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Evidence for increased chain stiffness of polydiacetylene in solution

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Evidence has been found of increased chain stiffness of isolated polydiacetylene molecules in solution, associated to an increased side-group interaction, and in at least one case, to an increased and more temperature dependent electronic conjugation length: Bromoform solutions of poly-3BCMU (3B) and poly-4BCMU (4B) were studied by visible and IR absorption spectroscopy and by small angle neutron scattering. The polymers are more rigid than in other solvents: for 3B, $b > 600 \text{ \AA}$ at 45°C and for 4B, $b = 420 \pm 40 \text{ \AA}$ at 25°C . Hydrogen bonding between neighboring side groups is observed, decreasing upon increasing temperature. For 3B, the visible absorption spectrum is slightly red shifted, the more so the lower the temperature, indicating an influence of chain stiffness on electronic conjugation length.

I. INTRODUCTION

Possibly the most intriguing and investigated property of polydiacetylene solutions¹ is their so-called chromic transition (color change) upon solvent quality variation produced by a change either of solvent composition² or temperature.³ The repeat unit of a polydiacetylene is $(-\text{CR}=\text{CR}'-\text{C}\equiv\text{C}-)_n$ where R and R' are side chains. Solutions of poly3- and poly4-BCMU, in which R and R' are $(-\text{CH}_2)_p \text{ OCONH}-\text{CH}_2-\text{COO}(\text{CH}_2)_3\text{CH}_3$ with $p = 3$ and 4, respectively, have been extensively studied, and for temperature dependent color change the best documented system is poly-4BCMU in toluene.⁴

Poly-*p*BCMU chains are highly conjugated, but the side groups are not. Thus, optical absorption in the visible corresponds to electronic transitions not involving the side groups, and the color change indicates a major modification of the polymer backbone electronic structure. In good solvents, these macromolecules are dissolved as isolated coiled worm-like chains.^{5,6} Thus, soluble polydiacetylenes offer a good opportunity for studying geometrical conformation, electronic configuration, and their interplay.⁷ In particular, one would like to understand the configuration change occurring at the chromic transition.

There are two conflicting models for these transitions in the literature. In one model, the color change is associated with aggregation,⁵ interchain interactions in the aggregates leading to straighter, less coiled, chains, hence larger electronic conjugation lengths. Indeed, the corresponding visible absorption spectra (of "blue" state for poly-3BCMU, "red" for poly-4BCMU) are very similar, if not identical, to those of the polymer solid obtained by precipitation from the solution.⁸ However, the transition conditions (temperature of solvent composition) are generally found to be independent of polymer concentration, and this has been considered as proving that the transition is an intrachain phenomenon^{4,9,10}. Molecules in the blue or red state may be less solu-

ble than in the yellow state, so aggregation may still usually occur at the transition, but it was argued that sufficiently dilute red or blue true solutions exist. Light scattering results are controversial^{4,5,11} but small angle scattering studies always show evidence of aggregation.⁶ However, this is not, in itself, a proof that the initial step of the transition is not intramolecular.

An important feature of poly-*p*BCMU polymers is that H bonds can be formed between neighboring side groups on the same side of the chain; ever since the discovery of chromic transitions it was claimed that formation of continuous lines of such bonds on both sides of a chain running parallel to the conjugated backbone was a key feature of the transition.²

Since, in good solvents, polydiacetylenes have similar persistence lengths, whether or not their side groups can form intramolecular H bonds,² it is plausible to assume that their worm-like chain conformation is entirely controlled by the conjugated backbone.

Cases where side groups would influence the polymer conformations could be considered as "intermediate" between the good solvent yellow solution and the red state, and might contribute to an understanding of the chromic transition. Claims of the optical detection of intermediate states have been made,¹¹ but optical absorption only shows coexistence of the two states: yellow and red for instance. In one case however, optical evidence for a different state ("orange" state) was obtained,¹² the color changing very gradually with temperature, with no evidence of a well-defined color transition, nor of hysteresis.

However, visible spectroscopy cannot by itself provide a proof of the existence of a well-defined intermediate state, nor of the absence of aggregation. On the other hand, small angle neutron scattering can prove the occurrence or nonoccurrence of aggregation.

It would be interesting to search for "precursor" effects to the transition—a change in the yellow state as the transition is approached. These were looked for in toluene solutions of poly-4BCMU, and no evidence for such effects was

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found at least down to 5° above the temperature where color change begins: Neutron scattering shows neither an increase in chain stiffness, nor change in average side-group conformation⁶ and IR absorption shows no change in H-bonding between side groups.¹³

In this paper, we look for the existence of true polydiacetylene solutions in which the polymer is more rigid than in the yellow state—or, as one might say, the “reference” state. The electronic conjugation on the polymer chain itself can be studied by visible absorption spectroscopy, information on the state of the possible H bonds is obtainable by IR absorption, and small angle scattering yields information on the conformation (geometry) of the polymer and its state as a single chain or an aggregate. All three experimental methods are used here: after describing materials and experimental methods used in Sec. II, we report on visible absorption, IR absorption, and small angle neutron scattering, in Secs. III–V, and the results are discussed in Sec. VI.

II. MATERIALS AND METHODS

The polymers used in this work were kindly provided by Dr. M. A. Müller,¹⁴ and were the same as those used in the neutron scattering study.⁶ The radiation dose used for the solid state polymerization was limited to 3 Mrad. This may explain why their polydispersity is less than most materials investigated to date.^{2,4} We have found that the molecular weight distribution, and presumably the amount of shorter chains, has some influence on the chromic transition.¹⁵ Some differences in literature data may be explained in this way.

Visible and IR absorption spectra were taken using a Beckman Acta III Spectrophotometer and a Bomem Interferometer, respectively. A furnace equipped with “Infrasil” quartz cells was built, allowing 0.1° stability between room temperature and 80 °C, with fast thermal equilibration. Typical concentrations were $2\text{--}5 \times 10^{-4}$ g/ml for visible and 10^{-3} g/ml for IR spectra.

Small angle neutron scattering experiments were performed at ILL, Grenoble, France, using the diffractometers D11 and D17. The scattering vector range was 5×10^{-3} to 7×10^{-2} Å⁻¹.

Polymer concentrations were 1 or 1.5 mg/ml. Data were processed and put on absolute scale using the same standard procedures as before.⁶

The Bromoform used contained as usual 0.1% to 0.3% ethanol as a stabilizer. One should therefore consider the possibility of preferential adsorption. Still, slow degradation may occur at elevated temperature and under visible light illumination. This degradation is considerably slowed down by the addition of 0.1% to 0.4% of triethylamine.¹⁴ It was verified already earlier that presence of the latter has no influence on the results. All data were taken under conditions in which degradation was negligible during the whole measurement time.

III. VISIBLE ABSORPTION

Spectra of a poly-3BCMU solution in CHBr₃ at several temperatures are shown on Fig. 1: There is a continuous red shift from 80 to 30 °C, but the absorption band remains

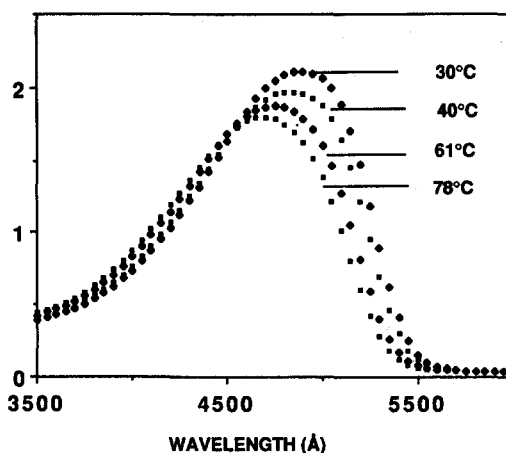


FIG. 1. Visible and near UV absorption of a 3B solution in CHBr₃ at four temperatures from about 30 to 80 °C.

structureless and no long wavelength absorption (around 600 nm) is detected. If the concept of conjugation length is applicable, this may correspond to a continuous change of conjugation length distribution, with an increase of the average length. The small apparent increase in oscillator strength would be in agreement with that point of view.¹⁶

In this temperature range, there is no evidence of any kinetic effect: There is no hysteresis, and no detectable change of the absorption spectrum over two hours at 30 °C for instance, i.e., the relative absorbance change is less than 1% at all wavelengths. The existence of very slow processes, taking days or more, is not ruled out by our present experiments.

If, however, the same solution is cooled down, for instance near 10 °C (just above the melting point of CHBr₃) for 10 min, and the absorption spectrum recorded near 20 °C immediately after, a different spectrum is obtained (Fig. 2). It shows coexistence of yellow and blue spectra, similar to that observed at 20 °C in a 82% CHCl₃/18% THF mixed solvent [Fig. 2(a)], or generally in several mixed solvent systems.^{2,11,13} These color changes in CHBr₃ show large hysteresis, as does, for instance, the thermochromic transition of 4B in toluene,¹⁷ and at longer times precipitation is observed.

In conclusion, the spectral changes observed above 30 °C are different from the usual chromic transition. If the latter is associated to aggregation, the former may not be. This is suggested by the absence of hysteresis. The continuous variation of the maximum absorption wavelength, and the absence of any new longer wavelength absorption, also suggest that no new electronic species appear on cooling. The final answer to the question of aggregation is provided by SANS (Sec. V).

The temperature dependence of the wave number of maximum absorption ν_m of *p*-3BCMU in CHBr₃ and of several other solutions is reported in Fig. 3. Clearly, 3B in CHBr₃ shows a special behavior: ν_m is smaller and changes more rapidly with *T*, 17 cm⁻¹/K compared to the shift of 11 cm⁻¹/K found in the other cases. The fact that 4B in CHBr₃, in DMF and, in toluene above the color transition temperature and 3B in DMF all have similar spectra, indi-

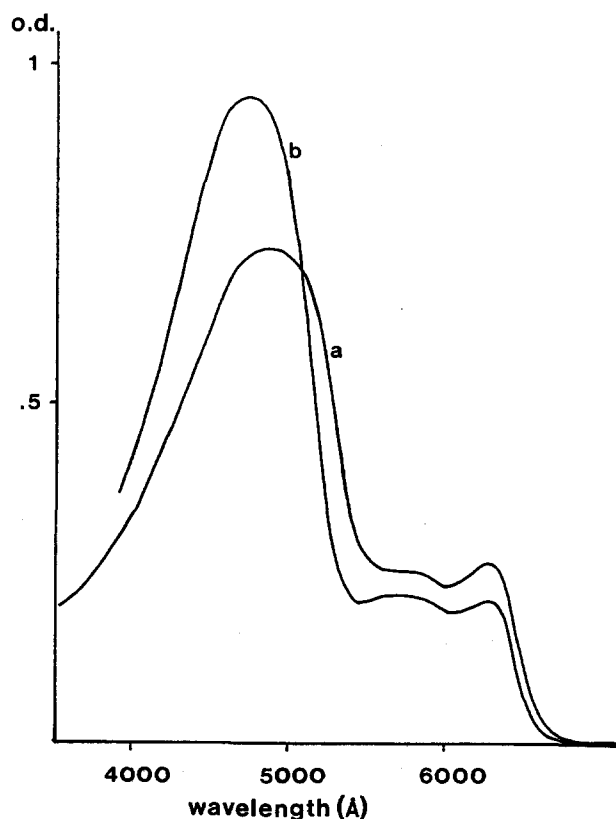


FIG. 2. Absorption of solutions showing simultaneously a yellow and a blue spectrum (the latter presumably associated to aggregates) at room temperature. (a) 3B in 82% CHCl_3 -18% THF. (b) 3B in CHBr_3 .

icates that this difference is not simply a solvent effect. It seems likely that electron conjugation is more extended in 3B in CHBr_3 than in the reference yellow state in DMF. If there is a relation with chain rigidity, one would expect 3B in CHBr_3 to be more rigid as well.

Note that the visible absorption of 4B in CHBr_3 and its variation with temperature do not differ significantly from that of the reference yellow state.

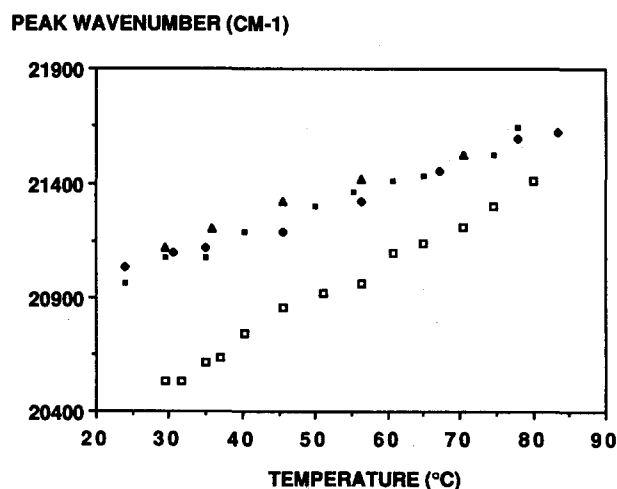


FIG. 3. Temperature dependence of the peak absorption wavelength of solutions of 3B and 4B in several solvents. \square 3B in CHBr_3 , \blacksquare 4B in CHBr_3 , \blacklozenge 4B in DMF, \blacktriangle 3B in DMF.

IV. INFRARED ABSORPTION

Formation of hydrogen bonds between CONH groups of neighboring side groups may contribute to this increased rigidity. In fact, this has been assumed ever since the discovery of these materials.²

Several absorption bands correspond to CONH vibrational modes.^{2,18} We have studied the region 3300 – 3450 cm^{-1} , where the absorption is most sensitive to changes in bonding, since the corresponding mode is almost purely a NH stretch.¹⁹

The frequency and oscillator strength of the corresponding absorption are both very strongly dependent on the bonding situation. Free NH groups absorb near 3435 cm^{-1} whereas N–H groups engaged in H bonds absorb much more strongly and at lower frequency^{19,20}. A regular array of H bonds between neighboring side groups in 3- and 4-BCMU polymers, as found in the polymer crystals and in red 4B gels in toluene, corresponds to absorption near 3320 cm^{-1} .⁸ However, absorption at intermediate frequency with intermediate strength may exist, as has been shown in other cases as well.¹⁸

Ethanol, present as a stabilizer, has a broad absorption band in the same region. As the amount of stabilizer may not be constant in various samples, fresh solutions were always used and solvent absorption was measured at the same temperature at the same time as solution absorption, so that it could be reliably subtracted.

The temperature dependence of the IR absorption of poly-3BCMU in CHBr_3 between 3200 and 3500 cm^{-1} , after subtraction of the background solvent and ethanol absorptions, is shown on Fig. 4. The band on the right, whose position is independent of T , is associated to free (non-H bonded) NH groups. Its intensity increases from 30 to 65 $^\circ\text{C}$, then stays constant. The band on the left shifts towards higher frequencies as T increases, and its intensity decreases much more rapidly. It is also much broader. The absorption maximum is never observed at 3320 cm^{-1} . Qualitatively, this can be understood by assuming that the N–H groups which are not free take a whole range of configurations, which average

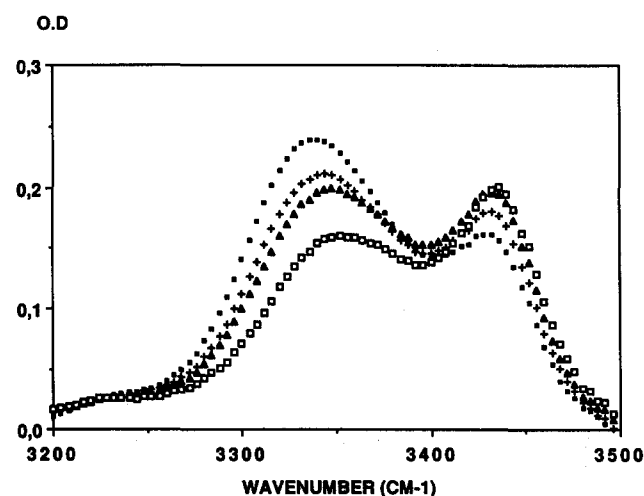


FIG. 4. IR absorption (after background subtraction) of a 3B solution in CHBr_3 at four temperatures from about 30 to 80 $^\circ\text{C}$. \blacksquare : 30 $^\circ\text{C}$; \blacktriangle : 40 $^\circ\text{C}$; $+$: 51 $^\circ\text{C}$; \square : 78 $^\circ\text{C}$.

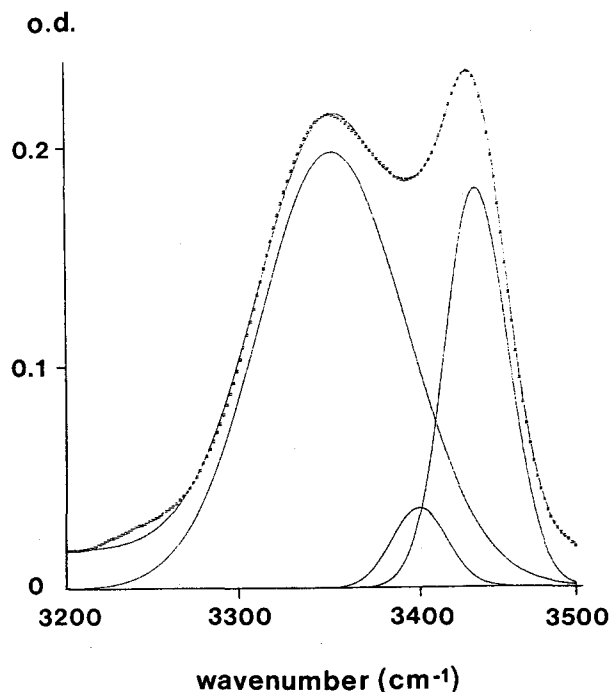


FIG. 5. A three-Gaussian fit of an IR absorption spectrum at 65 °C. Gaussian band parameters are, respectively, for the amplitude (in arbitrary units), the FWHM and the peak position in cm^{-1} : 0.20, 100 cm^{-1} , 3355 cm^{-1} ; 0.04, 37.4 cm^{-1} , 3404 cm^{-1} , and 0.18, 43 cm^{-1} , 3439 cm^{-1} .

becomes farther from the “perfectly bonded” one as T increases, the average oscillator strength decreasing correspondingly.

In order to get a more quantitative evaluation, the following fitting procedure was used: The absorption obtained after background subtraction, as shown on Fig. 4, was fitted as a sum of Gaussians, their position, width, and height, being adjustable. Using two Gaussians, one obtains a fairly good fit, but still imperfect between the peaks. Adding a third Gaussian there, very good fits are always obtained. The third Gaussian is always a minor contribution, and the posi-

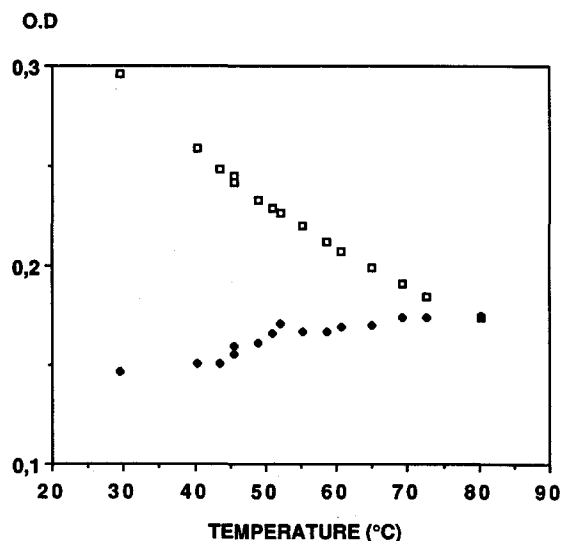


FIG. 6. Temperature dependence of the integrated IR absorption of free NH bonds (\blacklozenge) and partially H-bonded NH (\square).

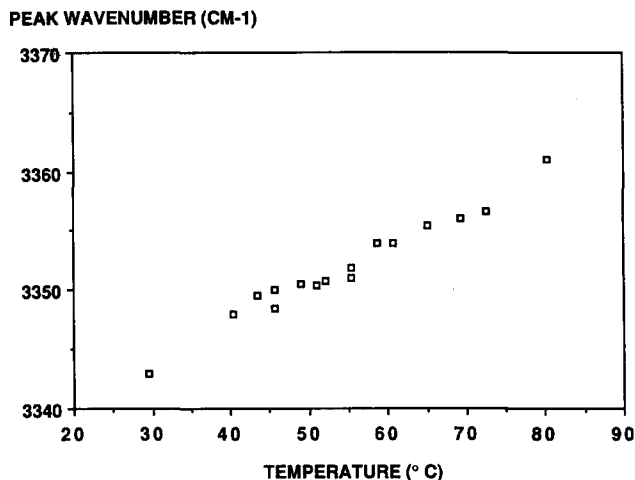


FIG. 7. Temperature dependence of the peak absorption wave number of the Gaussian associated to partially H-bonded NH in fits like in Fig. 5.

tion and intensity of the two main peaks, as well as their temperature behavior, are almost insensitive to its addition. An example is shown in Fig. 5. In this figure, the Gaussian on the right is associated to “free NH” absorption. Its position, 3435 cm^{-1} , and width, 40 cm^{-1} , are independent of temperature, its intensity increases by about 25% up to 70 °C (Fig. 6). Disregarding the intermediate, smaller Gaussian, the temperature dependence of the intensity and peak position of the third one, associated to “non-free” NH, are plotted on Figs. 6 and 7, respectively: on going from 30 to 80 °C, the intensity decreases by 60% and the peak position moves by 15 cm^{-1} , but remains always at a higher frequency than that of H-bonded NH stretch in 3BCMU solid or “blue” phase.^{8,20}

Since the total number of NH bonds is constant, the intensity variation is a proof that the oscillator strength of non-free NH stretch is not constant, being maximum for the completely bonded state, absorbing at 3320 cm^{-1} . This had already been observed in amorphous polyamide.¹⁹

The absorption band of the non-free state, being skewed by such intensity variation effects, should therefore be a Gaussian only if all such bonds have the same geometry, which is highly unlikely. We believe that the large linewidth (it is fitted to a Gaussian with FWHM $\approx 90 \text{ cm}^{-1}$) is at least in part due to a distribution of geometries corresponding to a distribution of frequencies, and of bond strengths. In such a case, the maximum absorption does not necessarily correspond to the most frequent geometry, but may be displaced towards smaller frequency.¹⁹ The third, intermediate, Gaussian introduced into the fit, might simply be a way to introduce this skewness.

The present IR data show that a sizable fraction of CONH groups are engaged in weak H-bonding interaction, and that by increasing T there are less and weaker such bonds; for comparison, a typical yellow state spectrum is shown on Fig. 8. From Figs. 6 and 7, we estimate that at least a third of possible bonds are formed. The accuracy of absolute absorption coefficients in the present data is not good enough to allow more quantitative calculations.

These bonds are much weaker than those present in blue or red cast films^{2,20} or in red 4BCMU gels in toluene.¹³

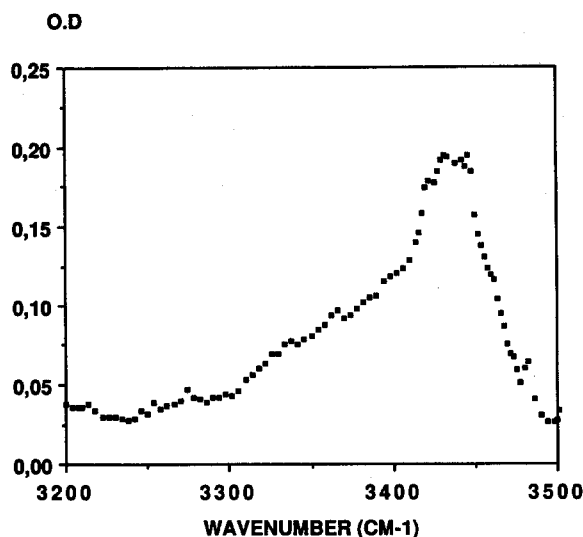


FIG. 8. IR absorption in the N-H stretch region of a yellow solution: short 4B chains in toluene at 80 °C.

Nevertheless, they may suffice to increase the conjugated chain rigidity beyond that solely due to the conjugated nature of the chain. IR and visible absorption data are therefore qualitatively fully consistent.

The worm-like chain rigidity is temperature dependent, the statistical length being theoretically proportional to T^{-1} , but the variation corresponding to the accessible T range in common solvents remains small. Due to the existence of a temperature dependent set of H bonds, the macromolecule acquires a T -dependent structure, its statistical length may vary faster, and be larger than for the reference polydiacetylene worm-like chain. Systems like 3B/CHBr₃ may open the way for the experimental study of the relation between rigidity, i.e., geometrical disorder, and electron delocalization.

V. NEUTRON SMALL ANGLE SCATTERING

The spectroscopic data presented above do not prove that poly-3BCMUs are present in CHBr₃ as truly dissolved isolated macromolecules. Absolute measurements of small angle scattered intensity allow to measure the mass per unit length of the scattering objects, thus providing a sensitive tool for the study of aggregation.⁶

The dimensionless structure factor $g(q)$ is given by

$$g(q) = \frac{\Sigma^{\text{coh}}(q)}{K^2 CN} \frac{m}{C},$$

where q is the scattering vector, m the molar mass (g/mol), C the polymer concentration (g/cm³), K^2 the neutron contrast factor (cm²), N Avogadro's number, and Σ^{coh} the absolute coherent cross section per unit volume of the solution (in cm⁻¹). This can be done at various C and T .

If the scattering object can be viewed as rod-like at some length scale, then $g(q)$ is proportional to q^{-1} in the corresponding q range. The scattering function of a worm-like chain obeying the Porod-Kratky model²¹ has been calculated.²² For $qb \gg 7$, one finds $qg(q) = \pi M_L/m = \text{constant}$, where b is the Kuhn statistical length, a measure of chain rigidity, and the height of this plateau in absolute units is a

measure of the mass per unit length M_L .

For solutions of 3B and 4B in good solvents, the yellow reference state, it has been shown that $b \approx 310$ Å at 295 K, and M_L is that of the isolated chain in the *trans* configuration of the double bonds.⁶

Solutions of 3B and 4B in CDBr₃ correspond to a very unfavorable contrast situation: for 3B chains in CDBr₃, the calculated contrast factor is only $K^2 = 49$ barns (10⁻²⁴ cm²), more than one order of magnitude smaller than those in our studies of 3B/DMF—a reference yellow state,⁶ so that a complete study would be inordinately lengthy and costly. Moreover, if preferential absorption of ethanol occurs, it might decrease the contrast by up to a factor of 3. The poor contrast made it impractical to collect data at different polymer concentrations, so as to calculate the single chain scattering function by the Zimm extrapolation procedure. Therefore, the contribution of interchain interactions is not eliminated for 3B/CDBr₃, and may not be negligible at the lowest q reached.

Results of measurements on solutions of 3B and 4B in CDBr₃ are shown on Fig. 9 and compared to those on 3B/DMF obtained earlier.⁶

These results lead to several conclusions:

(1) There is a q range in which $qg(q)$ is constant. 3B and 4B in CDBr₃ are therefore semirigid objects as in the reference yellow state.

(2) The corresponding plateau is below that of 3B in DMF. Therefore, both polymers, at the temperatures of the experiments (45 °C for 3B, 25 °C for 4B) do not form aggregates, as 4B forms in its red phase in toluene.⁶ At the length scales studied in the neutron experiment, they are isolated chains. Since this scale goes up to about 1000 Å, much longer than any conjugation length of the electrons on the conjugated backbone, the optical results reported above pertain to isolated polydiacetylene chains.

(3) Since the length of one repeat unit of a polydiacetylene chain cannot be much more than 5 Å, the three curves

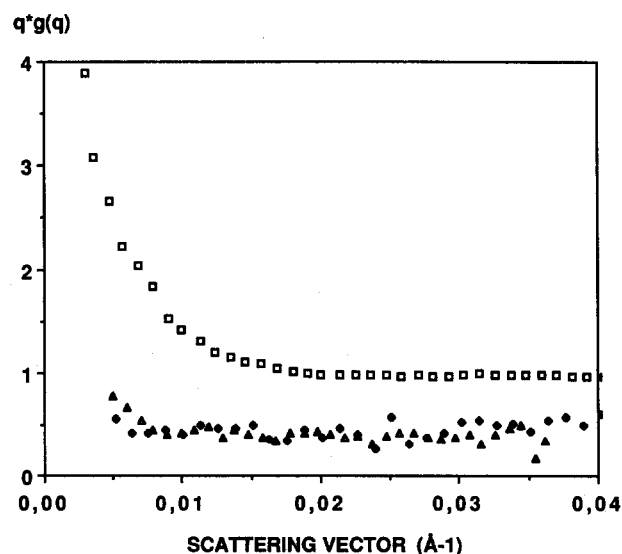


FIG. 9. Scattering functions plotted as $qg(q)$ vs q in absolute values for three solutions: 3B in DMF (standard yellow solution) (□), 3B in CDBr₃ at 45 °C (◆), 4B in CDBr₃ at 25 °C (Δ).

on Fig. 9 should be at the same height within $\sim 10\%$. Clearly, this is not the case, suggesting that, in the CDBr_3 solutions, a wrong (too large) contrast factor was used in the calculations. This is as yet an unsolved question. The most likely explanation is preferential adsorption of some of the perdeuterated ethanol stabilizer. If the coherently scattering moiety is polymer plus ethanol, a smaller contrast is expected. The experimental values would correspond to approximately one adsorbed ethanol on 5 or 4 monomer units in 3B and 4B, respectively.

(4) The 3B/DMF values increase above the corresponding plateau below $Q \sim 2 \times 10^{-2} \text{ \AA}^{-1}$. Clearly, the plateau extends farther on the 4B/ CDBr_3 curve. For 3B, it is not even certain that the points at the lowest q values are significantly above the plateau. As mentioned above, the interchain contribution could not be eliminated from the experimental data, so that the observed values may be smaller than the ones corresponding to the single chain scattering function at low q . By comparing with the 3B/DMF data, where the influence of interchain interactions was measured,⁶ and taking into account that we are dealing here with more rigid objects, one can conclude that the correction is significant below 10^{-2} \AA^{-1} . Therefore, curve fitting to the theoretical scattering function^{21,22} does not yield as accurate a value of the statistical length as for 3B/DMF. In the case of 4B in CDBr_3 , a good approximation is $b = 420 \pm 40 \text{ \AA}$. This is $\sim 30\%$ more than in the reference yellow state at the same temperature.⁶

In the case of 3B, only a lower limit can be given: b should be larger than 600 \AA or twice the value found for 3B in DMF.

VI. CONCLUSIONS

These results show that isolated polydiacetylene chains in solution do not always have the same rigidity at the same temperature. The same polymer can have greatly different statistical lengths $b = K_R/k_B T$, where K_R is the elastic modulus, in different solvents. However, polymers with few H bonds formed between their side groups, such as 3B or 4B in DMF, or 4B in toluene above 65°C , all have the same statistical length and the same value was found in *p*TS12, a polymer in which no H-bonding is possible.³ It was proposed that this may correspond to the intrinsic rigidity of the chain, due to its conjugated nature. This hypothesis is supported by theoretical calculations.²³ Here we show that much larger rigidities can be observed. No case of decreased rigidity has been found.

This increased rigidity is observed in systems showing a sizable amount of H-bonding. However, since the observed hydrogen bonds are not complete, it is likely that they do not play exactly the role assumed in the earlier discussions of polydiacetylene conformation²: Rather than forming perfectly flat short platelets, they slightly increase locally the worm-like ribbon rigidity.

This increased rigidity is correlated to changes in the electronic structure of the backbone but these changes are modest: The effect is negligible for 4B in CDBr_3 , or at least is smaller than solvent effects; for 3B, the statistical length is at least doubled, but the conjugation length is not comparably

increased. Still, the observed difference further supports the model in which electron localization is the result of the worm-like conformation of the chain rather than of a number of defects which strongly interrupt conjugation: a potential continuously fluctuating by small amounts is enough to localize the wave functions in one dimension. However, there is not a simple monotonous relation between b and for instance the wavelength of maximum absorption λ_m : Although 4B is more rigid in CHBr_3 than in DMF, the visible absorption spectra are very similar. The elastic coupling between 1D arrays of H bonds and the conjugated chain is likely to depend on the intermediate alkyl group size.

It would be interesting to study whether the effects observed here would be seen as well in solvents where a gradual "thermochromic" change from yellow to orange is observed.¹¹

The present results are also relevant to the study of the chromic transitions: They show that it is possible to produce controlled changes of the conformation of polydiacetylenes in a much wider range than can be done simply by changing temperature. True solutions exist in which the isolated chain is much more rigid than in good solvent, and still is yellow. It is tempting to relate the aggregation, including that observed below room temperature for 3B in CHBr_3 , to a temperature induced increase in rigidity; since the rigidity at the onset of the chromic transition is dependent on the solvent used, interactions should be introduced in a proper treatment of these transitions.

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