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4-Vinylazobenzene: Polymerizability and Photochromic Properties of Its Polymers

Angelina Altomare, Francesco Ciardelli, Nicola Tirelli,[†] and Roberto Solaro*

Department of Chemistry and Industrial Chemistry, University of Pisa,
via Risorgimento 35, 56126 Pisa, Italy

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ABSTRACT: The polymerizability of 4-vinylazobenzene; (VAB), a vinyl monomer containing an azobenzene chromophore directly attached to the polymerizable double bond, was investigated in the presence of radical, anionic, cationic, and Ziegler−Natta type catalysts. The homo- and copolymerization of VAB with (−)-menthyl methacrylate, carried out in the presence of AIBN as a radical initiator, afforded a fairly high yield of photochromic polymeric materials. On the contrary, no high molecular weight product was formed in the presence of cationic, anionic, and anionic coordinate catalysts, whereas polymeric products were obtained by anionic copolymerization of VAB with styrene. Determination of ^{13}C relaxation times allowed us to evaluate the poly(VAB) molecular mobility, also, in comparison, that of 4-isopropylazobenzene, a low molecular weight model compound, and of other polymeric systems containing azobenzene chromophores spaced from the main chain. Thermally and photoinduced *trans* → *cis* and *cis* → *trans* isomerization rates were almost independent of molecular weight and chemical composition of the investigated samples, thus suggesting that azobenzene isomerization implies an in-plane inversion of the phenyl ring most distant from the polymer backbone. Asymmetric perturbation of the azobenzene chromophores, attributable to the presence of short ordered segments along the polymer chain of MnMA/VAB copolymers, was evidenced by circular dichroism. The limited dependence of the intensity of dichroic bands on copolymer composition was interpreted in terms of distribution and mobility of VAB units.

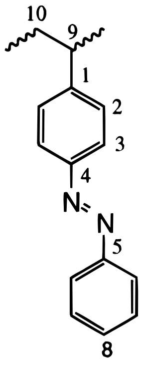
Introduction

Photochromic polymers are attracting ever increasing interest for both fundamental and applied significance,[1−3] particularly in view of their possible exploitation in nonlinear optics and optoelectronics.[4−8]

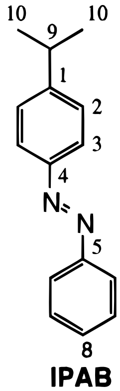
For many years our group has been active in a research line focused on the investigation of photochromic and chiroptical properties of optically active polymeric materials containing photoactive groups in the side chain.[10−16] Particular attention was devoted to establish useful correlations between polymer properties and macromolecular structure. In this respect, the influence of the distance of the photoactive chromophore from the main chain appeared to be of paramount importance in determining both chiroptical and photochromic properties of the investigated polymers.

Rather recently, the synthesis and the radical homopolymerization of 4-vinylazobenzene (VAB), a vinyl monomer containing an azobenzene chromophore directly attached to the polymerizable double bond, was reported.[17] No information on VAB ionic polymerization and on the photochromic properties of VAB polymers is, however, still available.

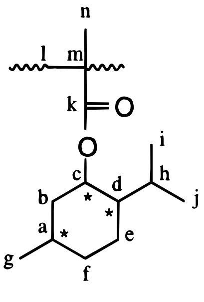
In the present paper, the results of an investigation on the homo- and copolymerizability of VAB in the presence of radical, cationic, anionic, and Ziegler−Natta catalysts are reported. Photochromic and chiroptical properties, 1D and 2D NMR spectra, and molecular dynamics in solution are discussed in terms of the chemical structure of the polymeric products.



poly(VAB)



IPAB



poly(MnMA)

Experimental Section

Commercial solvents, reagents, and monomers were purified according to well-established procedures.

4-Bromoazobenzene having mp 100−101 °C was prepared in 73% yield by reaction of 7.49 g (70 mmol) of nitrosobenzene with 8.66 g (64 mmol) of 4-bromoaniline in 400 mL of acetic acid, for 40 h at reflux.[17,18]

FT-IR (KBr): $\bar{\nu}$ = 3080−3040 (ν(CH) aromatic), 1569 (ν(C=C) aromatic), 835, 768, and 682 cm^{-1} (δ(CH) aromatic).

4-Vinylazobenzene (VAB) having mp 70−71 °C was prepared in 53% yield by reaction of 4-bromoazobenzene with ethylene: A 250 mL autoclave was loaded under nitrogen with 150 mL of anhydrous dimethylformamide, 5.00 g (19 mmol) of 4-bromoazobenzene, 115 mg (0.38 mmol) of tri-*o*-tolylphosphine, and 43 mg (0.19 mmol) of palladium diacetate; a pressure of 70 bar of ethylene was added, and the autoclave was then heated at 130 °C for 24 h. After the usual workup the product was eluted on silica gel with a 3:2 cyclohexane/toluene mixture, then recrystallized from ethanol, and finally sublimated under vacuum.[17,19]

FT-IR (KBr): $\bar{\nu}$ = 3080−3050 (ν(CH) aromatic and olefinic), 1628 (ν(C=C) olefinic), 1583 (ν(C=C) aromatic), 837, 768, and 688 cm^{-1} (δ(CH) aromatic).

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* To whom correspondence should be addressed.

[†] Present address: Department of Materials, Institute of Polymers, ETH Zürich, Universitätstrasse 6, 8092 Zürich, Switzerland.

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^{1}H-NMR ($CDCl_3$): $\delta = 7.95$ (m, 4H, aromatic protons ortho to the azo group), 7.55 (m, 5H, aromatic protons meta and para to the azo group), 6.8, 5.9, and 5.4 ppm (3 dd, 3H, vinyl protons).

UV−vis ($CHCl_3$): λ_{max} (ϵ) = 441 (900 mol L^{-1} cm^{-1}) and 329 nm (18 000 mol L^{-1} cm^{-1}).

4-Isopropylazobenzene (IPAB) having mp 49 °C was prepared in 78% yield by reaction of 7.49 g (70 mmol) of nitrosobenzene with 8.66 g (64 mmol) of 4-isopropylaniline in 400 mL of acetic acid, for 40 h at reflux.

FT-IR (KBr): $\bar{\nu} = 3100-3000$ (ν(CH) aromatic), 3000−2800 (ν(CH) aliphatic), 2000−1660 (δ(CH) aromatic overtones), 1590 (ν(C=C) aromatic), 1444 ($\delta_{as}(CH_3)$), 1384 and 1362 ($\delta_s(CH_3)$), 840, 766, 736, and 688 cm^{-1} (δ(CH) aromatic).

^{1}H-NMR ($CDCl_3$): $\delta = 8.0$ (m, 4H, aromatic protons ortho to the azo group), 7.5 (m, 3H, aromatic protons meta and para to the azo group), 7.4 (m, 2H, aromatic protons ortho to the vinyl group), 3.04 (m, 1H, CH aliphatic), and 1.36 ppm (d, 6H, CH_3).

(−)-Menthyl methacrylate (MnMA) having bp 106−108 °C/5 mmHg and $[\alpha]_D^{25}$ −91.8 (neat) was prepared in 58% yield by the procedure reported elsewhere.[20]

$MgCl_2$-supported Ziegler−Natta catalyst (BO200) was kindly supplied by Dr. F. Masi of EniChem, Milan, Italy.

(Tetraphenylcyclopentadienyl)zirconium trichloride was kindly supplied by Dr. G. Conti of the University of Pisa, Italy.

Polymerization Experiments. Polymerization experiments were performed according to common procedures. Data relevant to individual experiments are summarized in Table 1, whereas some typical examples are reported by the following.

Radical Homopolymerization of 4-Vinylazobenzene (Run R1). A solution of 0.5 g (2.5 mmol) of 4-vinylazobenzene and 12 mg (75 μmol) of AIBN in 10 mL of anhydrous dioxane was placed in a 25 mL glass vial. After three freeze−pump−thaw cycles, the vial was sealed under vacuum and heated at 60 °C for 3 h. After cooling at room temperature, the reaction mixture was poured into 100 mL of methanol. The precipitate was filtered out, dissolved in chloroform, reprecipitated in methanol, and finally dried under vacuum to yield 0.155 g (31% yield) of an orange polymeric product.

IR (cast film): $\bar{\nu} = 3100-3000$ (ν(C−H) aromatic), 2970−2860 (ν(C−H) aliphatic), 2226 (ν(C≡N)), 1730 (ν(C=O)), 1598 and 1514 (ν(C=C)), 1448 ($\delta(CH_2)$ and $\delta_{as}(CH_3)$), 1388 ($\delta_s(CH_3)$), 1300−1000 (ν(C−O−C)), 846 and 826 cm^{-1} (δ(C−H) aromatic).

^{1}H-NMR ($CDCl_3$): $\delta = 0.5-2.0$ (CH_3, CH_2, and CH), 3.0−4.3 (CH_2−N and CH_2−O), and 6.5−8.0 ppm (CH aromatic).

Homopolymerization of 4-Vinylazobenzene in the Presence of $MgCl_2$-Supported (BO/Al) Ziegler−Natta Catalyst (Run Z1). A solution of 10 μmol of triisobutylaluminum in 1 mL of *n*-heptane was added under an argon atmosphere to 2.5 mL (2.5 μmol of Ti) of a suspension of BO200 in *n*-heptane. After 10 min, a solution of 0.5 g (2.5 mmol) of 4-vinylazobenzene in 10 mL of anhydrous toluene was quickly added under stirring. The reaction mixture immediately turned dark brown. After 15 h of stirring at room temperature, the reaction mixture was poured into 100 mL of methanol. No solid polymeric product was formed.

Homopolymerization of 4-Vinylazobenzene in the Presence of (Tetraphenylcyclopentadienyl)zirconium Trichloride/Methylalumoxane (CpZr/MAO) Catalyst (Run Z2). A solution of 0.5 g (2.5 mmol) of 4-vinylazobenzene in 10 mL of anhydrous toluene was quickly added under stirring to a catalyst suspension obtained by reaction of 1 mL (2.5 μmol of Zr) of a 2.5 mM solution of CpZr in toluene with 5 mmol of MAO. The orange solution immediately turned dark brown. After 12 h of stirring at room temperature, the reaction mixture was poured into 100 mL of methanol. No solid polymeric product was formed.

Anionic Homopolymerization of 4-Vinylazobenzene (Run A1). A solution of 0.5 g (2.5 mmol) of 4-vinylazobenzene in 10 mL of anhydrous dioxane was placed in a 25 mL glass vial under a dry argon atmosphere; then 0.5 mL (50 μmol) of a 0.1 M solution of butyllithium in hexane was added under stirring. The orange solution immediately turned dark brown. After 3 h the reaction mixture was poured into 100 mL of methanol. No solid polymeric product was formed.

Cationic Homopolymerization of 4-Vinylazobenzene (Run C1). A solution of 0.5 g (2.5 mmol) of 4-vinylazobenzene in 10 mL of anhydrous dioxane was placed in a 25 mL glass vial under a dry argon atmosphere. The solution was cooled at −10 °C; then 0.5 mL (50 μmol) of a 0.1 M solution of $BF_3{\cdot}OEt_2$ in dioxane was added under stirring. The orange solution immediately turned dark brown. After 2 h the reaction mixture was poured into 100 mL of methanol. No solid polymeric product was formed.

Anionic Copolymerization of 4-Vinylazobenzene and Styrene (Run VS1). A solution of 0.5 g (2.5 mmol) of 4-vinylazobenzene and 50 mg (0.5 mmol) of styrene in 10 mL of anhydrous dioxane was placed in a 25 mL glass vial under a dry nitrogen atmosphere; then 0.5 mL (50 μmol) of a 0.1 M solution of butyllithium in hexane was added under stirring. The orange solution immediately turned dark brown. After 3 h the reaction mixture was poured into 100 mL of methanol. The precipitate was filtered out, dissolved in chloroform, reprecipitated in methanol, and finally dried under vacuum to yield 0.127 g (23% yield) of an orange polymeric product.

Radical Copolymerization of 4-Vinylazobenzene and (−)-Menthyl Methacrylate (Run VM1). A solution of 0.5 g (2.5 mmol) of 4-vinylazobenzene, 0.56 g (2.5 mmol) of menthyl methacrylate, and 12 mg (75 μmol) of AIBN in 10 mL of anhydrous dioxane was placed in a 25 mL glass vial. After three freezing−thaw−pumping cycles, the vial was sealed under vacuum and heated at 60 °C for 3 h. After cooling at room temperature, the reaction mixture was poured into 100 mL of methanol. The precipitate was filtered out, dissolved in chloroform, reprecipitated in methanol, and finally dried under vacuum to yield 0.35 g (33% yield) of an orange polymeric product.

Sample Characterization. FT-IR spectra were recorded by a Perkin-Elmer model 1600 spectrophotometer.

NMR spectra were recorded at room temperature on 5−10% $CDCl_3$ solutions by a Varian Gemini 200 spectrometer. ^{1}H-NMR spectra were recorded at 200 MHz, by using the following experimental conditions: 11.968 data points, 3 kHz spectral width, 30° pulse, 2 s acquisition time, 1 transient. 2D COSY spectra were recorded at 200 MHz, by using the following experimental conditions: 1024 data points, 1742 Hz spectral width, 8 transients, 1.7 s delay. A total of 256 spectra were recorded in order to have a 1742 Hz spectral width in the second dimension. Final spectra have been symmetrized.

^{13}C-NMR spectra were recorded at 50.3 MHz, under full proton decoupling, by using the following experimental conditions: 23 936 data points, 15 kHz spectral width, 70° pulse, 0.8 s acquisition time, 44 000 transients. 2D ^{13}C−^{1}H HETCOR spectra were recorded at 50.3 MHz, by using the following experimental conditions: 2048 data points, 14 992 Hz spectral width, 128 transients, 1.0 s delay. A total of 512 spectra were recorded in order to have a 1946 Hz spectral width in the second dimension. ^{13}C T_1 measurements were performed at 50.3 MHz, by using the $\pi-\tau-\pi/2$ pulse sequence and the following experimental conditions: 23 936 data points, 15 kHz spectral width, 70° pulse, 0.8 s acquisition time, 1024 transients, 6 s delay between sequences, delay between pulses τ = 0.023, 0.047, 0.094, 0.188, 0.375, 0.75, 1.5, 3.0, and 6.0 s.

UV spectra were recorded between 250 and 650 nm at 25 °C on chloroform solutions in 1 cm quartz cells by a JASCO Uvidec 510 spectrophotometer.

Photoisomerization experiments were carried out in 1 cm quartz cells placed within a JASCO Uvidec 510 spectrophotometer equipped with a magnetic microstirrer. Chloroform solutions of the investigated samples, having 0.2 absorbance at 366 nm, were irradiated at 366 nm by a quartz optical fiber placed on top of the cell and connected to a 150 W Hamamatsu Hg/Xe lamp equipped with a narrow bandwidth (10 nm) interferential filter. The 330 nm absorbance was monitored with time at 1 s time intervals.

Optical rotatory measurements were performed at 25 °C in 1.0 dm quartz cells by an automatic Perkin-Elmer model 141 spectropolarimeter having sensitivity ±0.001°.

Table 1. Homopolymerization and Copolymerization of 4-Vinylazobenzene under Different Experimental Conditions

	comonomer		catalyst		solvent			
run[a]	type	amt (mmol)	type	amt (mmol)	type	amt (mL)	temp (°C)	conv[b] (%)
R1			AIBN	15	dioxane	10	60	31
C1			BF_3OEt_2	10	THF	10	−10	0
C2			BF_3OEt_2	10	THF	10	−100	0
A1			C_4H_9Li	10	dioxane	10	20	0
A2			C_4H_9Li	10	dioxane	10	20	0
Z1			BO/Al	*d*	toluene	10	20	0
Z2			CpZr/MAO	*d*	toluene	10	20	0
VS1	St	0.5	C_4H_9Li	50	dioxane	10	20	23
VM1	MnMA	2.5	AIBN	75	dioxane	10	60	33
VM2	MnMA	22.5	AIBN	75	dioxane	10	60	47
M1[c]	MnMA	8.9	AIBN	75	dioxane	10	60	48

[a] VAB 0.5 g (2.5 mmol); duration 3 h. [b] Evaluated as 100(polymer weight/monomers weight). [c] Run carried out in absence of VAB. [d] 2.5 μmol of transition metal.

Table 2. Characterization of Photochromic Polymers Obtained by Copolymerization of VAB and MnMA

		polymer			
sample	VAB in the feed (% mol)	VAB (% mol)	T_g[a] (°C)	$\bar{M}_n$[b]	$\bar{M}_w/\bar{M}_n$[b]
R1	100	100	149	9000	1.8
VS1	90	88	n.d.	12200[c]	2.6
VM1	50	86	136	7600	1.5
VM2	10	15	138	7100	1.5
M1	0	0	140	8600	2.3

[a] Evaluated by DSC. [b] Evaluated by GPC. [c] Bimodal distribution of molecular weights: $\bar{M}_n = 25\,900$, $\bar{M}_v/\bar{M}_w = 1.5$ (82 wt %) and $\bar{M}_n = 4700$, $\bar{M}_n/\bar{M}_w = 1.1$ (18 wt %).

Circular dichroism (CD) measurements were performed in the 250−600 nm spectral region on polymer solutions in chloroform by a JASCO model J 500 A dichrograph.

Polymer number- ($\bar{M}_n$) and weight-average ($\bar{M}_w$) molecular weights were determined in THF by a Perkin-Elmer model 10 liquid chromatograph equipped with two PL mixed C 5 μm columns, a Perkin-Elmer LC-75 UV detector, and a JASCO 830 RI detector, by using polystyrene standards for calibration.

Differential scanning calorimetry (DSC) measurements were performed by a Mettler TA-4000 instrument between −50 and +250 °C at 10 °C/min heating rate on 5−10 mg polymer samples under a nitrogen atmosphere.

Results and Discussion

Polymer Synthesis. The polymerizability of 4-vinylazobenzene (VAB) was investigated under several different experimental conditions (Table 1). In accordance with previous findings,[17] radically initiated polymerization of VAB afforded a 31% yield of poly(VAB) having a number-average molecular weight of 9000 and a polydispersity index of 1.8 (Table 2). Fairly high yields of polymeric products having $\bar{M}_n$ = 7000−8000 were also observed in the radically initiated copolymerization of VAB and (−)-menthyl methacrylate (MnMA). The significantly larger contents of VAB units in the copolymers as compared with the corresponding polymerization feed (Table 2) indicate that VAB has a much higher reactivity than MnMA. The Kelen−Tüdös method, modified for the rather large conversions, allowed us to estimate, within the limits of just two sets of data, the following reactivity ratios: $r_{VAB} = 5.5$ and $r_{MnMA} = 0.6$.

No polymeric product was obtained when the polymerization was carried out in the presence of either a $MgCl_2$-supported Ziegler−Natta catalyst or a homogeneous system obtained by reacting (tetraphenylcyclopentadienyl)zirconium trichloride and methylaluminoxane, two catalytic systems highly active in the polymerization of α-olefins and styrene.[21,22] Analogous negative results were obtained when VAB homopolymerization was performed in the presence of BF_3OEt_2 as cationic initiator.

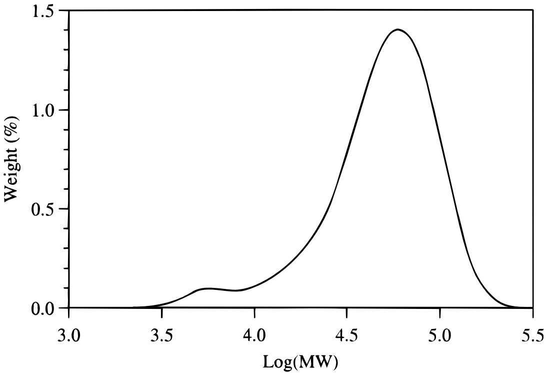

Figure 1. Molecular weight distribution of the anionic copolymer of VAB with styrene (sample VS1).

These results indicate that the electron withdrawing effect of the azobenzene substituent on the vinyl double bond effectively inhibits the formation of a carbocation (cationic polymerization) and poisons the active sites present in Ziegler−Natta type catalysts.

No polymeric product was formed when homopolymerization experiments were performed in the presence of C_4H_9Li as anionic initiator. It is, however, worth noting that the anionic copolymerization of a 5/1 VAB/styrene mixture, carried out under the same experimental conditions, afforded 23% conversion to a copolymer containing 88% VAB units, in accordance with a slightly lower reactivity of styrene as compared to VAB. These findings seem to suggest that the presence of the azo group completely inhibits the initiation step, which can be effectively carried out by styrene, whereas it does not significantly interfere with the propagation steps.

GPC analysis evidenced that the VAB/St copolymerization product was constituted by an 82/18 mixture of two fractions having $\bar{M}_n$ 25 900 and 4700, respectively (Figure 1). However, no significant difference in the GPC traces could be evidenced by using either 254 or 440 nm detection wavelength, where both monomeric units (254 nm) or only VAB units (440 nm) have significant absorbance, thus demonstrating that both fractions have almost the same chemical composition. No sound explanation of this result can be put forward at present.

Differential Scanning Calorimetry (DSC). DSC analysis of the polymerization products in the 0−200 °C temperature range evidenced the presence of a second-order transition attributed to the glass transition in the 130−150 °C range. The glass transition temper-

Table 3. Assignments, T_1 Relaxation Times, and Correlation Times (τ) of Signals Present in ^{13}C-NMR Spectra of IPAB and Poly(VAB)

carbon	IPAB			poly(VAB)		
atom	δ (ppm)	T_1 (s)	$10^{10}\tau$ (s)	δ (ppm)	T_1 (s)	$10^{10}\tau$ (s)
C_1	152.22	>29	n.d.	147.78	0.90	n.d.
C_2	127.01	3.46	0.14	128.25	0.13	4.3
C_3	122.67	3.76	0.13	122.82	0.28	1.7
C_4	151.02	>22	n.d.	151.35	1.52	n.d.
C_5	152.75	>21	n.d.	152.92	2.33	n.d.
C_6	122.91	3.44	0.14	122.82	0.28	1.7
C_7	128.94	3.67	0.13	128.93	0.35	1.4
C_8	130.56	1.20	0.39	130.51	0.13	4.3
C_9	34.04	5.16	0.09	40.89	0.11	5.4
C_{10}	23.77	1.68	0.13	41−46	0.07	8

atures (T_g) of VAB/MnMA copolymer samples were slightly lower than those of the corresponding homopolymers (Table 2), in accordance with a substantially random distribution of monomeric units. In no case were endothermic peaks attributable to the melting of the sample observed, thus suggesting that either the melting point is above the decomposition temperature (250−300 °C) or the analyzed polymers are amorphous.

NMR Analysis. The ^{1}H-NMR spectrum of IPAB, the low molecular weight model compound of poly(VAB) exhibited a doublet at 1.36 ppm and a multiplet at 3.04 ppm, attributable respectively to methyl and methylene protons, and a series of overlapping signals at about 7.4, 7.5, and 8.0 ppm. The 2D-COSY NMR spectrum allowed us to attribute these peaks to protons bound to C-2, C-7 and C-8, C-3, and C-6, respectively.

The ^{1}H-NMR spectrum of poly(VAB) presented in the aromatic proton region a series of overlapping signals at about 6.7, 7.0, 7.4, 7.7, and 7.8 ppm, having relative intensities of 1.8, 0.2, 3.0, 2.0, and 2.0, respectively. The 2D-COSY NMR spectrum evidenced off diagonal signals between peaks at 6.7 and 7.7 ppm and at 7.4 and 7.8 ppm. A weak cross-peak was also observed between signals at 7.0 and 7.7 ppm. These data allowed us to attribute peaks at 6.7, 7.4, 7.7, and 7.8 ppm, respectively, to aromatic protons bound to C-2, C-7 and C-8, C-3, and C-6. The large upfield shift of the signal of aromatic protons ortho to the main chain, as compared to the low molecular weight model compound, can be attributed to the partial overlap of neighboring aromatic groups. The small signal at about 7.0 ppm can be tentatively assigned to C-2 protons experiencing a smaller shielding effect, possibly due to locally different tacticity and/or conformation of the main chain.

Attribution of the signals present in the ^{13}C-NMR spectra of different polymer samples (Table 3) was performed on the basis of additive group contributions,[17] relative intensity, and 2D HETCOR spectra. Assignment of quaternary aromatic carbons, made only from group contributions, may be partially incorrect.

^{13}C-NMR spectra of copolymers of VAB and MnMA corresponded to the sum of the spectra of the two homopolymers as far as the number of the peaks are concerned, whereas their relative intensity varied with the chemical composition of the samples. Peaks at about 176.9, 75.9, 52.7, 47.5, 45.9, 40.3, 34.5, 31.5, 25.8, 23.1, 22.2, 21.5, 18.1, and 15.4 were attributed respectively to C_k, C_c, C_m, C_d, C_l, C_b, C_f, C_a, C_h, C_e, C_g, C_j, C_n, and C_i of the MnMA units.[23] No signal clearly attributable to junctions between different units was detected. However, peaks sensitive to main chain tacticity showed a small, continuous variation of peak shape and position with copolymer composition, thus suggesting an influence of comonomer distribution. Overlap of these two different effects prevented a quantitative evaluation of both polymer tacticity and monomer distribution.

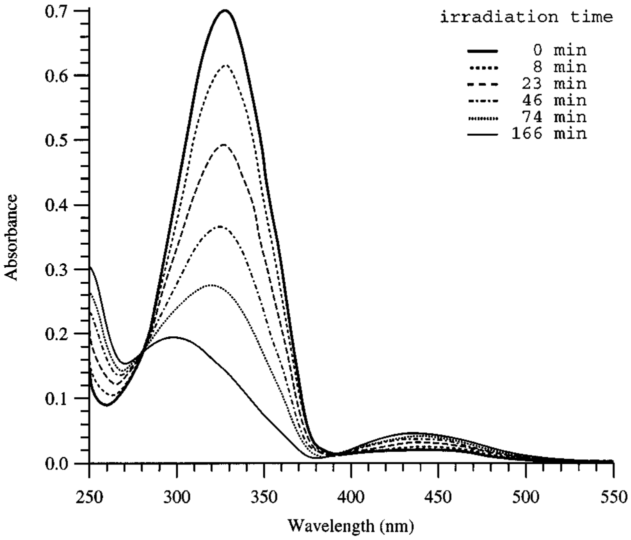

Figure 2. Variation of the UV absorption spectrum of poly(VAB) under irradiation at 366 nm in chloroform solution at 25 °C.

To gain information about molecular mobility ^{13}C-NMR relaxation times (T_1) of poly(VAB) and, for comparison, IMBAC were measured at 50.3 MHz, in chloroform solution at room temperature (Table 3).

Correlation times were evaluated from the corresponding T_1, under the rather crude assumption that the only relaxation process is dipolar and that only directly bonded hydrogen atoms contribute to the relaxation process (Table 3).[24]

Relaxation times and correlation times of IPAB evaluated therefrom evidenced an appreciable mobility of all carbons directly bound to hydrogen atoms ($\tau = (0.09-0.14) \times 10^{-10}$ s) in fair agreement with an overall isotropic tumbling model with a single correlation time. The cylindrical symmetry of the molecule is reflected by the somewhat larger correlation time of the C_8 carbon ($\tau = 0.39 \times 10^{-10}$ s).

T_1 and τ values of poly(VAB) carbons indicated a significantly reduced mobility of polymer chains, as compared with the low molecular weight model compound. As expected, this effect was more pronounced for main chain carbons and segmental mobility increased with the distance from the main chain. Relaxation times and hence mobility of aromatic carbons in poly(VAB) were 2 or 3 times smaller than those of poly(4-(methacryloyloxy)azobenzene),[25] confirming the relative flexibility of methacrylate segments with respect to hydrocarbon chains. Also the different distance of azobenzene chromophores from the polymer backbone must be taken into account.

Photochromic Properties. UV absorption spectra of VAB polymers in chloroform solution at 25 °C (Figure 2) showed in the 250−550 nm spectral region two absorption bands with maxima at about 327 nm ($\epsilon \approx$ 21 000 mol^{-1} l cm^{-1}) and 440 nm ($\epsilon \approx$ 900 mol^{-1} L cm^{-1}), attributable to the first $\pi \rightarrow \pi^*$ and n $\rightarrow \pi^*$ electronic transitions of the azobenzene chromophore, respectively. No significant difference, as far as intensity and position of the peaks are concerned, could be detected among the spectra of the different samples, independent of their nature and chemical composition.

On irradiation at 366 nm in the first $\pi \rightarrow \pi^*$ electronic transition, the azobenzene chromophores undergo a

Table 4. UV Absorption and Photochromic Properties of VAB Polymers in Chloroform Solution at 25 °C

sample	VAB (% mol)	λ_1 (nm)	ϵ_1[a]	λ_2 (nm)	ϵ_2[a]	10^4k_1[b] (s^{-1})	10^3k_2[c] (s^{-1})	A_∞/A_0[d]
R1	100	326.5	20 500	441.5	900	4.4 ± 0.3	7.0 ± 0.3	0.14 ± 0.02
VM1	86	328.0	21 700	441.5	730	4.0 ± 0.4	6.6 ± 0.4	0.13 ± 0.02
VM2	15	328.5	20 800	441.0	790	3.9 ± 0.3	6.9 ± 0.3	0.14 ± 0.02
IPAB		327.5	19 400	437.5	790	3.8 ± 0.2	7.2 ± 0.4	0.04 ± 0.03

[a] Expressed in mol^{-1} L cm^{-1}. [b] *Trans* → *cis* photoisomerization rate constant under irradiation at 366 nm. [c] *Cis* → *trans* photoisomerization rate constant under irradiation at 437 nm. [d] Ratio of the 330 nm absorbance at the photostationary state (A_∞) and at $t = 0$ (A_0).

trans → *cis* photoisomerization process. Correspondingly, shape, intensity, and position of the UV absorption bands are modified (Figure 2). Photoisomerization kinetics were investigated at 25 °C on chloroform solutions having an absorbance lower than 0.3 at the irradiation wavelength (366 nm). At the photostationary state, the UV spectra of the investigated polymer samples were characterized by the presence of two bands at 298 and 440 nm, having respectively $\epsilon \approx 5700$ and 1800 mol^{-1} L cm^{-1}.

When samples irradiated at 366 nm were irradiated at 437 nm, in the first n → π^* electronic transition, their 330 nm absorbance steadily increased to the starting value before irradiation, thus confirming the photoreversibility of the isomerization process.

In all cases UV spectra recorded at different irradiation times were characterized by the presence of two isosbestic points at about 280 and 390 nm (Figure 2), thus confirming that only two absorbing species, namely the *cis* and the *trans* azobenzene isomers, are present in solutions.

Kinetic data were fitted to equation $\ln[(A_0 - A_\infty)/(A_t - A_\infty)] = kt$, where A_0, A_t, and A_∞ are the 330 nm absorbance at time 0, t, and ∞, respectively.[26] First-order kinetics were observed for all investigated samples under irradiation at either 366 (k_1) or 437 nm (k_2). The experimental values of kinetic constants were averaged over four experiments and corrected for the variations of lamp intensity,[26] as measured by a photodiode. The recorded k_1, k_2, and A_∞/A_0 values (Table 4) showed only a slight dependence on nature and chemical composition of the investigated samples, analogously to what was observed for other azobenzene containing polymers.[27]

When kept in the dark, the 330 nm absorbance of irradiated samples steadily increased up to the starting value before irradiation, thus confirming the thermal reversibility of the photoisomerization process. Also in this case, the process obeyed a first-order kinetics. The thermal isomerization rate constants (k_T), measured on chloroform solutions of IPAB and poly(VAB) at 25, 35, 45, and 55 °C, ranged between 3.4×10^{-6} s^{-1} and about 4.4×10^{-5} s^{-1}. Arrhenius plots (Figure 3) of experimental data allowed us to evaluate an activation energy (ΔH^*) of about 16 kcal/mol for both samples.

The absence of an appreciable influence of the stiff polymer backbone on azobenzene *trans* → *cis* and *cis* → *trans* isomerization rates seems to indicate that both thermal and photoinduced processes occur by in-plane translation of the benzene ring further from the main chain rather than by rotation around the N=N bond.[28-33]

Chiroptical Properties. Chiroptical properties of VAB/MnMA copolymers were investigated only by circular dichroism (CD), as the large absorption of the azobenzene chromophore prevented the measurement of their optical rotation.

The CD spectra of the investigated samples, recorded in chloroform solution at 25 °C, exhibit in the 250−600 nm spectral region the presence of two positive and one negative dichroic bands at about 444, 345, and 305 nm (Figure 4), in close correspondence with azobenzene UV absorption bands. This result has to be attributed to an asymmetric perturbation of azobenzene chromophores induced by neighboring optically active MnMA units, thus unequivocally demonstrating that copolymer macromolecules are formed by radical polymerization of VAB/MnMA mixtures.[34]

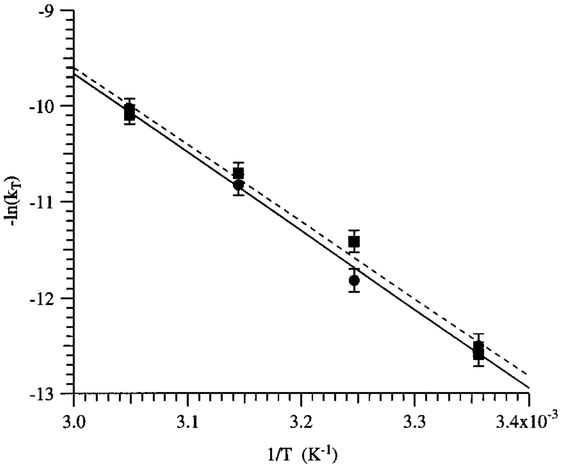

Figure 3. Arrhenius plot of the thermal *cis* → *trans* isomerization rates of poly(VAB) (■) and IPAB (●) in chloroform solution.

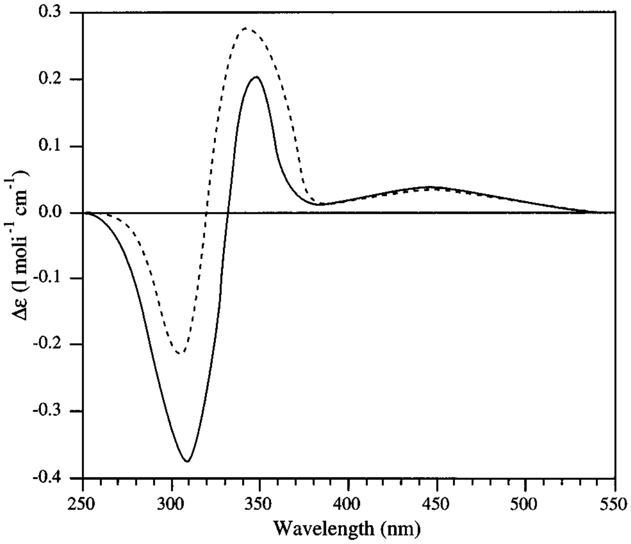

Figure 4. CD spectra of poly(VAB-*co*-MnMA) samples containing 14 (—) and 85% (- - -) of MnMA units, in chloroform solution at 25 °C.

The first positive band at 444 nm ($\Delta\epsilon = +0.04$ mol^{-1} L cm^{-1}) corresponds to the n → π^* electronic transition, whereas the two bands of opposite sign ($\Delta\epsilon = \pm 0.3$ mol^{-1} L cm^{-1}) at lower wavelength can be attributed to an exciton splitting of the 320 nm band.[35] The rather low ellipticity of this couplet seems to indicate that in solution only small sections of the polymer chain assume conformations suitable for exciton interactions.

Within the limits of experimental errors (±15%), the intensity of all dichroic bands is almost independent of copolymer composition, in spite of the rather large variation of the content of optically active MnMA units from 14 to 85%. This behavior can be tentatively attributed to the reduced mobility of the azobenzene chromophore inserted in blocks of VAB units. In this case the asymmetric perturbation of flanking MnMA residues can be easily transmitted over several neighboring aromatic units that are close enough to interact in suitable chiral conformations. On the other hand, at low VAB content, most azobenzene chromophores should experience the influence of chiral (−)-menthyl groups, but only the few neighboring ones can give rise to an exciton splitting. Moreover, the presence of rather flexible next-neighboring methacrylate units should significantly enhance the rotational freedom of the aromatic chromophores, thus making less effective the asymmetric perturbation by chiral co-units.

The independence of CD spectra from copolymer composition could be attributed also to a significant decrease of polymer stereoregularity with increasing content of chiral units. It is well-known that the structure of the inserted monomers can affect the stereochemistry of polymer propagation. Even though large variations of main chain tacticity are not expected to occur in the radical copolymerization of VAB with MnMA, this possibility cannot be completely ruled out.

Concluding Remarks

The polymerizability of 4-vinylazobenzene (VAB), a vinyl monomer containing an azobenzene chromophore directly attached to the polymerizable double bond, was investigated in the presence of radical, anionic, cationic, and both soluble and heterogeneous Ziegler−Natta type catalysts.

Fairly high yields of photochromic polymeric materials were obtained by radical polymerization of VAB, either alone or with (−)-menthyl methacrylate, carried out in benzene at 70 °C in the presence of AIBN. No high molecular weight product was formed on the contrary by VAB homopolymerization in the presence of cationic, anionic-coordinate, and anionic catalysts. Polymeric products were obtained only by anionic copolymerization of VAB with styrene.

Determination of ^{13}C relaxation times allowed us to evaluate the poly(VAB) molecular mobility, also in comparison with 4-isopropylazobenzene, a low molecular weight model compound, and other polymeric systems containing the azobenzene chromophore spaced from the main chain.

Thermal and photoinduced *cis* → *trans* and *trans* → *cis* isomerization rates were almost independent of molecular weight and chemical composition of the investigated photochromic polymers. These data seem to indicate that the isomerization of azobenzene chromophores implies an in-plane inversion rather than an out-of-plane rotation of the phenyl ring further from the main chain.

CD spectra of VAB/MnMA copolymers demonstrates that side-chain azobenzene chromophores are chirally perturbed by neighboring optically active MnMA units. The presence of two bands of opposite sign in correspondence with the $\pi \rightarrow \pi^*$ electronic transition strongly indicates that in solution segments of the polymer chains assume conformations of one prevailing chirality, suitable for exciton interactions. The limited influence of copolymer composition on the intensity of dichroic bands can be tentatively attributed to the different distribution of monomeric units, that in turn affects both chromophore mobility and induced chirality.

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