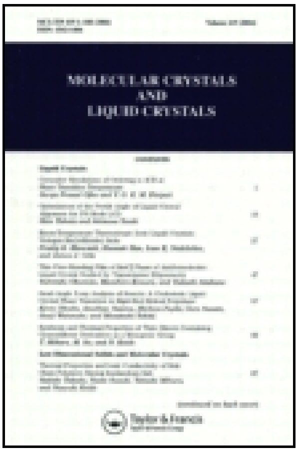


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Side-Chain Azobenzene Polymers: Synthesis and Photochemical Properties

Vitaliy Smokal [a], Oksana Krupka [a], Bouchta Sahraoui [b] & Alexey Kolendo [a]

[a] Taras Shevchenko National University of Kyiv, Kyiv, Ukraine
[b] LPhA, University of Angers, Angers, France

Version of record first published: 03 Mar 2011

To cite this article: Vitaliy Smokal, Oksana Krupka, Bouchta Sahraoui & Alexey Kolendo (2011): Side-Chain Azobenzene Polymers: Synthesis and Photochemical Properties, Molecular Crystals and Liquid Crystals, 536:1, 115/[347]-121/[353]

To link to this article: http://dx.doi.org/10.1080/15421406.2011.538316

Mol. Cryst. Liq. Cryst., Vol. 536: pp. 115/[347]–121/[353], 2011
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2011.538316

Side-Chain Azobenzene Polymers: Synthesis and Photochemical Properties

VITALIY SMOKAL,[1] OKSANA KRUPKA,[1]
BOUCHTA SAHRAOUI,[2] AND ALEXEY KOLENDO[1]

[1]Taras Shevchenko National University of Kyiv, Kyiv, Ukraine
[2]LPhA, University of Angers, Angers, France

A series of methacrylic monomers containing azobenzene moiety with alkyl spacer and different substituents is synthesized. Their photophysical and photochemical properties have been investigated. The photophysical properties of these compounds are investigated by ^{1}H NMR, IR, and UV spectroscopies.

Keywords Azo polymers; free radical polymerization; methacrylic monomers

1. Introduction

In the last few years, a growing interest of researchers was paid to the development of materials which exhibit nonlinear optical (NLO) properties for applications such as optical signal processing and information storage [1–17]. The desirable properties of azo materials are attributed to the highly efficient photo-reversible *trans-cis* isomerization of azobenzene moieties. Generally, this phenomenon is induced by light with frequencies above a half of that of the main resonance of a material [18], and its efficiency is resonantly enhanced via the one-photon absorption. The photo-isomerization is accompanied by significant changes in dipole moments of molecules, thus giving rise to a third-order nonlinearity [19,20]. Therefore, azobenzene compounds are studied as materials for nonlinear optical applications.

In this work, we will present a detailed photophysical study of a series of azobenzene polymers (Fig. 1). The effects of UV irradiation on the absorption are investigated and discussed.

2. Experimental

2.1. *Instruments for Characterization*

^{1}H NMR (500 MHz) spectra were recorded by a "Mercury-400" spectrometer using $CDCl_3$ and DMSO-d_6 as solvents. Chemical shifts are in ppm from the internal standard tetramethylsilane.

Address correspondence to Oksana Krupka, Taras Shevchenko National University of Kyiv, 60,Volodymyrska Str., 01033 Kyiv, Ukraine. E-mail: oksana_krupka@yahoo.com

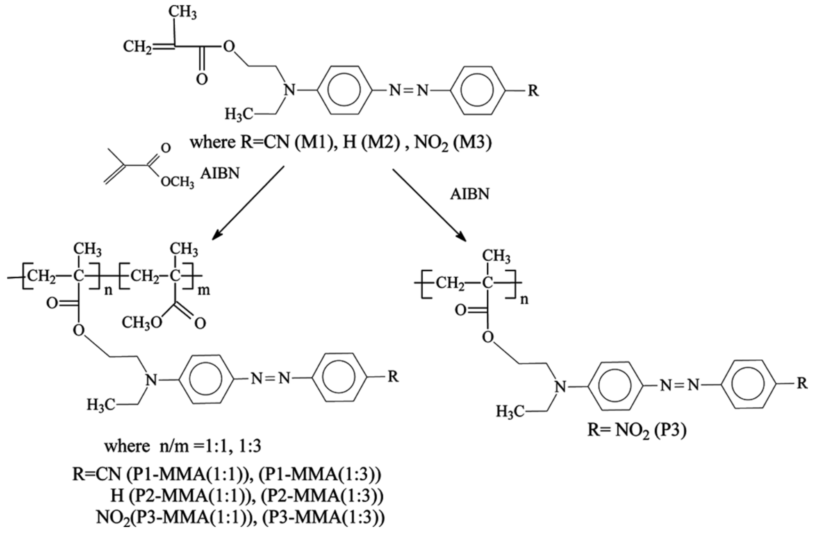


Figure 1. Synthesis of azobenzene polymers.

UV-VIS measurements were performed at room temperature in a solution in a quartz cell with a Perkin-Elmer UV/VIS/NIR Lambda 19 spectrometer.

Differential Scanning Calorimetry: a Q20 DSC model was used to determine the glass (T_g) and phase transition temperatures of all polymers. The sample was initially stabilized. After the first scan, it was heated at a rate of 10°C/min up to 200°C and then cooled to 20°C. Finally, a second scan was performed at a heating rate of 10°C/min up to 200°C giving the values of T_g. The glass transition temperatures by the midpoint of the heat capacity jump are given.

Size exclusion chromatography: The molecular weights and the molecular weight distribution of all polymers were determined with a system equipped with a Spectra SYSTEM AS1000 autosampler, with a guard column (Polymer Laboratories, PL gel 5 μm Guard, 50 × 7.5 mm) followed by 2 columns (Polymer Laboratories, 2 PL gel 5 μm MIXED-D columns, 2 × 300 × 7.5 mm), and with Spectra SYSTEM RI-150 and Spectra SYSTEM UV2000 detectors. The eluent used is THF at a flow rate of 1 ml/min at 35°C. Polystyrene standards ($580–4.83 \times 10^3$ g/mol) were used for calibration.

2.2. *Materials Synthesis*

Standard distillation procedures were performed for triethylamine and THF just prior to the use. 2,2′-Azobis(isobutyronitrile) (AIBN) was recrystallized twice from absolute methanol. Methacrylic chloride was vacuum-distilled, immediately before the use. Methylmethacrylate (MMA) was washed with aq NaOH to remove inhibitors and dried with $CaCl_2$ under nitrogen at a reduced pressure. All other reagents and solvents were commercially available and used as-received.

4′-[(2-Methacryloyloxyethyl)ethylamino]-4-cyanoazobenzene (M1). A solution of 4′-[(2-hydroxyethyl)ethylamino]-4-cyanoazobenzene (3 g, 0.01 mol) and triethylamine (1.11 g, 0.011 mol) was dissolved in THF (35 mL). The solution was kept in an ice bath for 10 min. A solution of distilled methacryloyl chloride (1.15 g, 0.011 mol) in THF (10 mL) was added slowly to the reaction mixture. After the addition of methacryloyl chloride, the solution was stirred for 12 h at ambient temperature. The solvent was removed by the rotary evaporation, and the residue was washed with a solution of sodium carbonate (0.8 g) in water (40 mL). After removing the solvent, the resulting material was purified by column chromatography (silica gel, ethyl acetate/hexane 1/8). Red solid residue, yield: 87%. ^{1}H NMR ($CDCl_3$), d (ppm): 7.89, 7.87 (d, 4H, Ar), 7.75, 7.73 (d, 2H, Ar), 6.82, 6.8 (d, 2H, Ar), 6.1 (s, 1H, CH_2), 5.6 (s, 1H, CH_2), 4.36 (m, 2H, OCH_2), 3.7 (m, 2H, NCH_2), 3.55 (m, 2H, NCH_2), 1.94 (s, 3H, CH_3), 1.25 (m, 3H, NCH_2CH_3).

4′-[(2-Methacryloyloxyethyl)ethylamino]-azobenzene (M2). Azomonomer **M2** was synthesized using the above procedure for azomonomer **M1**. The product was purified by column chromatography (silica gel, ethyl acetate/hexane 1/8). Orange solid residue, yield 75%. ^{1}H NMR ($CDCl_3$), d (ppm): 7.83, 7.85 (d, 4H, Ar), 7.48 (t, 2H, Ar), 7.38 (t, 1H, Ar), 6.8 (d, 2H, Ar), 6.11 (s, 1H, CH_2), 5.6 (s, 1H, CH_2), 4.36 (m, 2H, OCH_2), 3.71 (m, 2H, NCH_2), 3.51 (m, 2H, NCH_2), 1.95 (s, 3H, CH_3), 1.24 (m, 3H, CH_3).

4′-[(2-Methacryloyloxyethyl)ethylamino]-4-nitroazobenzene (M3). Azomonomer **M3** was synthesized in the same way as azomonomer **M1**. The solid was recrystallized from methanol. Dark red crystals, yield 80%. ^{1}H NMR ($CDCl_3$), d (ppm): 8.33, 8.31 (d, 2H, Ar), 7.92 (t, 4H, Ar), 6.83, 6.81 (d, 2H, Ar), 6.1 (s, 1H, CH_2), 5.6 (s, 1H, CH_2), 4.37 (m, 2H, OCH_2), 3.74 (m, 2H, NCH_2), 3.56 (m, 2H, NCH_2), 1.94 (s, 3H, CH_3), 1.24 (m, 3H, CH_3).

Polymerization. Polymers were synthesized by free-radical polymerization in toluene. The homo-polymerization was carried out in a 10-wt. % dry toluene solution of a monomer with AIBN as a free radical initiator (1 wt.% of monomer) at 80°C 35 h in the argon atmosphere. Previously, the initial mixture was degassed with repeated freeze-pump-taw cycles. The polymerization was stopped by pouring the reaction mixture into methanol. The polymer was redissolved in THF and then precipitated in methanol. This procedure was repeated several times to ensure the removal of the unreacted methacrylic monomer, and finally the homo-polymer (**P3**) was dried under vacuum at 50°C overnight. The synthesis of copolymers based on azobenzene methacrylic monomers **M1**, **M2**, **M3**, and MMA was a typical polymerization procedure [21]. The copolymerization ratios in the corresponding polymers **P1-MMA** (1:1), **P1-MMA** (1:3), **P2-MMA** (1:1), **P2-MMA** (1:3), **P3-MMA** (1:1), and **P3-MMA** (1:3) were calculated on the basis of the integrated peak areas of ^{1}H NMR spectra in DMSO-d_6.

3. Results and Discussion

The 4′-[(2-hydroxyethyl)ethylamino]-4-cyanoazobenzene and 4′-[(2-hydroxyethyl)-ethylamino]azobenzene were prepared by coupling the diazonium salt of 4-aminobenzonitrile or aniline correspondingly with 2-(*N*-ethylanilino)ethanol according to the procedure published previously [22]. The 4′-[(2-hydroxyethyl)ethylamino]-4-nitroazobenzene is commercially available (Aldrich). The azobenzene methacrylate monomers were synthesized by the reaction of azobenzene alcohols with methacryloyl chloride in the presence of triethylamine as a nucleophilic catalyst and a hydrochloric acid acceptor. The polymers were synthesized by the radical polymerization using AIBN as a radical initiator.

Table 1. Characteristics of azobenzene polymers

Sample	Mole ratio in the copolymer n/m[a]	Mn[b]	Mw/Mn[b]	T_g[c]
P1-MMA (1:1)	1:1.1	28000	1.85	125
P1-MMA (1:3)	1:3	16000	1.79	120
P2-MMA (1:1)	1:1	42000	1.7	123
P2-MMA (1:3)	1:3.2	57000	1.82	128
P3-MMA (1:1)	1:1.1	34000	1.86	130
P3-MMA (1:3)	1:3.2	19000	1.77	128
P3	–	17000	1.92	118

[a] Determined by ^{1}H NMR integration.
[b] Measured by GPC.
[c] Measured by DSC.

Polar substituents such as –CN and –NO_2 in azobenzene compounds can act as retarding agents of the free radical polymerization reaction. Therefore, the long reaction time is needed to synthesize polymers with a high yield. The structures of obtained polymers were confirmed by ^{1}H NMR spectra. The compositions of the copolymers were well controlled as the initial ratio of the azobenzenes monomers and MMA (Table 1). However, the MMA saturation was observed practically for all copolymers due to a high polymerization ability of MMA. Glass transition temperatures (T_g) are presented in Table 1. The molecular weights of copolymers are in the range 16000–57000, and the polydispersity indices are between 1.7 and 1.92 as evaluated by the GPC analysis (Table 1).

The UV-vis spectra of the azopolymers show two absorption bands which are due to benzene rings and the intense band assigned to the vibronic coupling between the n-π^* and π-π^* electronic transitions of azobenzene polymers [5]. The electron-donor and electron-acceptor substituents in the synthesized polymers increase the charge-transfer character of the π-π^* transition and consequently shift the π-π^* band to the red (Fig. 2). Thereby, **P3-MMA** (1:3) exhibits a maximum absorption at the

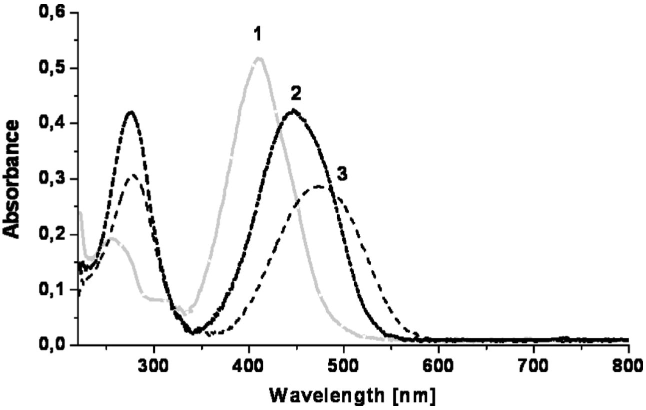
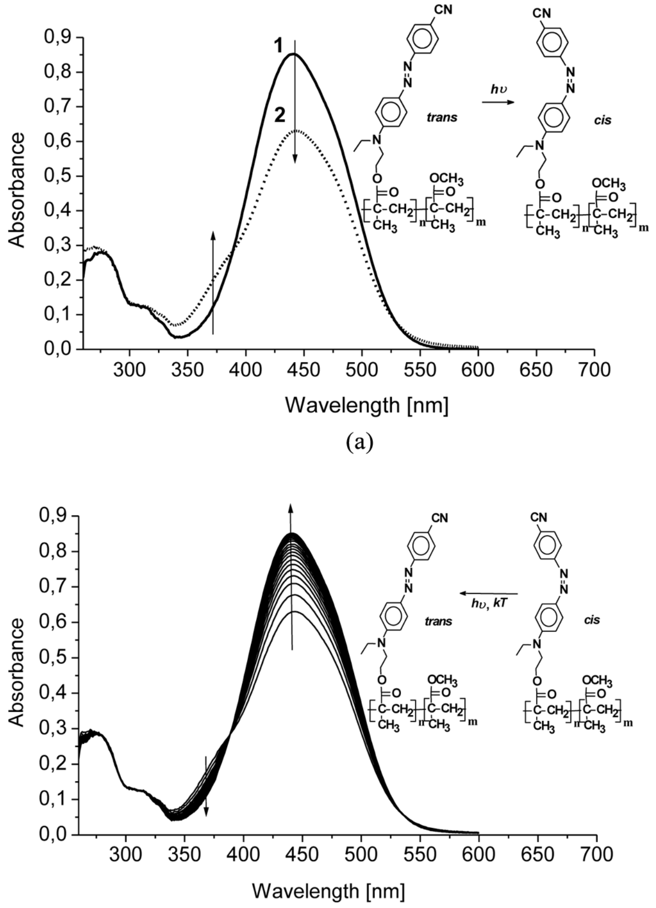


Figure 2. UV-vis spectra of **P2-MMA** (1:3) – 1, **P1-MMA** (1:3) – 2, **P3-MMA** (1:3) – 3 in THF.



(a)

(b)

Figure 3. Changes in the absorption spectra of **P1-MMA** (1:3) in THF: **a** – before (1) and after the 30-s period (2) of irradiation at wavelengths $\lambda > 300$ nm revealing the *trans-cis* transformation; **b** – during the reversible process of *cis-trans* isomerization.

longest wavelength (475 nm) among the investigated compounds, which can be explained by the strongest charge-transfer interaction occurring between the electron-donor group (amino) and the electron-acceptor group (nitro) characteristic of the "pseudo-stilbene" types in Rau's classification [23].

The common photochemical properties of all azobenzene compounds are their ability for the photoisomerization through a rotation about the N–N bond and via the inversion of one or both of the nitrogens through a linear *sp*-hybridized transition state, in which the double bond was retained. As example, Figure 3a shows changes in the absorption spectra of **P1-MMA** (1:3) due to the optically induced transition to the *cis*-isomer. This state is metastable; the reverse transition from the *cis*- to the *trans*-state occurring gradually, even without exposure to UV light (via thermal relaxation), is shown in Figure 3b.

The reversible switching of the *trans*-*cis*-*trans* isomerization of **P1-MMA** (1:3) is demonstrated in Figure 4 by alternate cycles, where the descents and the ascents

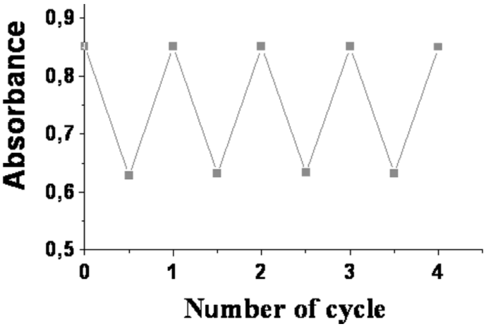


Figure 4. Absorbance at 440 nm *versus* the number of cycle for **P1-MMA** (1:3) in THF (descents and ascents correspond to the *trans-cis* and *cis-trans* transitions, respectively).

correspond, respectively, to *trans-cis* and *cis-trans* transitions. This photoisomerization is completely reversible and free from side reactions. These properties are also typical of copolymer **P2-MMA** (1:3). However, the thermal back isomerization of **P3** and **P3-MMA** (1:3) is too fast (milliseconds) at room temperature [24]. Therefore, the isomerization cannot be observed reasonably.

4. Conclusions

We have synthesized polymers based on 4′-[(2-methacryloyloxyethyl)ethylamino]-4-azobenzenes containing various electron-acceptor groups via the free radical polymerization. We have confirmed that these materials exhibit the repeating *trans-cis-trans* izomerisation process. Polymers with analogous properties are promising materials for photonic applications to the optical data storage, surface-relief holography, and optical switching.

Acknowledgment

The authors would like acknowledge the support of COST MP0702 action.

References

[1] Toussaere, E., & Labb, P. (1999). *Opt. Mat.*, *12*, 357.
[2] Ubukata, T., Seki, T., & Ichimura, K. (2000). *Adv. Mater.*, *12*, 1675.
[3] Ichimura, K. (2000). *Chem. Rev.*, *100*, 1847.
[4] Lagugne-Labarthet, F., Bruneel, J. L., Rodriguez, V., & Sourisseau, C. (2004). *J. Phys. Chem. B*, *108*, 1267.
[5] Czaplicki, R., Krupka, O., Essaidi, Z., El-Ghayoury, A., Grote, J. G., Kajzar, F., & Sahraoui, B. (2007). *Opt. Express*, *15*, 15268.
[6] Zettsu, N., Ogasawara, T., Mizoshita, N., Nagano, S., & Seki, T. (2008). *Adv. Mater.*, *20*, 516.
[7] Centore, R., Fort, A., Panunzi, B., Roviello, A., & Tuzi, A. (2004). *Inorg. Chim. Acta.*, *357*, 913.
[8] Sekkat, Z., Knoesen, A., Lee, V. Y., & Miller, R. (1997). *Phys. Chem. B*, *101*, 4733.
[9] Krupka, O., El-Ghayoury, A., Rau, I., Sahraoui, B., Grote, J. G., & Kajzar, F. (2008). *Thin Solid Films*, *516*, 8932.

[10] Rodriguez, F. J., Sanchez, C., Villacampa, B., Alcala, R., Cases, R., Millaruelo, M., & Oriol, L. (2004). *Polymer*, *45*, 2341.
[11] Jecs, E., Kreicberga, J., Kampars, V., Jurgis, A., & Rutkis, M. (2009). *Opt. Mater.*, *31*, 1600.
[12] Ikeda, T., & Tsutsumi, O. (1995). *Science*, *268*, 1873.
[13] Yu, Y., & Ikeda, T. (2004). *J. Photochem. Photobiol. C: Photochem. Rev.*, *5*, 247.
[14] Liang, Z., Ming, H., Wang, P., Zhang, J., Xie, J., & Zhang, Q. (2004). *J. Appl. Phys.*, *90*, 5866.
[15] Yesodha, S. K., Sadashiva Pilai, C. K., & Tsutsumi, N. (2004). *Prog. Polym. Sci.*, *29*, 45.
[16] Wijekoon, W., Lee, K. S., & Prasad, P. N. (2007). In: *Physical Properties of Polymers. Handbook*, Mark, J. E. (Ed.), Springer: Berlin, 795.
[17] Sekkat, Z., & Knoll, W. W. (2002). *Photoreactive Organic Thin Films*, Academic Press: New York.
[18] Correa, D. S., Cardoso, M. R., Goncalves, V. C., Balogh, D. T., De Boni, L., & Mendonc, C. R. (2008). *Polymer*, *49*, 1562.
[19] Yamada, R., Matsuda, H., & Yankelevich, D. (1998). *Appl. Phys. Lett.*, *72*, 1021.
[20] Brzozowski, L., & Sargent, E. H. (2001). *J. Mat. Sci: Mat. Electr.*, *12*, 483.
[21] Robello, D. G. (1990). *J. Polym. Sci., Part A: Polym. Chem.*, *28*, 1.
[22] Ho, M. S., Natansohn, A., Barrett, C., & Rochon, P. (1995). *Can. J. Chem.*, *73*, 1773.
[23] Rau, H. (1990). In: *Photochemistry and Photophysics*, Rabek, J. F. (Ed.), CRC Press: Boca Raton, 119.
[24] Xie, S., Natansohn, A., & Rochoni, P. (1993). *Chem. Mater.*, *5*, 403.