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γ-Ray Polymerization of Urethane-Substituted Diacetylenes: Reactivity and Chain Lengths

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ABSTRACT: γ-Ray polymerization of two diacetylenes (3BCMU and 4BCMU) was studied, in particular at low doses below 5000 rad. Reactivity is very high, leading to large polymerization G values of 2.4×10^4 and 6.9×10^4, respectively. Molecular weight distributions were measured for 4BCMU, leading to $M_n \approx 2.6 \times 10^6$ (chain length 2.5 μm) with small dispersion. A large chain initiation G value, $G_i = 14$, is derived.

I. Introduction

Solid-state polymerization leading in the cases of interest to macroscopic conjugated polymer single crystals is a unique property of several substituted diacetylenes (DAs).[1,2]

The polymerization reaction

$$n(\mathrm{R{-}C{\equiv}C{-}C{\equiv}C{-}R'}) \Rightarrow {=}(\mathrm{RC{-}C{\equiv}C{-}CR'})_n{=}$$

can be induced thermally and/or by radiation (UV, X- or γ-rays, electrons, etc.) but the reactivity is greatly dependent on the nature of the substituents R and R′. Poly(diacetylene)s (PDAs) have raised a great interest since they form perfectly periodic conjugated polymer chains which can be modeled as 1-D crystals. The optical and electronic properties of the corresponding 3-D PDA crystals show a great anisotropy and have been the subject of many studies, particularly in nonlinear optics.[3]

Recently, we have been studying PDA chains dispersed in their crystalline monomer matrix, keeping the polymer concentrations so low ($<10^{-3}$ in weight) that chains can be considered as isolated in the sense that their mutual interactions are negligible.[4−6] The properties of these chains as 1-D crystals can be compared to those of isolated disordered single chains in dilute solutions, provided of course that the corresponding PDA is soluble.

The DAs in our study are urethane-substituted diacetylenes commonly known as 3BCMU and 4BCMU, where the side groups R and R′ are identical and have the general formula

$$-(\mathrm{CH_2})_n-\mathrm{OCO}-\mathrm{NH}-\mathrm{CH_2}-\mathrm{COO}-\mathrm{C_4H_9}$$

where $n = 3$ or 4, respectively. The corresponding polymers are soluble in organic solvents such as chloroform, THF, DMF, etc.[7] They thus can be studied in different physical states from the isolated chain in solution to gels, amorphous spin-cast films, and single crystals.

Urethane-substituted DAs are known to be highly reactive to irradiation but not thermally reactive.[8] This last property is useful in our study of isolated chains in their monomer matrix, since we need to keep the polymer content very low and constant over the experimental study.

The present paper concerns the polymerization of 3BCMU and 4BCMU under γ-irradiation. Since we are interested in very dilute solid solutions of polymer in the corresponding monomer crystal, our study is focused on the effect of low γ doses on crystals (section III). It was found that the reactivity is very high, leading to large polymerization G values. The reactivity of crystals is larger than that of powders, which have been formerly studied by Patel.[9]

Since these PDAs are soluble, chain length determination by standard methods of polymer physics is possible, though difficult for crystals at low polymer conversion because of the very small amount of polymer matter available. Results on poly-4BCMU are reported in section IV. The average molecular weights are very large. From these values, a chain initiation yield can be derived. Its high value is discussed in section V.

Up to now, the study of PDA chain length as a function of γ-ray-induced polymer conversion has been performed only once, on a non-urethane DA known as pTS-12.[10,11] In this case, chains formed during the early stages of polymerization are short (average number of repeat units per chain $N \approx 50$), while chains formed later in the polymerization process are much longer ($N \approx 1400$). This has been related to the large mismatch between monomer and polymer in the chain direction. To account for short chains in the early stages of polymerization, the effect of strain on the chains corresponding to this large mismatch has been invoked; indeed, a theoretical model[12] of the solid-state polymerization kinetics under strain predicts that short chains are formed in the early stages of polymerization when such a mismatch is present. As polymerization proceeds, this mismatch decreases, allowing formation of longer chains. In the present case of 3BCMU and 4BCMU, the situation is very different, as presented and discussed below.

II. Experimental Section

Materials. 4BCMU monomer was obtained from Lancaster Chemicals (67800 Bischheim, France), and 3BCMU had been

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synthesized by Dr. G. N. Patel.[7] Monomer powders were purified by recrystallization in acetone. Single crystals were grown by slow crystallization in acetone at 4 °C in the dark. They are obtained as transparent platelets; typical dimensions of the crystals studied were as follows: area, a few square millimeters; thicknesses, 50−100 μm for 4BCMU and 20−50 μm for 3BCMU. Very fine powders were prepared by rapid precipitation from acetone solutions upon addition of large quantities of hexane.

γ-Irradiations. γ-Irradiations were carried out at room temperature using ^{60}Co sources of different activities: dose rate ca. 25 rad/min for low doses (<2500 rad) and ca. 1800 rad/min for higher ones. The dose rates were measured experimentally using the $Fe^{II}-Fe^{III}$ reaction. The energies actually absorbed by the samples have been corrected taking into account the differences in electron densities between water and 4BCMU or 3BCMU. The correction factors ("electronic factor") were 0.915 and 0.908 for 4BCMU and 3BCMU, respectively.

Polymer Solutions. Pure polymer powder was prepared by extraction from monomers γ-irradiated to high doses (6−8 Mrad), yielding polymer contents of approximately 90 and 50% for 4BCMU and 3BCMU, respectively. Polymer solutions were prepared in chloroform.

Absorption Spectroscopy. Absorption spectra between 350 and 700 nm were taken at room temperature in a Beckman Acta III spectrophotometer. For crystals, light polarized either parallel or perpendicular to the chain direction was used.

Size Exclusion Chromatography (SEC). SEC is a powerful technique for measuring average molecular masses and therefore characterizing the molecular mass distribution.[13]

A differential refractometer (Waters R401) and a UV−visible absorption spectrophotometer (Beckman) operating at 350 nm were used as concentration detectors. A low-angle laser light scattering spectrometer (LALLS; Chromatix CMX 100) was used as the molecular mass detector. Its use has the advantage of yielding directly the relation between elution volume and molecular mass without calibration with monodisperse standards. Moreover, it allows molecular weight measurement using rather small amounts of polymer.

The eluent was distilled THF. Five columns from Polymer Laboratories (PL GEL) were used, with porosities between 50 and 10^5 nm. The upper exclusion limit of this column set is 4×10^7 g·mol^{-1} for linear polystyrene; from known persistence lengths,[14] this yields a limit of $(3-6) \times 10^6$ g·mol^{-1} for poly-4BCMU. Such molecular masses allow scattering measurement on poly-4BCMU in the Guinier range with the low-angle LALLS detector used.

Calibration of the SEC chain, including determination of volumes between detectors and apparatus constants, was carried out using various solutions of several monodisperse polystyrene standards.

Poly-4BCMU solutions were prepared in THF; a small amount (0.3%) of triethylamine was added in order to avoid degradation. Prior to injection, these solutions were filtered through 0.45 μm filters, and their concentrations were then controlled by UV−vis absorption: no loss of polymer was observed after filtration. Injected volume was 150 μL in all cases. Total elution time was ~1 h.

For data analysis, separately measured refractive index increment d*n*/d*c* and molar absorption coefficient ϵ values were used: $dn/dc = 0.20 \pm 0.01$, cm^3·g^{-1} at 632.8 nm, and $\epsilon = (3.0 \pm 0.1) \times 10^3$ L·mol^{-1}·cm^{-1} at 350 nm. The average molecular weights M_w and M_n were then determined using standard relations.[13]

III. Reactivity under γ-Irradiation

1. Method. One wants to know the exact polymer content in weight X in a sample irradiated by a given dose D. X is the ratio of the polymer mass over the total sample mass. The dose is accurately known by calibration of the used γ source as described above.

Polymer masses can be determined spectroscopically. The absorbance of a solution containing the amount of polymer to be determined is compared to that of a standard solution of known concentration in the same solvent at the same temperature. The absorption spectrum of a solution of pure polymer in a given solvent at a given temperature does not depend on the average molecular weight nor on polydispersity, provided the chains are not too short.[4] Standard solutions were prepared with pure 3BCMU or 4BCMU polymers dissolved in chloroform at concentrations of a few 10^{-5} mol·L^{-1} (expressed in monomer units). The corresponding absorption spectra are shown in Figure 1. Spectra of 3BCMU and 4BCMU polymers in this solvent are slightly different. In both these DAs, the monomer does not absorb in this wavelength range, and it was checked that its presence in the solution does not affect the polymer absorption spectrum. Therefore, it is not necessary to extract from the monomer the small amount of polymer formed by low-dose irradiation, and dissolving the whole sample is sufficient.

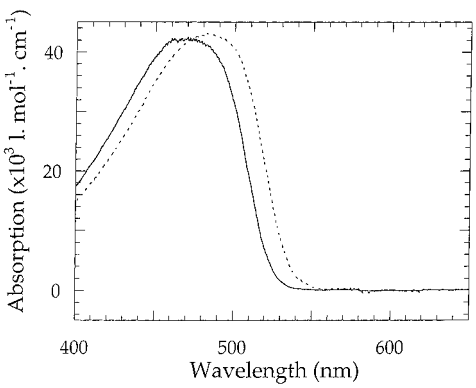

Figure 1. Absorption spectra of solutions of poly-3BCMU (dashed line) and poly-4BCMU (solid line) in chloroform at room temperature.

From the standard solutions, absorption coefficients α_{max} at the wavelength of maximum absorption are derived: for poly-4BCMU at $\lambda_{max} = 470$ nm, $\alpha_{max} = 42\ (\pm 2) \times 10^3$ L·mol^{-1}·cm^{-1}; for poly-3BCMU at $\lambda_{max} = 482$ nm, $\alpha_{max} = 43\ (\pm 2) \times 10^3$ L·mol^{-1}·cm^{-1}. α_{max} is defined by

$$I = I_0 \exp(-\alpha_{max} d)$$

where I is the transmitted light intensity, I_0 is the incident light intensity, and d stands for the optical path length through the solution.

Once these values of α_{max} are known, the exact polymer content X in any solid sample can be deduced from the optical density of the corresponding solution and the total sample weight.

An accurate determination of α_{max} is essential in this work, since all polymer contents are derived from absorption measurements. There are only very few data in the literature on the absolute absorption coefficients of PDA solutions. Shand et al.[15] found $\alpha_{max} \approx 40 \times 10^3$ L·mol^{-1}·cm^{-1} (see their Figure 6) for poly-3BCMU in $CHCl_3$, and Patel et al.[16] found $\alpha_{max} \approx 38 \times 10^3$ L·mol^{-1}·cm^{-1} (see their Figure 1) for poly-3BCMU and poly-4BCMU in $CHCl_3$. In all cases, the values of λ_{max} are the same as ours. Considering the many possible systematic errors, the agreement may be considered good. The slight red shift of λ_{max} for poly-3BCMU compared to poly-4BCMU corresponds to slight differences in polymer chain conformation in solution: it has been shown[17] that the persistence length of poly-

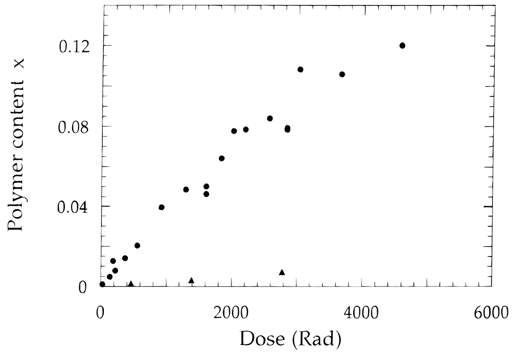

Figure 2. Polymer contents, *X*, in weight of 4BCMU crystals (filled circles) and fine powders (filled triangles) as a function of dose.

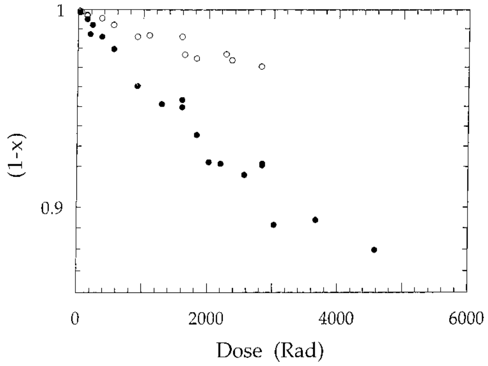

Figure 3. Semilogarithmic plot showing the fraction $(1 - X)$ of unreacted monomer in 3BCMU (open circles) and 4BCMU (filled circles) crystals as a function of dose.

3BCMU is larger than that of poly-4BCMU in $CDBr_3$, and that this corresponds to a red shift of the absorption.

2. Results. For 4BCMU crystals, Figure 2 (filled circles) shows the polymer conversion X in crystals against doses D up to 5000 rad. All doses were corrected using the electronic factor as described above. In his work on irradiated powders, Patel[9] found smaller reactivities than in our crystal data, by a factor of up to 6. This suggests that the crystal size and perfection play a part in the reactivity. This assumption was checked by irradiating crystals and very fine powders with exactly the same dose. The results on such powders appear as filled triangles in Figure 2: the corresponding reactivity is 1 order of magnitude smaller than that of macroscopic crystals. At high doses, larger than ca. 1 Mrad, our crystal results agree with those reported by Patel, suggesting that reactivity differences between powders and crystals fade out with increasing dose.

The dispersion of our crystal results is mostly explained by experimental uncertainties, without invoking different reactivities from crystal to crystal. Defects may, in principle, influence chain initiation and termination. Our observations suggest that in the present experiments defects do not play an important part in the crystals' reactivity. Thus we assume that the measured reactivity is about the maximum one, but the question about the ultimate reactivity of a perfect crystal remains open.

The reactivity $\Delta X/\Delta D$ for 4BCMU crystals appears constant up to $X \approx 0.1$. This amounts to having an exponent $n = 1$ in an Avrami equation. It can be seen as a further experimental confirmation of Wegner's original model of DA polymerization.[1] The constancy of reactivity is more clearly seen in Figure 3, where the crystal data for 4BCMU (filled circles) are plotted on a semilogarithmic scale. The slope is $s^{(c)} = 3.7 \times 10^{-5}$ rad^{-1}. In radiation chemistry, this reactivity is usually expressed as a G value, which can be defined here as the number G_p of monomer molecules incorporated in a polymer chain for 100 eV deposited in the sample. Using the relation $1\ rad = 10^{-5}\ J{\cdot}g^{-1} = 6 \times 10^{13}\ eV{\cdot}g^{-1}$, the derived value is $G_p^{(c)} = 6.9 \times 10^4$.

For powders, the corresponding values are $s^{(p)} = 2.5 \times 10^{-6}\ rad^{-1}$ and $G_p^{(p)} = 5 \times 10^3$. The studied powders are about 15 times less reactive than crystals.

For 3BCMU, Figure 3 shows (open circles) the polymer conversion in crystals against doses up to ca. 3000 rad. Here again, the reactivity is approximately constant but ≈3 times less than that of 4BCMU. The slope is $s^{(c)} = 1.2 \times 10^{-5}\ rad^{-1}$, leading to $G_p^{(c)} = 2.4 \times 10^4$. The reactivity of 3BCMU powders at low doses has not been studied in detail,[3] but it seems that the low-dose reactivity of crystals is larger than that of powders. Polymerization slows down considerably beyond doses of ~3 Mrad and, contrary to 4BCMU, complete polymerization is not observed even beyond 15 Mrad, a dose for which Patel[9] measured for 3BCMU powders a polymer content around 0.6. Our own measured values on crystals around 6 Mrad agree with Patel's value at the same dose. In 3BCMU as well, reactivity differences between powders and crystals hold at low polymer content only.

IV. Size Exclusion Chromatography

Five different samples were studied, as shown in Table 1. Samples labeled nC correspond to solutions prepared from crystals containing approximately n% of polymer in weight. Sample C_m was prepared from a mixture of crystals that contained 10−12% of polymer. Sample P was prepared from a very fine 4BCMU monomer powder that had been irradiated with the same dose as sample 10C. It contains approximately 0.6% of polymer, in agreement with the dose dependence curve shown in Figure 2.

For polymer concentration determination, it was observed that the UV absorption signal was much more accurate than the RI signal, although both gave the same results. Figure 4 shows the UV and LALLS chromatograms, as well as the relation between elution volume and molecular weight for sample 2C (see Table 1). Note that the peak broadening toward larger elution volumes is not related to a mass distribution. It is only due to retention of poly-4BCMU chains inside columns, as indicated by the nearly constant calibration curve $\log_{10} M$ versus V_e shown.

The average molecular weights M_w and M_n measured for the different solutions studied are given in Table 1. The two concentration detectors yield almost the same results, and the variations from sample to sample are within the experimental uncertainties, as demonstrated by the fact that sample 6C gave smaller masses than both sample 2C (corresponding to lower polymer content in the irradiated crystal) and sample 10C (corresponding to larger polymer content). So, for all samples for which $X \leq 0.1$, $M_w = (2.5 \pm 0.1) \times 10^6\ g{\cdot}mol^{-1}$.

Polydispersity indices are very low for all nC samples. This is a surprising result. The larger polydispersity of sample C_m indicates that M_w begins to decrease for chains formed beyond $X \approx 0.1$.

The powder sample P has a much smaller M_w value than the 10C sample prepared under the same conditions, and its polydispersity index is much larger. The

Table 1. M_w and M_w/M_n Determined with either RI−LALLS or UV−LALLS Coupled Detectors

sample	X^a	polym concn of injected soln (g·L^{-1})	RI and LALLS detectors: M_w (g·mol^{-1})	RI and LALLS detectors: M_w/M_n	UV and LALLS detectors: M_w (g·mol^{-1})	UV and LALLS detectors: M_w/M_n
10C	0.09	0.644	2.5×10^6	1.04	2.6×10^6	1.04
6C	0.065	0.745	2.2×10^6	1.03	2.3×10^6	1.04
2C	0.02	0.466	2.4×10^6	1.01	2.6×10^6	1.02
C_m	0.106	0.429	2.4×10^6	1.2	2.4×10^6	1.2
P	0.006	0.18			7.5×10^5	1.4

[a] From UV−visible absorption of the injected solution.

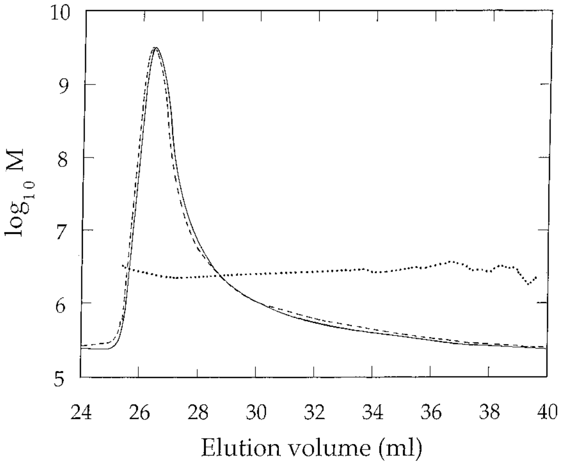

Figure 4. Elution of a solution of poly-4BCMU (sample 2C) in THF. The solid and dashed lines show the 350 nm UV and LALLS signals, respectively, in arbitrary units, as a function of elution volume. The dotted line shows the corresponding variation of polymer molecular mass M on a logarithmic scale (ordinates on the left): all elution fractions correspond to the same molecular mass.

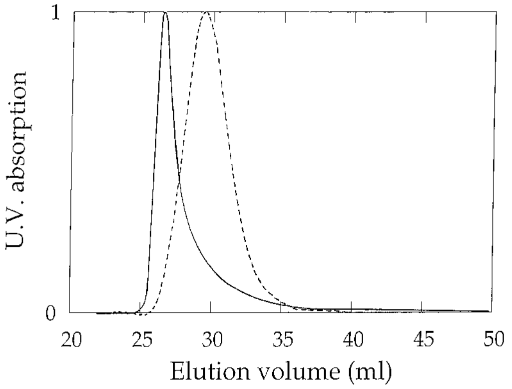

Figure 5. Comparison of the 350 nm UV signals for the crystal (sample 10C) and powder (sample P) irradiated with the same dose. Solid line: sample 10C; in this case also, all elution fractions correspond to the same mass. Dotted line: sample P, the broadening here is related to an actual molecular mass distribution.

corresponding chromatograms are presented in Figure 5.

V. Discussion

1. Chain Initiation in 4BCMU. From the values of G_p and M_n obtained in sections III and IV, respectively, a G value for chain *initiation* G_i in 4BCMU crystals is deduced

$$G_i = G_p\frac{m}{M_n} = 14 \pm 1$$

in other words, on average 1 chain is initiated each time ~7 eV are deposited in the crystal.

G_p is independent of X up to about $X = 0.1$ (Figure 3), and M_n is the same within experimental uncertainty for $X = 0.02$, 0.05, and 0.1. Therefore G_i is independent of X in the same range: it is highly unlikely that M_n would change much between $X = 0$ and $X = 0.02$, since the observed constancy of G_p would then imply a change of G_i exactly balancing that of M_n.

This value of G_i is very large. There are very few quantitative data on chain initiation in the solid-state γ-ray-induced polymerization of diacetylenes, such data require determination of G_p and M_n on the same sample, or two identical ones, and the determination of M_n requires in practice the obtained PDA to be soluble. To our knowledge, this has been achieved only once up to now, in the work of G. Wenz on TS-12.[10,18] He found a constant G_i value at the early stages of polymerization, as we do, but his $G_i = 1.2$, an order of magnitude smaller than the value found here.

Patel[9] studied the γ-ray polymerization of 4BCMU, presumably in the form of small crystallites, and obtained G_p values. Unfortunately, M_n was not measured but taken from data corresponding to much higher polymer content, i.e., larger doses, where M_n decreases considerably, so his inferred values of G_i are uncertain. Contrary to Wenz and to us, Patel found a dose-dependent G_p: the value for $X \approx 0$ seems comparable to our crystal data, but beyond $X \approx 0.01$, a $G_p \sim 1.5 \times 10^4$, which is intermediate between our crystal and powder values. So, although no quantitative conclusion can be drawn, qualitatively Patel's work supports the large G_i that we find.

Chain initiation can conceivably occur either from a neutral excited state of the DA or from an ionized monomer. The first process is documented in photopolymerization of DAs; the efficiency of the second, if it occurs, is unknown. It should be pointed out that the $-C{\equiv}C-C{\equiv}C-$ reactive centers of the 4BCMU molecule contain <10% of the total number of electrons in the material. Thus, >90% of the Compton electrons come from the side groups. They interact with the medium predominantly by generation of electron−hole pairs, and most of these pairs will be created on side groups as well. Their recombination will generate neutral excitations. The lowest neutral excited state of 4BCMU is located on the diacetylene at ≈4.2 eV,[19] corresponding to a weak band in the monomer crystal UV absorption spectrum. Thus, excitation can be funneled to the reactive center for polymerization.

Comparing the average energy needed to initiate one chain (7 eV) with this 4.2 eV energy, the difference seems very small; this implies that at most 40% of the total deposited energy is lost as heat and that the probability for chain initiation from an excited state is close to one. The origin of such a high reactivity is then still an open question.

In powders, M_n is $\sim 5 \times 10^5$, i.e., 5 times smaller than in crystals. Such an M_n corresponds to a chain length of ~0.5 μm. Recently, small 4BCMU crystals prepared—

as we did here—by rapid precipitation were imaged by electron microscopy and sizes of a few tenths of a micron were determined.[20] This suggests that the chain length in such crystallites may be limited by the crystal size. This is not enough to account entirely for the observed reduction of G_p, by a factor of ca. 15. Then in powders chain initiation seems less efficient than in good-quality crystals, by a factor of about 3: defects within the crystallites may also play a part in reducing the polymerization rate.

2. Chain Lengths. From our results, chain lengths do not depend significantly on polymer content up to $X = 0.1$. However, our M_n value is larger than the one determined from crystals containing ~65% of polymer, where $M_n \approx 6.7 \times 10^5$.[14] The derived value for N is then 1310. This means that chains are on the average 4 times shorter in these highly polymerized crystals.

M_w/M_n is close to 1 in our crystals. So, as long as the polymer content is low, $X \leq 0.1$, all chains grow to approximately the same length, suggesting an intrinsic length limiting mechanism.

VI. Conclusion

It has been shown in this paper that crystal size and quality indeed influence the polymerization rate of the DA 4BCMU under γ-irradiation. For single crystals of low polymer content ($X \leq 0.1$), a constant and very large chain initiation rate was found ($G_i = 14$). Chains grow to large length (2.5 μm) with a very small dispersion in length. These two striking properties raise interesting questions about the microscopic chain initiation, growth, and termination processes in DA solid-state polymerization.

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Appendix. Absolute Absorption Coefficients of Polymer Chains in Their Monomer Crystalline Matrix

Once the polymer content obtained after irradiation at a given dose is known, it is possible to determine accurately the absorption coefficient of the polymer in its crystalline monomer matrix by directly measuring the absorption spectra for crystals provided the thickness of the crystal is known. As for solutions, the absorption spectrum in the visible range (Figure 6) is only due to chain absorption. This absorption is so highly dichroic that spectra polarized parallel and perpendicular to the chain direction cannot be obtained accurately on the same sample. Spectra in the parallel polarization could only be obtained for X smaller than 10^{-3}. Spectra in the perpendicular polarization were measured up to $X = 0.1$ in 4BCMU and 0.03 in 3BCMU. No differences in the absorption spectrum shapes as a function of X were observed. The derived values for $\alpha_{\|}$ and $\alpha_{\perp}$ at room temperature are as follows: for 4BCMU at $\lambda_{\max} = 626$ nm, $\alpha_{\|} = (7.4 \pm 1.8) \times 10^5$ cm^{-1}, $\alpha_{\perp} = (2.0 \pm 0.3) \times 10^3$ cm^{-1}; for 3BCMU at $\lambda_{\max} = 635$ nm, $\alpha_{\|} = (1 \pm 0.2) \times 10^6$ cm^{-1}, $\alpha_{\perp} = (1.6 \pm 0.4) \times 10^3$ cm^{-1}. The dichroïc ratios derived from these values of α are 350 for 4BCMU and over 650 for 3BCMU. For 4BCMU, we could find a combination of crystal thickness and polymer content for which spectra in both polarizations could be obtained, though the spectrum in the parallel polarization was nearly saturated at $\lambda_{\max}$, while the perpendicular one was just detectable. The resulting observed dichroic ratio was then ≥200.

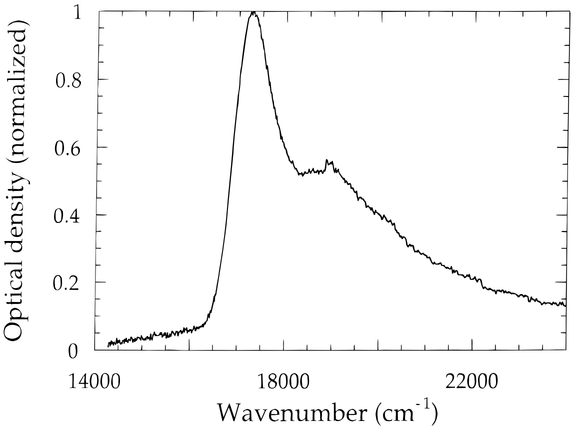

Figure 6. Room temperature absorption spectrum of 4BCMU isolated chains ($X = 10^{-4}$) in their monomer crystalline matrix.

$\alpha_{\perp}$ for 4BCMU is in agreement with our previously measured value.[4] $\alpha_{\|}$ for 4BCMU had not been measured directly, and we had inferred an $\alpha_{\|}$ value from the measured $\alpha_{\perp}$ assuming that the dichroic ratio of 120 we had measured on thin single films of fully polymerized 4BCMU[6] was still valid for diluted chains. It now appears that the dichroic ratios are much larger in the case of isolated chains. Indeed, Horvath and Weiser[21] have calculated $\alpha_{\|}$ for a bulk poly-4BCMU crystal by Kramers−Kronig inversion of the reflectance spectrum and found $\alpha_{\|} = 2.8 \times 10^5$ cm^{-1}. This value agrees with our measurements on single-crystal polymer thin films and also corresponds to a dichroic ratio of about 120.

The values of $\alpha_{\perp}$ found for the isolated chains are typical of all PDAs, once taken into account the actual number of chains per cm^3, i.e., the different side group sizes of different PDAs. It is the value of $\alpha_{\|}$ which appears especially large for isolated chains. This remains an open question.

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