

See discussions, stats, and author profiles for this publication at:
<https://www.researchgate.net/publication/229310496>

Ultrafast photoinduced ring-closure dynamics of a diarylethene polymer

ARTICLE *in* CHEMICAL PHYSICS LETTERS · JUNE 2002

Impact Factor: 1.9 · DOI: 10.1016/S0009-2614(02)00706-6

CITATIONS

26

READS

49

7 AUTHORS, INCLUDING:



Francesco Stellacci

École Polytechnique Fédérale de Laus...

192 PUBLICATIONS 7,169 CITATIONS

SEE PROFILE



Giuseppe Zerbi

Politecnico di Milano

494 PUBLICATIONS 11,047 CITATIONS

SEE PROFILE



Salvatore Stagira

Politecnico di Milano

279 PUBLICATIONS 4,784 CITATIONS

SEE PROFILE

Ultrafast photoinduced ring-closure dynamics of a diarylethene polymer

C. Bertarelli ^{a,*}, M.C. Gallazzi ^a, F. Stellacci ^a, G. Zerbi ^a, S. Stagira ^b,
M. Nisoli ^b, S. De Silvestri ^b

^a *Dipartimento di Chimica, Materiali e Ingegneria Chimica, Politecnico di Milano, Piazza Leonardo da Vinci, 32, 20133 Milan, Italy*

^b *Dipartimento di Fisica, Politecnico di Milano, Piazza Leonardo da Vinci, 32, 20133 Milan, Italy*

Received 27 February 2002; in final form 24 April 2002

Abstract

The dynamics of the ring-closure reaction of poly-1,2-bis(2-methylthien-3-yl)perfluorocyclopentene in chloroform solution is investigated. Ultrafast transient absorption spectra are measured using 260 nm pump pulses. It is shown that the optical switching occurs on a sub-200 fs timescale. The presence of a transient band around 450 nm, which disappears in ~200 ps, is ascribed to excited-state absorption of the dithiophene moiety. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

The continuous and increasing interest in photochromism is ascribable to its potential applicability for various optoelectronic devices, mainly for rewritable optical memories [1]. Among all the switching systems, 1,2-diarylethenes [2–6] undergo a reversible light induced electrocyclisation between hexatriene to cyclohexadiene by a conrotatory mechanism according to the Woodward and Hoffmann rule [7]. Diarylethenes having heterocycles as aromatic rings and perfluorocyclopentene as ethylen bridge have been extensively studied in the last ten years because of the thermal and optical stability of the two isomers, their high

fatigue resistance, their high sensitivity and the rapid response that make them good candidates for technological applications [5,6,8,9]. Moreover, technology requires solid state materials; for this reason, for practical applications, photochromic molecules are usually embedded in amorphous polymeric matrices. Unfortunately matrices play an important role in the photochromic process and in most cases the presence of a polymer worsens the photochromic reactivity of the host molecule [10]. In order to obtain a bulk amorphous material belonging to the diarylethene class with enhanced photochromism, we have recently synthesised poly-1,2-bis [2-methyl thien-3-yl]perfluorocyclopentene (Poly-BMTFP), the first backbone photochromic polymer consisting entirely in diarylethene photochromic units in the main chain, as shown in Fig. 1 [11,12]. As previously reported, Poly-BMTFP is photochromic both in solution

* Corresponding author. Fax: +39-02-2399-3231.

E-mail address: chiara.bertarelli@polimi.it (C. Bertarelli).

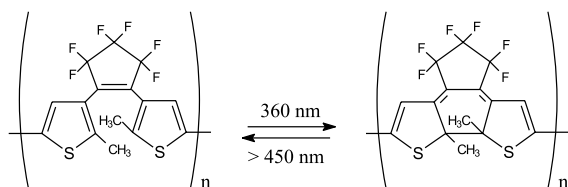


Fig. 1. Molecular structure of poly-1,2-bis(2-methylthien-3-yl)perfluorocyclopentene (Poly-BMTFP).

and in the solid state and its photochromic reactivity is better than that of the corresponding monomer. The cyclisation quantum yield is 0.86, a very high value which could be ascribed to a very high contribution of the antiparallel conformation in the open form and to the possible presence of cooperative motions. On the contrary, the low value of the ring-opening quantum yield ($\phi = 0.0015$) reveals that the reverse process is not efficient. The photochromic isomerisation is thermally irreversible: no thermochromism has been detected keeping the closed-form in the dark for three months at 80 °C. The molecular weight was determined by gel permeation chromatography in THF using polystyrene as standard: M_n values from different preparations were in the range between 2450 and 4350, M_w between 3000 and 5900. The solubility of the photochromic polymer decreases with the increase of the molecular weight.

The study of the optical switching dynamics is of particular interest for the potential applications of such materials. Time-resolved studies have been performed on other dithienylethene derivatives switching systems and revealed that the ring-closure and the ring-opening processes occur in the picosecond timescale, both in solution and in the solid state [13–19].

In this work we study the dynamics of the ring-closure process of Poly-BMTFP in solution, using femtosecond pump-probe measurements. The ring-closure reaction is induced by 260-nm pump pulses. We show that the photochromic reaction takes place on a sub-200-fs timescale.

2. Experimental

Transient absorption measurements were performed by using a conventional pump-probe

configuration. The laser system, which has been described elsewhere [20], consists of a Ti:sapphire laser system with chirped-pulse amplification, which provides 150-fs pulses at 780 nm, with energy up to 750 μ J at a 1-kHz repetition rate. The white-light supercontinuum, ranging from 430 to 760 nm, generated focusing a portion of the laser beam in a thin sapphire plate, was used as a probe. Excitation pulses at 260 nm were generated by focusing the fundamental beam in air. Fundamental and third harmonic pulses were then separated by multiple reflections on a dichroic mirror pair. The pulse duration, of ~ 150 fs, was determined with degenerate pump-probe measurement in dioxan.

In order to study the ring-closure reaction, the pump-probe measurements were performed flowing the Poly-BMTFP, in chloroform solution (Aldrich[®] spectrophotometric grade), through a 1-mm-thick flow cell. In this way the excitation of the closed form by successive pump pulses is avoided. Irradiation with a He–Ne laser was used to regenerate the open form of the sample. The concentration of the polymer solution was $\sim 10^{-4}$ M in order to have absorbance intensities between 0.5 and 0.8.

3. Results and discussion

Cw absorption spectra both of the open and the closed form of Poly-BMTFP in chloroform solution are shown in Fig. 2. The open form exhibits an UV absorption with a maximum at 326 nm. Under irradiation with UV light the open form converts into the more conjugated closed form characterised by a broad visible band having a maximum near 620 nm. Transient transmission spectra were measured in the range between 430 and 760 nm by using 260 nm excitation for delay times up to 200 ps. For every time delay the pump-probe spectra were measured several times and the results were averaged to give the transient transmission spectra reported in Fig. 3. Upon excitation a broad and featureless absorption band appears around 620 nm, whose amplitude remains nearly constant on a timescale of hundreds of picoseconds. The spectrum at a

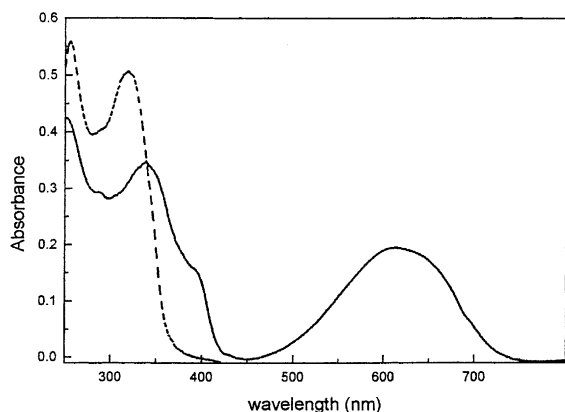


Fig. 2. UV-Vis absorption spectra of the open form (dashed line) and of the closed form (solid line) of Poly-BMTFP in chloroform solution.

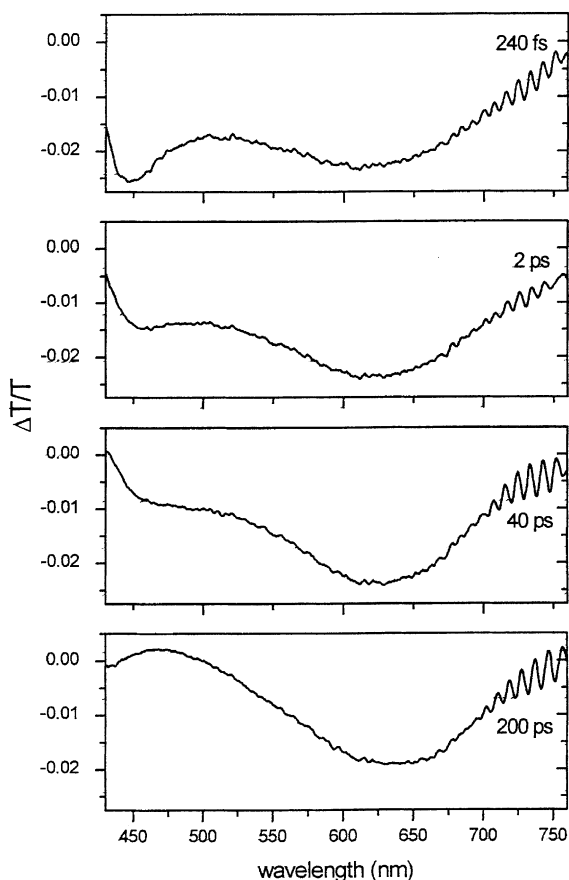


Fig. 3. Differential transmission spectra of Poly-BMTFP in chloroform solution for various pump-probe delays.

240-fs pump-probe delay clearly shows a narrower absorption band around 450 nm, characterised by a fast relaxation dynamics. The spectrum measured for a delay of 200 ps displays only the photoinduced absorption band around 620 nm. It is worth pointing out that the spectral position and shape of this band exactly correspond to those of the cw visible absorption band of the closed form (see Fig. 2). As a consequence this photoinduced absorption band is attributed to the ring-closure process. The relative simplicity of the time-evolving spectra associated to the ring-closure process of Poly-BMTFP when compared with similar experiments reported in literature [13–19] can be ascribed to the supposed absence of the parallel conformer of the open form, inactive to the light-induced switching process. In order to study in more details the temporal evolution of the ring-closure reaction, we have measured the transient transmission change (ΔT) at 620 nm as a function of the probe delay. The measured ΔT curve is displayed in Fig. 4. The fast rise of the reported curve follows the time integral of the pump-probe cross-correlation. Therefore we can conclude that the ring-closure reaction takes place on a sub-200 fs timescale, thus indicating that the molecule is characterised by a dynamics of cycling process faster than those so far reported for diarylethene derivatives [13–19].

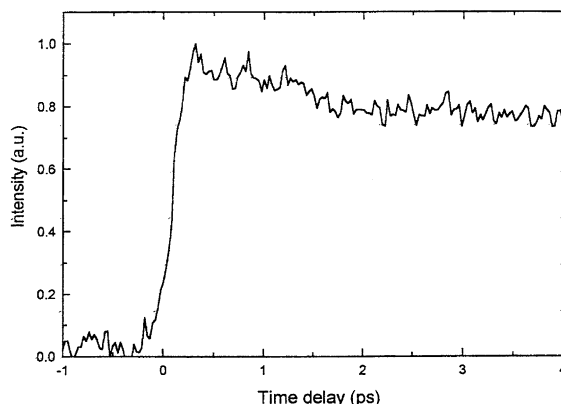


Fig. 4. Normalised pump-probe trace of Poly-BMTFP in chloroform solution at a probe wavelength of 620 nm.

The absorption band around 450 nm presents an instantaneous formation (shorter than the temporal resolution of the pump-probe setup), followed by a decay which leads to its complete disappearance after about 200 ps. The occurrence of additional bands that accompany the typical signal of the switching process has been already found in previous transient absorption studies of other photochromic diarylethene derivatives that showed time-evolving bands between 450 and 515 nm [13,14,17]. In more details, the dynamics of the ring-closure process of 1,2-bis (2,4,5-trimethyl-3-thienyl) maleic anhydride [13] revealed, beside the formation of the closed product, an absorption at 450 nm, persisting also in the nanosecond domain, which could not be ascribed to the switching process. Moreover, in the femtosecond study of the ring-closure process of a photochromic diarylethene containing a bithienyl derivative, Tamai et al. [14] observed the presence of an absorbance at 515 nm, decaying in the ps domain, due to the $S_n \leftarrow S_1$ absorption of the open ring form. Owrutsky et al. [17] came to the same conclusion for 1,2-bis(5-pyridyl-2-methylthien-3-yl)perfluorocyclopentene which exhibited an absorption at about 450 nm whose intensity decrease in few ps. In the case of Poly-BMTFP, the completely different dynamics of the measured absorption bands at 450 and 620 nm, leads to the hypothesis that two different processes are taking place and we assign the former band to the process of light excitation of the dithiophene moiety. Indeed a transient band near this wavelength has been already observed in oligothiophenes, and it has been assigned to the dithienyl S_1 excited-state absorption [21]. Starting by the same consideration Tamai et al. [14] in the femtosecond study of the ring-closure process of a photochromic diarylethene containing a bithienyl derivative, assigned the transient band nearly at 460 nm to $S_n \leftarrow S_1$ absorption of the dithiophene in the open form.

4. Conclusions

The kinetics of photochromic electrocyclisation reaction of poly-1,2-bis(2-methylthien-3-yl)perflu-

orocyclopentene has been investigated by using femtosecond pump-probe measurements. We have shown that the switching process occurs in the femtosecond domain and it is faster than in other diarylethene derivatives so far reported. Besides the formation of the closed isomer upon excitation at 260 nm of the open-form we have observed the occurrence of the $S_n \leftarrow S_1$ absorption of the dithiophene moiety as suggested by the presence of a transient band at 450 nm decaying on a picosecond timescale.

Acknowledgements

This work was partly supported by the Nanotechnology Program of CNR (Italy).

References

- [1] J. Whittall, in: H. Durr, H. Bouas-Laurent (Eds.), *Photochromism, Molecules and Systems*, Elsevier, Amsterdam, 1990.
- [2] M. Irie, M. Mohri, *J. Org. Chem.* 53 (1988) 803.
- [3] S. Nakamura, M. Irie, *J. Org. Chem.* 53 (1988) 6136.
- [4] K. Uchida, Y. Nakayama, M. Irie, *Bull. Chem. Soc. Jpn.* 63 (1990) 1311.
- [5] M. Irie, K. Uchida, *Bull. Chem. Soc. Jpn.* 71 (1998) 985.
- [6] M. Irie, *Chem. Rev.* 100 (2000) 1685, and references therein.
- [7] R.B. Woodward, R. Hoffmann, *The Conservation of Orbital Symmetry*, Verlag Chemie, Weinheim, Germany, 1970.
- [8] M. Hazanawa, R. Sumiya, Y. Horikawa, M. Irie, *J. Chem. Soc. Chem. Comm.* (1992) 206.
- [9] S.L. Gilat, S.H. Kawai, J.-M. Lehn, *Chem. Eur. J.* 1 (1995) 275.
- [10] K. Horie, I. Mita, *Adv. Polym. Sci.* 88 (1989) 77.
- [11] F. Stellacci, C. Bertarelli, F. Toscano, M.C. Gallazzi, G. Zotti, G. Zerbi, *Adv. Mater.* 11 (1999) 292.
- [12] F. Stellacci, F. Toscano, M.C. Gallazzi, G. Zerbi, *Synth. Met.* 102 (1999) 979.
- [13] H. Miyasaka, S. Araki, A. Tabata, T. Nobuto, N. Mataga, M. Irie, *Chem. Phys. Lett.* 230 (1994) 249.
- [14] N. Tamai, T. Saika, T. Shimidzu, M. Irie, *J. Phys. Chem.* 100 (1996) 4689.
- [15] H. Miyasaka, T. Nobuto, A. Itaya, N. Tamai, M. Irie, *Chem. Phys. Lett.* 269 (1997) 281.
- [16] J. Ern, A.T. Bens, A. Bock, H.-D. Martin, C. Kryschi, *J. Lumin.* 90 (1998) 76.
- [17] J.C. Owrutsky, H.H. Nelson, A.P. Baronavski, O.-K. Kim, G.M. Tsivgoulis, S.L. Gilat, J.-M. Lehn, *Chem. Phys. Lett.* 293 (1998) 555.

- [18] J. Ern, A.T. Bens, H.-D. Martin, S. Mukamel, D. Schmid, S. Tretiak, E. Tsiper, C. Kryschi, *Chem. Phys.* 246 (1999) 115.
- [19] J. Ern, A.T. Bens, H.-D. Martin, S. Mukamel, S. Tretiak, K. Tsyganenko, K. Kuldova, H.P. Trommsdorff, C. Kryschi, *J. Phys. Chem. A* 105 (2001) 1741.
- [20] G. Cerullo, S. Stagira, M. Nisoli, S. De Silvestri, G. Lanzani, G. Kranzelbinder, W. Graupner, G. Leising, *Phys. Rev. B* 57 (1998) 12806.
- [21] D.V. Lap, D. Grebner, S. Rentsch, H. Naarmann, *Chem. Phys. Lett.* 211 (1993) 135.