consistent with the experimental data. The measurements show that polydiacetylene solutions can be stored in the dark for up to four years but that solutions left open to the light can have shelf lives as short as ten days.

Introduction

Polydiacetylenes have attracted considerable interest over the last three decades. Initially, following the work of Wegner,[1] this interest centred on the high quality chain aligned, polymer single crystals formed by the solid state, topochemical polymerization of disubstituted diacetylene monomers.[2] These macroscopic crystal samples enabled the intrinsic properties of extended, conjugated, polymer chains to be explored.[3] The polymerization reaction was also extensively studied and a detailed picture of the reaction mechanism was elucidated.[4] From the early 1980s onwards there was a growing realisation that the polydiacetylenes provided the one-dimensional conjugated structures for which large third-order optical non-linearity had been predicted theoretically.[5] Over the last decade there have been extensive studies of the non-linear optical properties of single crystals, solutions and solution cast thin films of polydiacetylenes.[6–19] These have explored the microscopic origins of the non-linearity, determined the properties relevant for application in all optical devices and produced new polydiacetylenes designed to have enhanced non-linearity. Both single crystal and cast thin films offer properties suitable for application, and studies of polydiacetylene optical waveguides and devices have been published.[20–25]

Despite intense activity in both fundamental and applied research, comparatively little attention has been paid to the stability of polydiacetylenes. The polymers have routinely been subjected to differential thermal analysis and their decomposition temperatures recorded. However, detailed studies of thermal decomposition have been reported only for the bis-(toluene sulfonate) polymer, poly-pTS[26] and the bis-(*N*-carbazolyl) polymer, poly-DCH;[27–29] the chemical formulae of these polymers are given in Table 1. Chemical degradation for poly-DCH during attempts to render the crystals conductive by exposure to bromine has been studied thoroughly.[30,31] The photo-oxidation of poly-pTS crystals has been studied in some detail[32] but is not observed for poly-DCH, which also shows good stability under electron beam irradiation.[33]

The stability of soluble polydiacetylenes, which have larger pendent groups containing $(-\text{CH}_2-)_n$ units, see Table 1, has not been studied in much greater depth despite the intensive study of their optical and non-linear optical properties. Spectroscopic studies have explored the solvatochromism of poly-3BCMU and -4BCMU[34,35] and the nature of the photoexcited states in these materials has been investigated through studies of the photo-induced absorption spectra and their dynamics.[36] The non-linear optical properties of these polymers have been studied both for light propagating through thin films and for light waveguided in the films.[8,9,13,17,18,21,22] The related poly-9BCMU has received less attention but similar investigations of the non-linear optical properties have appeared.[11,24] Low loss, monomode, channel waveguides have been fabricated with poly-9SMBU and the quadratic electro-optical coefficient measured.[20,37] Degradation of solid films of the *n*BCMU polymers by ozone was investigated by Patel and Yee.[38] Photobleaching of poly-4BCMU spin coated films in air has been used to fabricate integrated waveguide structures.[39] This process has been studied in the related poly-3BCMU and physical and photo-oxidation mechanisms discussed.[40,41] The photodegradation of solutions of poly-3BCMU and -4BCMU was studied by Müller and Wegner[42] along with a number of other soluble polydiacetylenes. This study complemented earlier less comprehensive work.[43,44] Prolonged exposure of polymer solutions to ultrasound is also known to result in degradation.[45]

Table 1 Chemical formulae of soluble polydiacetylenes of the general formula $=(\text{CR}-\text{C}\equiv\text{C}-\text{CR})_m=$

acronym	R
pTS	$-(\text{CH}_2)-\text{OSO}_2\text{C}_6\text{H}_4\text{CH}_3$
pTS-12	$-(\text{CH}_2)_4-\text{OSO}_2\text{C}_6\text{H}_4\text{CH}_3$
DCH	carbazol-9-ylmethyl
*n*BCMU	$-(\text{CH}_2)_n-\text{OCONH CH}_2\text{CO}_2\text{C}_4\text{H}_9$
nR(*S*)MBU	$-(\text{CH}_2)_n-\text{OCONH C*H(CH}_3)(\text{C}_6\text{H}_5)$
DDA	$-(\text{CH}_2)_9-\text{OCOCH}_3$

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The published studies of solution photodegradation were undertaken by irradiating chloroform solutions with a high pressure mercury arc. The solutions bleach with both an overall loss of absorption strength and a shift of the absorption maximum to shorter wavelengths. This was taken to be the result of reduced mean chain length, which also gives rise to decreased solution viscosity and shorter elution times on gel permeation chromatography (GPC).[42] The degradation process was identified as random chain scission *via* a radical mechanism, with the possible involvement of the relatively unstable solvent, chloroform. The rate of degradation was observed to increase in the presence of triplet sensitisers, which provide free radicals, and oxygen, which can form either peroxyl radicals or singlet oxygen. Although these species may give rise to more complex degradation, their action was cited as supporting evidence for chain scission by radicals.[42] Photodecomposition occurred in a range of solvents, the decomposition rate varying in different solvents.[42,44] Slow spontaneous degradation was reported for poly-3BCMU in 1,2-dichloroethane at 70 °C.[42] However, no comparisons were made between the relative decomposition rates of different polymers, neither was the degradation studied under normal laboratory manipulation and storage conditions, *i.e.* under either ambient lighting or in the dark at room temperature.

The degradation of a series of related, soluble polymers has been studied under normal laboratory conditions. The polymers chosen were from the poly-*n*BCMU series with values of *n* ranging from 3 to 9 and the related chiral polymers poly-*nR*(*S*)MBU, which are known to possess helical backbones in the chain extended forms in solution and the solid-state.[46]

Experimental

The *n*BCMU monomers were prepared following the literature.[47] The monomers with chiral substituents were prepared in the same manner by condensation of either the *R*-(+)- or *S*-(−)-α-methylbenzyl isocyanates with the appropriate diacetylene diols. The starting diols were obtained by the oxidative coupling of terminal acetylenic alcohols.[48] Monomers were polymerized by ^{60}Co γ-ray irradiation with a dose in the range 10–50 MRad. Unreacted monomer was removed by repeated solvent extraction with acetone. Typical degrees of polymerization as determined by GPC were in the range 2000 to 3000.[49] These are in accord with values reported in the literature.[42–45]

Dissolution of the polymers in HPLC grade chloroform is slow at room temperature but is accelerated by gentle heating. The resulting bright yellow solutions were filtered through a glass frit to remove undissolved polymer and were stored in 100 ml Pyrex conical flasks, with Teflon sealed screw tops. The initial maximum absorbances were between 2 and 3, corresponding to concentrations in the range $1.1–1.6 \pm 0.1 \times 10^{-4}$ M. The solutions were stored either on a shelf, exposed to room lighting and indirect sunlight, or in aluminium foil wrapped flasks in a closed cupboard. All samples were subjected to similar thermal histories throughout the experiments.

Spectra were recorded using a Perkin-Elmer Lambda 9 spectrophotometer. Spectra were stored on floppy disk *via* a Perkin-Elmer data station interfaced to the spectrophotometer. The maximum absorption and its position were recorded automatically during each scan. Recorded spectra could be overlaid and difference spectra generated using the data station. Integrated intensities could not be determined directly from these data as spectra were recorded as a function of wavelength not energy. The graphical output was re-digitised and absorbance *versus* wavenumber data generated. The spectra were fitted using between one and eight unconstrained Gaussian functions to give an r^2 coefficient of determination greater than 0.999. The total integrated absorbance was calculated as the sum of the areas of the fitted Gaussian lines. This fitting was used to compare the variation in the values of the maximum absorbance, the total integrated absorption and the integrated absorption of the dissolved conjugated species during degradation, as described in the following section.

A fresh sample was pipetted from the storage vessel into a quartz cuvette prior to recording the spectrum. These samples were discarded after measurements. Spectra were recorded for samples from solutions that were stored for up to a maximum period of approximately 2000 d. For comparison purposes a solution of poly-9RMBU was degraded by irradiation with a 12 W low pressure Hg resonance lamp at a distance of 5 cm from a 1 cm square 6Q cuvette. Since the absorbance of chloroform at 253.6 nm is about 0.1 the whole of the solution is irradiated with the Hg resonance line.

Results

The spectra of all the solutions exposed to light show the same general trends as previously observed for UV-irradiated solutions of poly-pTS-12 in chloroform[42] and poly-DDA in dichloromethane,[44] *i.e.* an overall loss in absorption strength coupled with a shift of the absorption maximum to shorter wavelengths. There are, however, distinct differences in the behaviour of solutions exposed to UV radiation and those subjected to normal lighting and daylight. The spectra of the poly-9RMBU solution exposed to the 253.6 nm Hg resonance line for up to 20 min are shown in Fig. 1(*a*). These spectra show a small increase in absorption below 400 nm but with the intersection of successive spectra moving to shorter wavelengths, *i.e.* there is no isosbestic point. Identical behaviour has been reported for UV irradiated solutions of poly-DDA in dichloromethane.[44] The data for poly-pTS-12 in chloroform are cut-off at *ca.* 380 nm and so a precise comparison is not possible.[42]

In contrast, for the solutions exposed to lower intensity, broad band, visible radiation in these experiments, the increase in absorption strength during degradation occurs typically at wavelengths shorter than 300 nm. Typical spectral evolution is

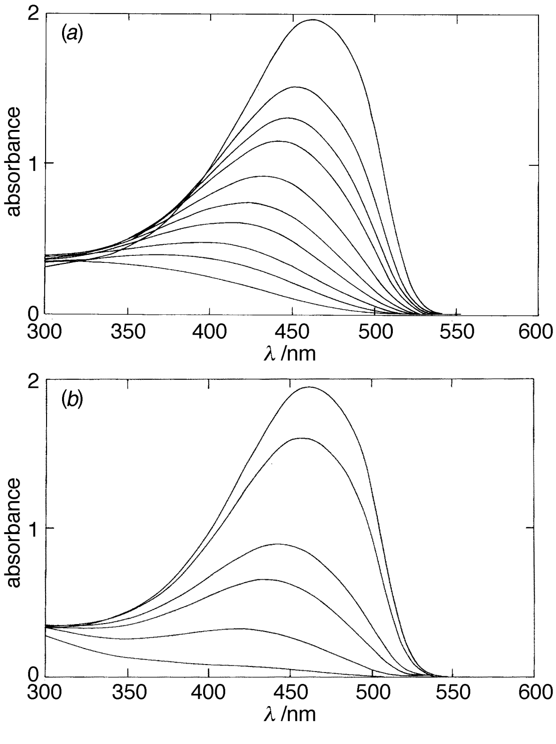


Fig. 1 Spectra of poly-9RMBU solutions in chloroform (*a*) exposed to UV light for periods of 0, 1, 2, 3, 5, 7, 9, 12, 15 and 20 min in order of decreasing absorption strength; (*b*) stored under ambient lighting for periods of 0, 16, 41, 56, 102 and 390 days in order of decreasing absorption strength

shown for poly-9RMBU, -3BCMU, -9BCMU and -9SMBU in Fig. 1(*b*), 2, 3 and 4. Similar changes in spectra were observed for poly-4BCMU, -4RMBU and -6BCMU. The spectral profiles are all similar but small differences are discernible; the most obvious is a weak shoulder at 350 nm in the spectra of poly-6BCMU. These minor differences probably reflect differences in the molecular weight distribution of the initial polymer samples.

Throughout the main phase of degradation, when the bulk of the polymer is lost, *i.e.* the integrated absorption intensity falls to between 20 and 30% of its initial value, an isosbestic point is visible near 300 nm, *cf.* Fig. 2–4. The behaviour becomes more complex in the later stages of the degradation process, *e.g.* poly-9BCMU beyond 150 d storage, Fig. 3. Comparison of the spectra for UV and white light degraded poly-9RMBU, Fig. 1(*a*) and 1(*b*), shows distinctly different spectral shapes after comparable reductions in absorption strength. These differences, though not large, show that the degradation process is not identical under UV and white light illumination.

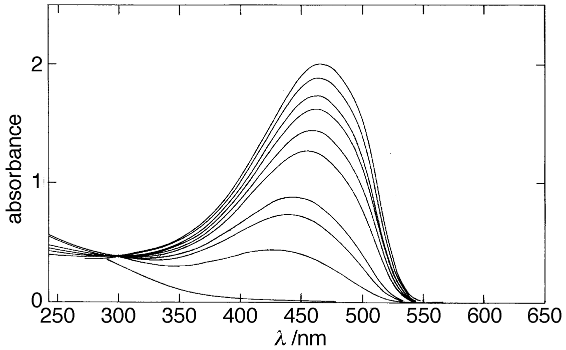


Fig. 2 Spectra of poly-3BCMU solution in chloroform stored under ambient lighting for periods of 0, 102, 218, 290, 470, 586, 856, 948, 1247 and 1964 days in order of decreasing absorption strength

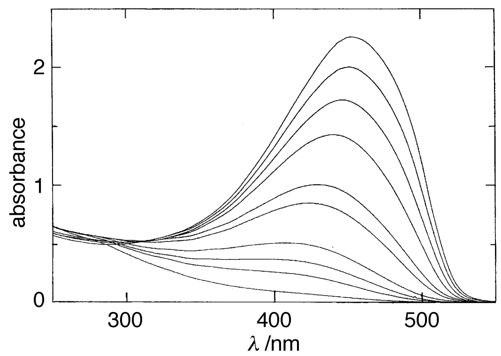


Fig. 3 Spectra of poly-9BCMU solution in choloroform stored under ambient light for 0, 36, 70, 102, 146, 163, 218, 245, 290 and 470 d in order of decreasing absorption strength

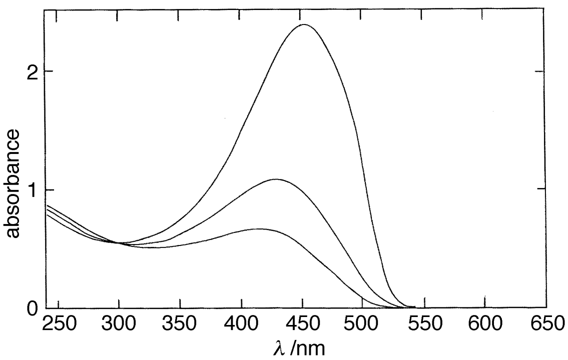


Fig. 4 Spectra of poly-9SMBU solution in chloroform stored under ambient lighting for 0, 72 and 144 d in order of decreasing absorption strength. An isosbestic point in apparent at 300 nm.

There are marked differences in degradation rate for the polymers studied. The polymers with the longest $-(CH_2)-$ sequences degrade most rapidly. This is indicated in Fig. 5 where the ratio of the maximum absorbance after a storage and exposure time t to the initial peak value, $A(t)/A(0)$, is plotted against t. The polymers with $n \geqslant 6$ have been completely bleached over a period of less than 300 d while those with $n \leqslant 4$ have suffered significantly less degradation. Indeed as shown in Fig. 5(*a*) the poly-3BCMU solution is fully bleached in a time in excess of 1500 d while the 4BCMU and 4RMBU polymers are not fully bleached even after 2000 d. It is notable that even after 1719 d storage in ambient light at room temperature in an oxygenated chloroform solution the poly-4RMBU absorption maximum is only just below half its initial value.

The numerical data that can be used to analyse the degradation process are: (*a*) the maximum absorbance, A, (*b*) the total integrated absorbance, ΣA, and (*c*) an integrated absorbance for the conjugated species present, ΣA_c. The first of these was available from the spectrometer output. The second was determined, as described in the Experimental section, for wavelengths longer than 300 nm. A typical set of digitised and fitted data is shown in Fig. 6. Determination of integrated absorbance of the conjugated species present required subtraction of an appropriate background from the measured absorption curves. This was not constant throughout the experiment since there were no degradation products present at the start of the experiment and the final, fully bleached samples had a negligible concentration of conjugated

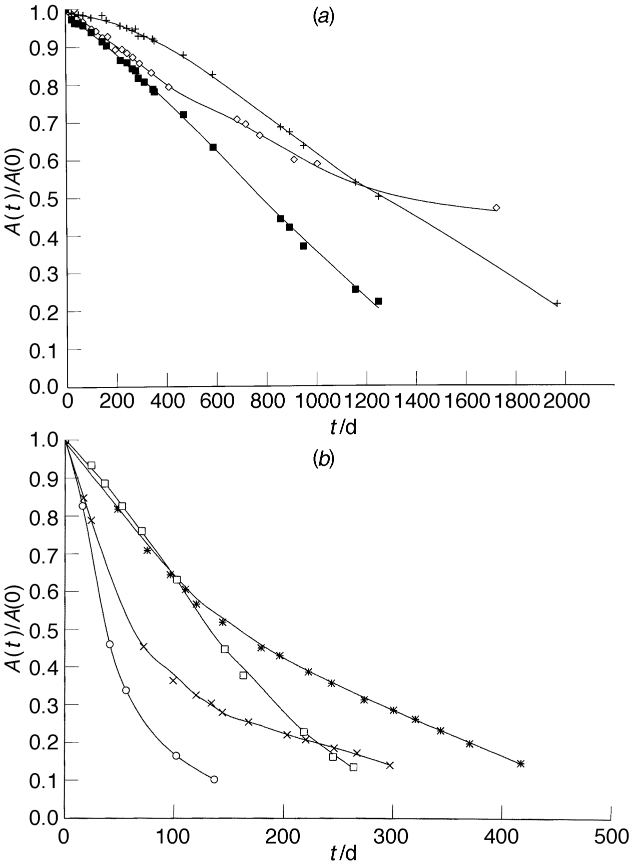


Fig. 5 Reduction in maximum absorption strength for degrading solutions as a function of time plotted as the ratio of the initial maximum absorption to the value measured after storage for a time t; (*a*)+, poly-4BCMU; ◇, poly-4RMBU; ■, poly-3BCMU; and (*b*) *, poly-6BCMU; □, poly-9BCMU; ○, poly-9RMBU and ×, poly-9SMBU. Lines are guides for the eye.

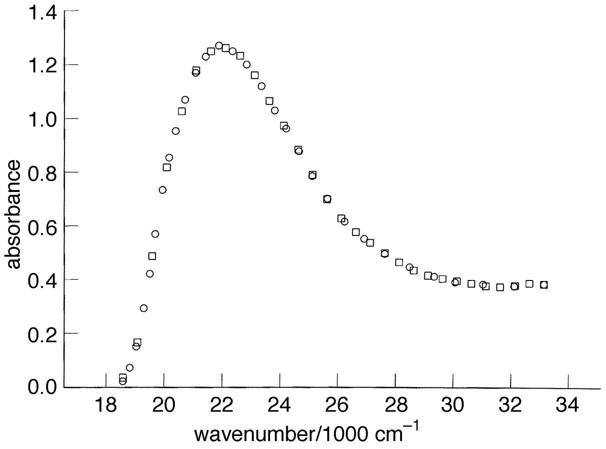


Fig. 6 Comparison of digitised data (○) taken from the spectrum of poly-3BCMU recorded after 586 d and the calculated spectrum (□) used to determine the total integrated absorbance

species. The spectrum of such samples, as shown for poly-3BCMU in Fig. 2, had an absorption onset at about 450 nm and the absorption rose above that of the initial spectrum at a wavelength below 300 nm, the position of the isosbestic point for this material. On the basis of these observations the calculations of integrated absorbance were performed, as noted above, for wavelengths greater than 300 nm. The integrated absorbance of the conjugated material was calculated for poly-3BCMU from the values of the total integrated absorbance initially, finally and after an exposure time t (ΣA_i, ΣA_f and ΣA_t) using eqn. (1).

$$\Sigma A_c = \Sigma A_t - \Sigma A_f \frac{\Sigma A_i - \Sigma A_t}{\Sigma A_i} \qquad (1)$$

The photodegradation can be characterised by the ratios of the measures A, ΣA and ΣA_c after an exposure time t to the initial value at time zero; the first of these was used in Fig. 5.

The values of the three ratios for poly-3BCMU are listed in Table 2 and plotted in Fig. 7(*a*). For comparison the ratios of the absorbance maximum and the total integrated absorbance for poly-9RMBU degraded in white and UV light are shown in Fig. 7(*b*) and 7(*c*) respectively. For the samples degraded in white light, the ratio of the total integrated absorbance and that of the maximum absorbance values are initially similar. This is to be expected because, in the early phase of degradation, the shift in absorbance maximum is small and the change in the shape of the spectrum is not marked. However, in the later stages of the degradation $A(t)/A(0)$ decreases more rapidly than the ratio of the total integrated absorbance. This is to be expected as there is still significant residual absorption between 300 and 500 nm, which contributes to the integrated absorbance, after an absorbance maximum is no longer discernible, *e.g.* Fig. 3. However, the ratios of absorbance maximum and the integrated absorbance of the conjugated material are similar throughout the degradation, see Fig. 7(*a*). Hence, the use of the ratio $A(t)/A(0)$ provides a simple, but reasonable basis for a comparison of the behaviour of the different polymers. Finally, it should be noted that the ratios differ most for the UV exposed poly-9RMBU sample. This is a consequence of the increase of absorbance below 400 nm, Fig. 1(*a*), which contributes significantly to the total integrated absorbance of the degraded samples. This further emphasises the different behaviour of UV and white light degraded samples noted above.

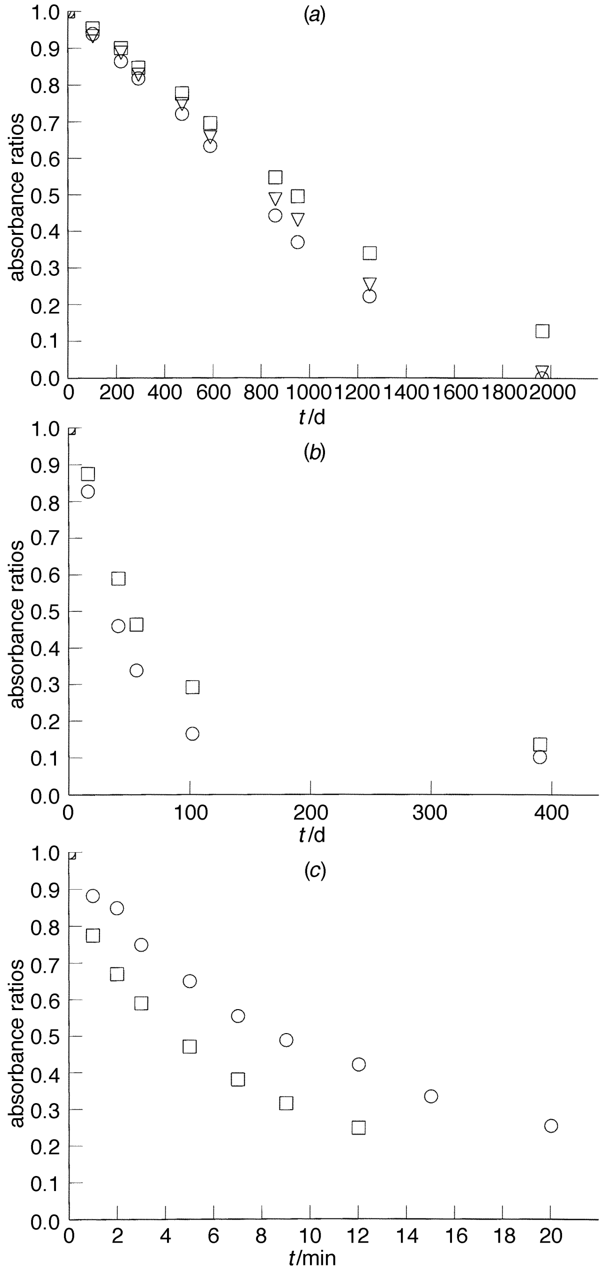


Fig. 7 Temporal variation of the ratios of absorbance maximum (○), the total integrated absorbance (□) and the integrated absorbance calculated with eqn. (1) (▽) for (*a*) poly-3BCMU, (*b*) poly-9RMBU (white light exposed) and (*c*) poly-9RMBU (UV exposed)

Table 2 Ratios of the absorbance maximum, total integrated absorbance and the integrated absorbance of the conjugated material calculated using eqn. (1), at time t to the initial values for poly-3BCMU

t/d:	0	102	218	290	470	586	856	948	1152	1247
$A(t)/A(0)$	1.0	0.94	0.87	0.82	0.72	0.63	0.44	0.37	0.25	—
$\Sigma A(t)/\Sigma A(0)$	1.0	0.95	0.90	0.85	0.77	0.70	0.55	0.50	0.34	0.13
eqn. (1)	1.0	0.93	0.89	0.83	0.75	0.66	0.49	0.43	0.25	0.02

At the longest exposure times it is possible that thermal degradation may play a significant role, since at elevated temperatures measurable degradation was reported to occur in 6 h.[42] To establish whether this was a relevant factor, a solution of poly-9RMBU was divided into two portions, one of which was exposed to ambient light, the other being kept in the dark under similar thermal conditions. The comparison of the degradation of these solutions is shown in Fig. 8. The light exposed sample showed the most rapid degradation of all the samples studied but the degradation in the dark was very slow. This sample was stored in the dark for 1200 d at room temperature and after a small initial decrease in absorbance, shown in Fig. 8, the subsequent fall was negligible,

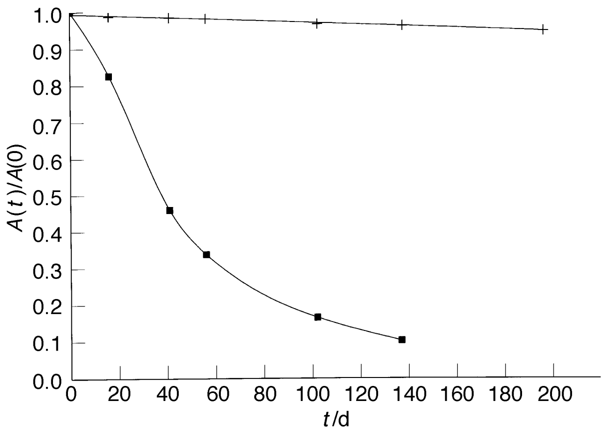


Fig. 8 Reduction in absorption strength ratios for poly-9RMBU; +, stored in the dark and ■, stored in ambient lighting. The solid curves are fits to the data.

with $A(t)/A(0)$ equal to 0.935 after 1200 d. Thermal degradation is, therefore, negligible for the slightly more stable $n=6$ and 9 polymers and cannot play a major role in the decomposition of the much more stable 3BCMU, 4BCMU and 4RMBU polymers.

Although the changes in spectral profile and peak absorbance during degradation of different polymers are not identical, the initial portions of the $A(t)/A(0)$ plots are approximately linear, as can be seen from Fig. 5, 7 and 8. As shown above, for poly-3BCMU the ratio of the maximum absorbance, $A(t)/A(0)$, can be taken as a reasonable representation of the change in the integrated absorption coefficient of the conjugated material. The initial slope of the curves in Fig. 5 can, therefore, be taken as a measure of the relative rates of degradation; values are listed in Table 3. These values can be compared directly for the groups of polymers (*a*) poly-3BCMU, -4BCMU and -9BCMU and (*b*) poly-4RMBU, -6BCMU and -9SMBU, within which the exposure histories were identical. The longer term behaviour of poly-9BCMU and both poly-6BCMU and -9SMBU may be influenced by differences in sample history, the initial 150 d being in the winter for poly-9BCMU and the summer for poly-6BCMU and -9SMBU and the converse for the later stages of degradation. However, the extensive use of artificial lighting in the laboratory would be likely to nullify any differences in natural light, the former being direct and the latter indirect. Variations in room temperature were small and unlikely to have an observable effect. In fact no long term variations are discernible in the traces for poly-3BCMU, -4BCMU and -4RMBU which extend over several years, as shown in Fig. 5(*a*). Note also that the slowing in degradation rate of poly-4RMBU after 500 d occurred at a time when the degradation rates of poly-3BCMU and -4BCMU were essentially constant, *i.e.* at about 750 d for these samples. Thus, the variations seen in Fig. 5 can be attributed to real differences in behaviour at the later stages of degradation while the variations in initial rate reflect a correlation between the structure of the pendent group and the resistance to degradation of the polymer.

Careful inspection of the spectra of the degrading solutions reveals little evidence of the occurrence of an enhanced population of short chain oligomers in the degradation products. For poly-9BCMU some very weak maxima can be discerned between 300 and 400 nm, Fig. 3. These are clearer when the spectra are plotted on an expanded scale, Fig. 9. Weak features have been observed in the same wavelength region in the fluorescence spectrum of a solution of poly-9RMBU either exposed to daylight or subjected to ultrasonic disruption.[50] Comparison with studies of analogous oligomers[51,52] suggests that the peaks at *ca.* 330, 360 and 385 nm correspond to molecules with two, three and four repeat units respectively. The absence of even these weak features from all the other spectra recorded suggests that the quantity of short chain oligomers produced by photodegradation with white light is extremely small.

Discussion

While the detailed shapes of the decay curves shown in Fig. 5 are not identical, they are all of the same general form. This is shown in Fig. 10 where the decay data are plotted on a normalised time scale, obtained by dividing the actual exposure time by the time taken for $A(t)/A(0)$ to fall to half its initial value ($t_{0.5}$). Values of $t_{0.5}$ are given in Table 3. The experimental results are dispersed about an exponential decay, plotted as a continuous line in Fig. 10. Such behaviour would occur if the

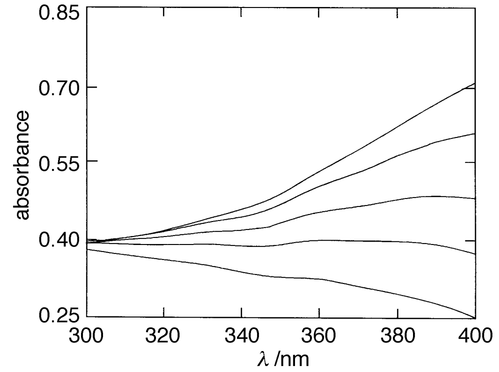


Fig. 9 Selected spectra for degrading poly-9BCMU solutions in the spectral range 300–400 nm

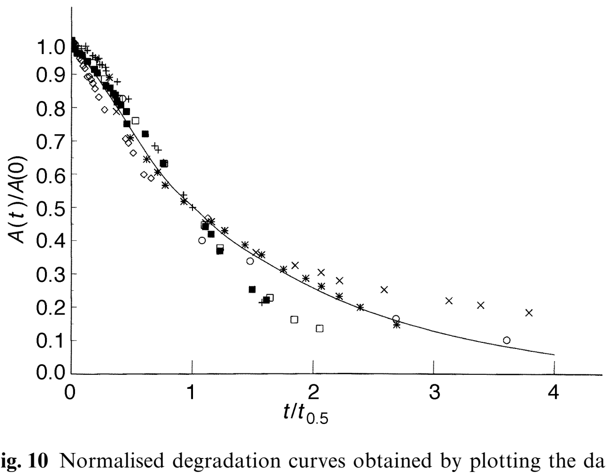


Fig. 10 Normalised degradation curves obtained by plotting the data of Fig. 5(*a*) and (*b*) against the ratio of the actual exposure time (t) and the time at which ($A(t)/A(0)$ equals 0.5 ($t_{0.5}$). The different polymers are denoted by the same symbols used in Fig. 5(*a*) and (*b*). The solid curve is an exponential decay.

Table 3 Initial rates of reduction in peak absorbance for polydiacetylene solutions exposed to room lighting (d[$A(t)/A(0)$]/dt in units of 10^{-9} s^{-1}) and the times for $A(t)/A(0)$ to fall to 0.5 ($t_{0.5}$ in days)

polymer	3BCMU	4BCMU	4RMBU	6BCMU	9BCMU	9RMBU	9SMBU
d($A(t)/A(0)$)/dt/10^{-9}s^{-1}	7.1	3.0	5.8	44	39	97	104
$t_{0.5}$/d	770	1250	1500	155	130	38	65

decay rate were directly proportional to the quantity of conjugated material left, *i.e.* if the degradation results from absorption by the polymer and the absorption spectrum remains constant throughout the degradation. The former constraint is clearly true for samples exposed to white light since the direct production of radical species by irradiation of the solvent is negligible. However, the latter constraint is not satisfied as the spectral profile changes during degradation as shown in Fig. 1–4. Allowing for the changes in spectral profiles, the curves in Fig. 10 should become slower than an exponential for times longer than $t_{0.5}$. The data for poly-6BCMU and -9RMBU lie close to the exponential curve throughout the degradation process. The degradation for poly-9SMBU is initially a little faster than the exponential but becomes slower at longer times. Poly-4RMBU appears to degrade somewhat faster than an exponential initially but this polymer only just exceeded a 50% reduction in maximum absorbance and showed a noticeable slowing of degradation, see Fig. 5(*a*). This behaviour appears to be atypical. The remainder of the polymers showed a behaviour exactly the opposite of that anticipated. The degradation curves for poly-3BCMU, -4BCMU and -9BCMU are initially slower than the exponential curve but beyond $t_{0.5}$ are faster than the exponential. These degradation curves are slightly sigmoidal in shape, which is suggestive of auto-catalytic action by the degradation products. An additional factor that could affect the degradation behaviour is the change in persistence length of the polymer chain as a function of molecular weight, as discussed below.

The small variation in the initial concentrations of the solutions, $1.1–1.6 \times 10^{-4}$ M is unlikely to affect the degradation behaviour. There is no discernible correlation between solution concentration and either the degradation rate or behaviour. The only apparent correlation between the structure of the polymers and the different degradation behaviour is that the polymers with chiral pendent groups do not show any sign of an auto-catalytic effect. However, the converse is not true since the achiral poly-6BCMU has a degradation curve close to exponential. There is a better correlation between the absolute degradation rate and the length of the $-(CH_2)_n-$ sequences in the pendent groups. The degradation rates for both chiral and achiral polymers are significantly slower for the $n=3$ and 4 polymers than the $n \geqslant 6$ polymers; see Fig. 5(*a*) and (*b*) and Table 3. The initial rates are lowest for $n=4$, slightly higher for $n=3$ and significantly greater for $n \geqslant 6$. For $n>6$ poly-9BCMU appears anomalous since its initial degradation rate is much less than that of the equivalent chiral polymers, poly-9RMBU and -9SMBU, and slightly slower than that of poly-6BCMU. For a given n the degradation rates of the chiral polymers are faster than those of the achiral polymer. The same overall ordering is observed for longer term degradation since $t_{0.5}$ is largest for $n=3$ and 4 and much smaller for $n \geqslant 6$. However, for poly-9BCMU $t_{0.5}$ is less than that for poly-6BCMU, giving a closer correlation with n.

It has been shown through extensive experimental studies that the solutions of polydiacetylenes in solvents such as chloroform behave as relatively stiff random coils with a ‘worm-like’ configuration described by the Porod–Kratky model, see ref. 45 and references therein. This structure results from the disruption of intramolecular H-bonds in good solvents, which allows the pendent groups to become disordered. Pendent groups with larger $-(CH_2)_n-$ sequences can adopt more disordered configurations with stronger steric hindrance and are more massive than those with small n values. Thus, they can be expected to produce greater backbone deformation. Distortion of the conjugated backbone from a planar conformation produces asymmetric π-electron distributions with a more reactive, radical-like character than for a fully extended backbone. This process is analogous to the formation of radicals in monomer molecules deformed by either thermal- or photo-excitation during the solid-state polymerization.[4] Thus, more deformed backbones will have a greater chemical reactivity with respect to either the chloroform, in which they are dissolved, or the co-dissolved oxygen or both potentially reactive substances. This qualitative model explains the observed trend of initial degradation rates to higher values and the normalised degradation times to lower values as the size of the pendent groups increases. Furthermore, steric hindrance prevents the chiral polymers from ever adopting a planar backbone.[46] Thus, they will always have a somewhat greater deformation than the equivalent achiral polymer, even in a good solvent, and hence a generally faster degradation rate.

As noted above, the dependence of the persistence length of the worm-like chain may also have some influence on the degradation behaviour. The Porod–Kratky model predicts a weak dependence of the persistence length (b) on the weight average degree of polymerization (n_w) [eqn. (2)],

$$b = [C_n \alpha_0{}^2 n_w{}^p l]/2 \qquad (2)$$

where l is the length of the repeat unit, C_n the characteristic ratio, which describes the chain stiffness due to steric factors, α_0 is the expansion constant, which depends on excluded volume and osmotic swelling, and p is an exponent, which is zero for a rigid, fully extended chain and $= ca.$ 0.24 for a randomly coiled polymer. For poly-4BCMU $\alpha_0 = ca.$ 1 and $p = 0.07$.[45] The persistence length falls from a value of about 30 nm when n_w is about 2000 to 24 nm when n_w is about 80. During the degradation process there will be an increase in curvature that, following the qualitative model set out above, would be expected to result in an increase in the rate of degradation. Thus, the different degradation behaviour observed is probably the result of the combined effects of the reduction in radiant energy absorbed, auto-catalytic activity of the degradation products and changes in persistence length as the degradation proceeds, all of which vary from polymer to polymer.

The spectra of all the samples studied have absorption maxima that shift to shorter wavelength as the degradation proceeds. This reflects a reduction in the average molecular weight of the residual polymer. Specific correlation between molecular weight and the absorption maximum has been established for poly-pTS-12,[42,43] and poly-4BCMU,[45] with a less complete evaluation for poly-3BCMU. These show that the relationship between these quantities is not transferable between different polydiacetylenes. The initial spectrum of the poly-4BCMU sample indicates a number average molecular weight of between 2000 and 3000 in agreement with GPC data.[45] When the energy of the absorption maximum is plotted against $A(t)/A(0)$ the curves have different origins but very similar shapes. A second universal plot is obtained by using the shift in the energy of the absorption maximum relative to its initial value, as shown in Fig. 11. The data for all the polymers are distributed in a narrow region about a common trend.

The behaviour shown in Fig. 11 can be explained in terms of the following model. The dependence of the energy of the first excited state and the molecular length is well established for polyenes. A similar correlation has been observed for molecules with an yne–ene bonding sequence with the energy varying as the inverse of the number of repeat units in the molecule $(1/N)$.[51,52] However, the extrapolation of this dependence to an infinite chain length gives a somewhat lower energy than that observed for polymer solutions. This is a consequence of the fact that the model oligomers lack the large pendent groups of the soluble polymers. Hence they are more rigid than the polymers, which are not fully extended planar molecules but worm-like chains with more localised, higher energy excited states. The experimental data from references 43, 45, 51 and 52 are shown in Fig. 12. The points for the oligomers and polymers are offset but have similar slopes. It therefore seems reasonable to use a linear relationship between the energy of the absorption maximum and $1/N$ for the

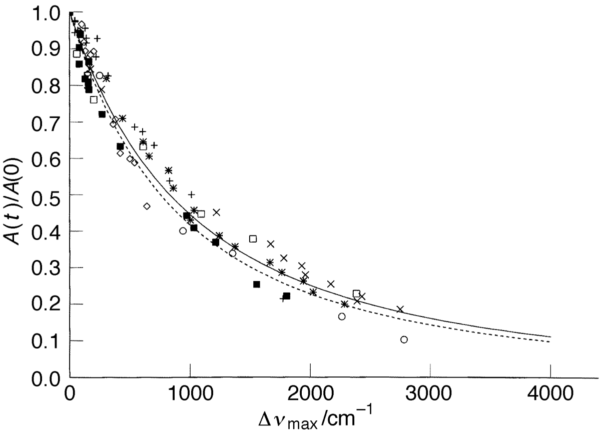


Fig. 11 Relative shift in energy of the absorption maximum, in units of cm^{-1}, *versus* $A(t)/A(0)$. The full and dash curves are calculated with eqn. (6) as described in the text. The different polymers are denoted by the same symbols as in Fig. 5 and 10.

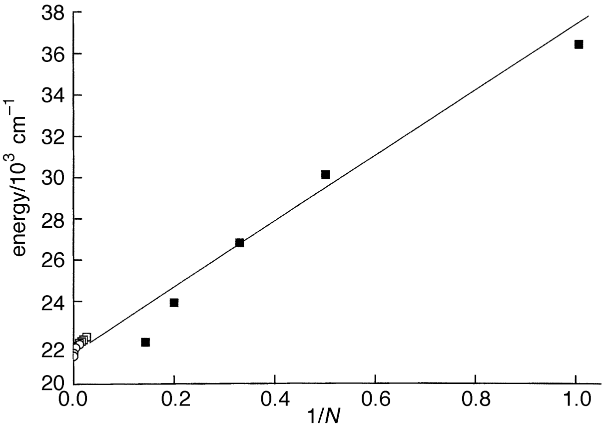


Fig. 12 Length dependence of the energy of the absorption maximum for model oligomers (■, average values calculated from ref. 51 and 52) and for soluble polydiacetylenes (○, poly-4BCMU[45]; □, poly-pTS-12[43]). The solid line indicates the trend of the energy *versus* $1/N$ for all the data points.

materials studied here [eqn. (3)],

$$E_N = E_\infty + \kappa/N \tag{3}$$

where κ is an empirical constant. Formally the absorption spectrum can be calculated as a sum of the absorption bands for chains of length N repeat units for all the lengths present in the sample.[53] For oligomers the absorption coefficient is proportional to N. However, such a dependence is inappropriate for long worm-like chains where the extent of the wavefunctions of the excited state is significantly smaller than the actual chain length. In this situation the absorption strength can be assumed to be independent of chain length. A simple approximation can be made for samples with a broad molecular weight distribution, a polydispersity of two is typical for polydiacetylenes,[43] and with broad, featureless bands, the longest oligomers have a broad absorption with very weak vibronic features.[52] This approximation is that the absorbance is proportional to N^2 since the band spacing becomes smaller as N increases as dE/dN is proportional to $1/N^2$.[54] Then we have eqn. (4),

$$A(t)/A(0) = N^2(t)/N^2(0) \tag{4}$$

and from eqn. (3) with N written as $N(t)$ and E_N as $E(t)$, eqn. (5),

$$N^2(t)/N^2(0) = [1 - \Delta E N(0)/\kappa]^{-1} \tag{5}$$

where $\Delta E = E(t) - E(0)$. Combining eqns. (4) and (5) gives eqn. (6).

$$A(t)/A(0) = [1 - f\Delta E]^{-2} \tag{6}$$

Eqn. (6) has one free parameter $f = N(0)/\kappa$ and was used to calculate the curves plotted in Fig. 11. With ΔE in units of cm^{-1} the continuous curve in Fig. 11 is for $f = 5 \times 10^{-4}$ cm and the dash curve is for $f = 5.5 \times 10^{-4}$ cm.

The data for the integrated absorbance shown in Fig. 7 can be replotted as a function of $t/t_{0.5}$ (Fig. 13) and the shift in absorption maximum (Fig. 14). These show that the UV degraded poly-9RMBU has a degradation behaviour close to exponential. However, the differences in the spectral profiles for UV and white light degraded samples (Fig. 1) result in the large differences for these samples seen in Fig. 14. The results in Fig. 14 can also be fitted to eqn. (6); the continuous curve, following the points for the white light degraded samples, is for $f = 4 \times 10^{-4}$ cm, a similar value to that used to fit the generic $A(t)/A(0)$ data in Fig. 11. However, the dash curve fitted to the UV degradation data requires a distinctly smaller value for f of 1.6×10^{-4} cm. The results shown in Fig. 10, 11, 13 and 14 indicate that absorption of the light by the solute molecules is the primary step in the degradation process for both UV and white light irradiation but that the subsequent degradation reactions are different.

As noted in the first Section, Müller and Wegner proposed random chain scission for poly-3BCMU and -pTS-12 on the

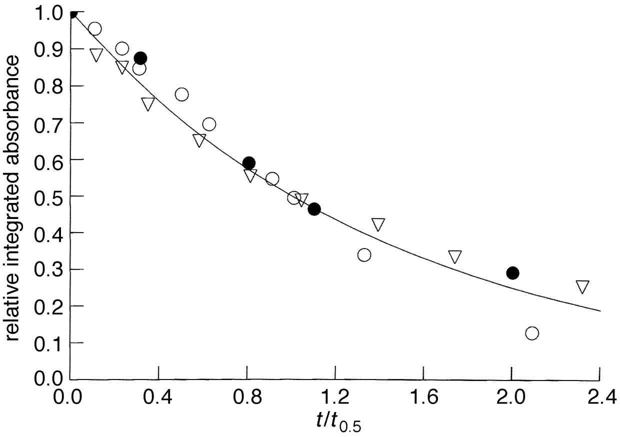


Fig. 13 Relative integrated absorbances of Fig. 7 plotted *versus* $t/t_{0.5}$; ○, poly-3BCMU, ●, poly-9RMBU exposed to white light and ▽, poly-9RMBU exposed to UV irradiation. The solid line represents an exponential time dependence.

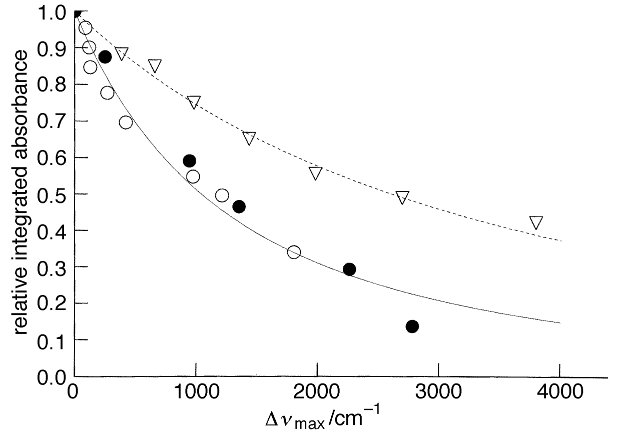
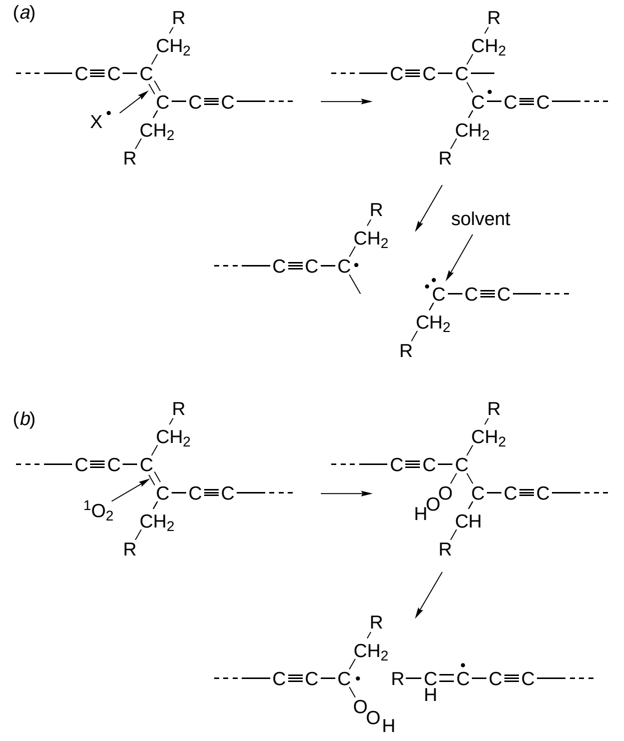


Fig. 14 Relative integrated absorbances of Fig. 7 plotted against the shift in energy of the absorption maximum; ○, poly-3BCMU, ●, poly-9RMBU exposed to white light and ▽, poly-9RMBU exposed to UV irradiation. The full and dash curves are calculated with eqn. (6) as described in the text.



Scheme 1 Proposed reaction mechanisms for scission of polydiacetylene–C=C– bonds (*a*) induced by radicals (after ref. 42) and (*b*) by singlet oxygen (after ref. 54)

basis of the change in molecular weight of UV degraded samples.[42] They suggested that the most likely degradation mechanism was initiation by UV excitation of the pendent groups, which is known to occur in organic compounds containing these groups, followed by free radical formation by either direct photolysis of the pendent group or a hydrogen abstraction reaction of photo-excited triplet states with the solvent or the polymer. Oxygen was shown to play an active role *via* either direct reaction with a radical to form a peroxyl radical or the formation of reactive singlet oxygen by the interaction of triplet oxygen with photoexcited triplet states. The latter would probably lead to the formation of hydroperoxides. Chain scission was then attributed to radical attack at either a double or a triple bond leading to the formation of a radical and a carbene as shown in Scheme 1(*a*). The reactive carbene was assumed to form a stable saturated chain end by reaction with either the solvent or other low molecular weight species present.

The spectra of films of poly-3BCMU degraded by either 360–405 nm radiation from a UV lamp or the 488 nm line from an Ar laser are dominated by the residual undegraded polymer since degradation proceeds progressively from the irradiated surface.[41] However, some increase in absorption was observed below about 400 nm similar to that of UV degraded solutions, Fig. 1(*a*) and ref. 44. Bands with peaks at *ca.* 280, 330 and 360 nm corresponding to monomers, dimers and trimers were observed during degradation but disappeared on completion of the degradation of the film. The films degraded exponentially as predicted by a model with a fixed quantum efficiency for the photodegradation of excited molecules. The degradation process was attributed solely to a photo-oxidation process as no degradation was observed *in vacuo*. Since neither the UV lamp nor the Ar laser can directly excite singlet oxygen triplet–triplet interaction of the photo-excited polymer and ground state oxygen molecules was identified as the reaction leading to singlet oxygen.[40] The attack of singlet oxygen was assumed to degrade the polymer successively through lower molecular weight oligomers to the monomer and then to unsaturated end products. However, the precise mechanism of the process was not discussed.

The data collected show that degradation of polydiacetylenes in solution is initiated by absorption of a photon by the polymer. For irradiation below 300 nm, as in reference 42, and for poly-9RMBU in Fig. 1, absorption by the pendent groups is the predominant process. However, for irradiation for wavelengths longer than 300 nm, *e.g.* white light and 488 nm Ar line, the predominant absorption is by the conjugated polymer backbone. On the evidence of this study the degradation reactions that follow from these two photo-excitation processes are different, *cf.* Fig. 1, 7 and 14. The former is well described by the random scission mechanism of ref. 42. The differences in absorption profile and the almost total absence of features associated with short chain oligomers for white light degraded samples suggests that photo-excitation of the polymer chain leads to a depolymerization process. Chain scission will degrade molecular weight but with an increase in the number of lower molecular weight chains present and an increase in absorbance for wavelengths greater than 300 nm [Fig. 1(*a*)]. Depolymerization will reduce the mean molecular weight with the increase in absorption occurring below 300 nm, where monomers and unsaturated degradation products absorb. While this general conclusion can be drawn from this study, in the absence of detailed chemical analysis of the degrading solutions the precise reaction mechanisms cannot be definitively identified.

The dependence of the degradation rate on the size of the pendent groups suggests that photo-excitation and reaction occurs at localised, deformed sites on the polymer backbone. Whether the initial step is due to reaction of the excited states with a radical character or of singlet oxygen generated at the site by triplet transfer cannot be determined without further experiments. Both processes would lead to the production of radical chain ends as shown for the reaction of singlet oxygen at a double bond in Scheme 1(*b*).[55] Random chain scission followed by depolymerization, which propagates for a short distance along the residual polymer chains, will lead to a rapid decrease in the degree of polymerization as the degradation proceeds.[56] If the depolymerization was initiated at the chain ends the degree of polymerization would fall in proportion to the fraction of polymer degraded. The shift in energy of the absorption maximum at $t_{0.5}$ indicates that the number average molecular weight has fallen from between 2000 and 3000 repeat units to between 30 to 50 repeat units. This large reduction indicates that depolymerization is initiated by random chain scission.

Depolymerization in solution will be aided by the dynamic deformation of the polymer chains. While thermal excitation is, on its own, insufficient to produce significant degradation at room temperature, the depolymerization following photo-excitation is likely to be aided by a thermal energy contribution. In contrast, solid films, while possessing local, static chain deformations, would lack this additional energetic contribution to the degradation process. Finally, we note that if photochemistry of the urethane groups played a significant role, as for UV irradiation, then faster degradation would be expected

Table 4 Suggested shelf-lives in days for polydiacetylene solutions in chloroform stored under ambient atmosphere and lighting at room temperature

polymer	3BCMU	4BCMU	4RMBU	6BCMU	9BCMU	9RMBU	9SMBU
shelf-life/d	170	400	180	30	30	10	10

for small *n* values, when the urethane group is closer to the polymer backbone. Some contribution from pendent group photochemistry could explain the slightly greater degradation rate for poly-3BCMU relative to poly-4BCMU and -4RMBU (Table 3).

Conclusions

Polydiacetylenes in solution in chloroform degrade when stored under normal laboratory conditions. The mechanism of degradation is different from that of UV induced degradation although the initial step in both instances is absorption of a photon by the polymer. The spectroscopic data favours depolymerization probably after singlet oxygen attack either at chain ends or where the polymer backbone is deformed from the ideal planar conformation. The latter process, leading to random chain scission, is favoured by the observed rapid decrease in molecular weight of the residual polymer. The influence of dynamic distortion of the backbone is indicated by the fact that the rate of degradation is greatest for the polymers with the largest pendent groups. The differences in rate are also reflected in the times taken for half the original conjugated materials to be degraded, $t_{0.5}$, given in Table 3. At this point, as noted above, the mean chain length will have been reduced from the range 2000–3000 repeat units to *ca.* 30–50 repeat units. Solutions stored for this length of time will, therefore, not provide films with properties comparable with those of the original polymer.

An effective shelf life under ambient illumination can be deduced from an estimate of the time to reduce the average chain length to half its original value. This will give chains with more than 1000 repeat units, which will give films with similar properties to those of films made from fresh solution. From the literature data this corresponds to a shift in the energy of the absorption maximum by $130 \pm 20\ \mathrm{cm}^{-1}$.[42,45] This criterion corresponds approximately to the condition that $A(t)/A(0)$ equals 0.9. The scatter in the measured shift in the absorption maxima at this level of degradation is large, *cf.* Fig. 11, and this condition errs on the safe side. For example for poly-3BCMU a shift of $130 \pm 20\ \mathrm{cm}^{-1}$ is observed for $A(t)/A(0)$ of the order 0.85. The recommended shelf lives are listed in Table 4. Thus, while storage under laboratory conditions of $n = 3$ and 4 polymers is possible for the order of six months, prolonged storage of solutions of polymers with $n \geqslant 6$ is not recommended without adequate precautions.

Storage of all the polymers under ambient atmosphere, but with the exclusion of light, enables even the most reactive polymers to be stored for periods in excess of four years. Solution life will also be extended by storage under an inert atmosphere. However, storage of solutions in the dark is probably a sufficient precaution since any gain from storage under inert gas is likely to be outweighed by the added inconvenience. For samples stored in the dark, minimising the periods of exposure to light is recommended.

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