

Synthesis and Polarized Light-Induced Birefringence of New Polymethacrylates Containing Carbazolyl and Azobenzene Pendant Groups

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ABSTRACT: Low T_g copolymers of [11(*N*-carbazolyl)undecylmethacrylate] and [2,5-dimethylphenyl-[(4-nitrophenyl)azo]-phenoxyalkylmethacrylate] have been synthesized and the polarized light-induced birefringence of thick films (70 μm) has been investigated at a constant deduced temperature relative to T_g ($T - T_g = 10$ °C). The optical properties of these copolymers have been studied in relation to the azo-dye content and the length of the alkyl spacer between the azo-dye and the methacrylic backbone. They have been compared with the dispersion of (4-methoxy-2,5-dimethylphenyl)-(4-nitrophenyl)diazene (DMNPAA) within a poly[11(*N*-carbazolyl)undecyl-methacrylate] and a poly[*N*-vinylcarbazole] (PVK) matrix. The experimental curves have been fitted by biexponentials, so emphasizing the effects of the copolymer structure on the kinetics of the writing process. The photoinduced orientation is more than three orders of magnitude higher in a grafted material compared to the dispersion version. The azo-dye concentration also has an important role in both the amplitude and the dynamics of the photo-orientation. © 2000 John Wiley & Sons, Inc. *J Polym Sci B: Polym Phys* 38: 205–213, 2000
Keywords: polymethacrylates; azo-dye; photoinduced birefringence; matrix structure; concentration

INTRODUCTION

Because the availability of efficient optical data storage systems is highly desirable, polymers combining high optical sensitivity and storage densities, short response time, and read-write reversibility are nowadays the focus of extensive scientific and industrial interest. For this purpose, azo-dyes are currently either dispersed¹ or grafted into polymer matrices,^{2–4} or in organic-

inorganic composite materials.⁵ Liquid crystals that can be oriented by weak optical fields and exhibit high birefringence have also been considered as new electro-optical materials.^{6–8}

Birefringence has been found to be photoinduced in an azo-dye doped polymer, so that special attention has been paid to the basic mechanism in view of improving the efficiency of this phenomenon. The photoinduced birefringence relied upon the local orientation of the azo groups and is the result of successive *trans-cis-trans* isomerizations initiated by a linearly polarized laser beam.^{1,9} This photo-orientation is responsible for the refractive index change.

Dispersion of an azobenzene in poly[*N*-vinylcarbazole] (PVK), plasticized and doped with a charge generator, has been reported as exhibit-

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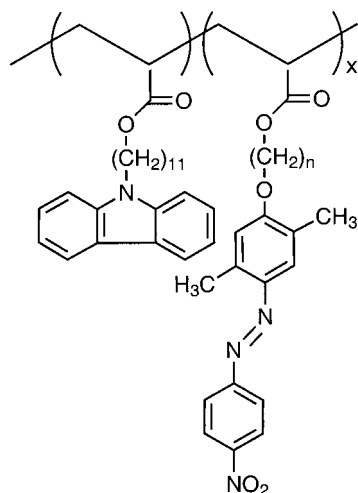


Figure 1. Structure of the carbazoyl azo-dye side chain copolymers. [11-(*N*-carbazoyl)undecylmethacrylate] and [2,5-dimethyl-[(4-nitrophenyl)azo]-phenoxyalkylmethacrylate].

ing a photorefractive effect.¹⁰ The low T_g of this type of material for photorefractive applications was found to increase the diffraction efficiency as a result of the improved orientation of the chromophore in the space-charge electric field.¹¹ This type of azo-dye doped PVK has also proved to be a useful polarized recording medium.¹² Diffraction grating, and more recently, photorefractive asymmetric two-beam coupling, have been studied by Rochon et al.¹³ in methacrylic polymers bearing azobenzene and carbazoyl pendant groups.

This paper reports the synthesis and optical storage properties of new low T_g copolymers of [11-(*N*-carbazoyl)undecylmethacrylate] and [2,5-dimethylphenyl-[(4-nitrophenyl)azo]-phenoxyalkylmethacrylate] (Fig. 1). Because of the dependence of the photoinduced orientation on molecular mobility, it is worth considering the possible effect of the azo-dye grafting, the azo-dye concentration, and the length of the alkyl spacer on the photoinduced birefringence. It is also important to compare the properties of these new materials with the previous materials reported in the scientific literature. The photoinduced birefringence properties of (4-methoxy-2,5-dimethylphenyl)(4-nitrophenyl)diazene (DMNPAA) dispersed in the photoconducting poly[*N*-vinylcarbazole], plasticized by *N*-ethyl carbazole, have therefore also been measured.

EXPERIMENTAL

General

¹H NMR spectra were recorded at 400 MHz with a Bruker AM 400 spectrometer. IR spectra were recorded with a Perkin–Elmer 1600 FT (Norwalk, CT) spectrometer. The glass-transition temperature was measured by differential scanning calorimetry (DSC) with a Dupont 9000 instrument, under a nitrogen atmosphere at a 20 °C/min heating rate. Measurement procedure was identical for all samples in order to have the same thermal history. Gel permeation chromatography was performed at 40 °C in chloroform with a Waters 610 apparatus. Molecular weights were calculated with respect to a polystyrene calibration.

Products and Solvents

Carbazole (Aldrich), *N*-ethylcarbazole (Acros) and *N*-vinylcarbazole (Fluka) were twice recrystallized from methanol before use. 11-bromoundecanol (Fluka), methacryloyl chloride (Janssen), sodium hydride (Aldrich, 60% dispersion in mineral oil), triethylamine (Janssen), *p*-nitroaniline (Janssen), 2,5-dimethylphenol (Acros), iodomethane (Aldrich), and 6-chlorohexanol (Janssen) were used as received. Tetrahydrofuran was dried over sodium/benzophenone and distilled just before use. *N,N*-dimethylformamide was dried over phosphorus pentoxide and then distilled. Poly[*N*-vinylcarbazole] was synthesized by radical polymerization of the *N*-vinylcarbazole monomer, initiated by azobisisobutyronitrile (AIBN) and followed by two precipitations in methanol.

Monomer Synthesis

Synthesis of N-(11-hydroxyundecyl)Carbazole

According to a known procedure,¹⁴ carbazole **1** (10 g, 0.06 mol) was dissolved in 300 mL dry THF in a 500 mL single-necked flask under nitrogen atmosphere. The solution was immediately transferred into a second single-necked 500 mL flask containing 11-bromoundecanol (15.06 g, 0.06 mol) and sodium hydride (4.8 g, 0.12 mol) dissolved in 50 mL dry THF. The reaction mixture was then heated at 50 °C for 5 h. After cooling to room temperature, the reaction mixture was filtered and THF was removed under reduced pressure. The crude product was further dissolved in 200 mL diethylether, washed with water, and the or-

ganic layer was dried over magnesium sulfate before removal of the solvent under reduced pressure. Recrystallization from methanol yielded 5.5 g (27%) of *N*-(11-hydroxyundecyl)carbazole. mp = 75 °C. NMR: δ (ppm, CDCl₃) 8.07, 7.46, 7.37 and 7.21 (8 H, m, N(C₆H₄)₂), 4.27 (2H, t, J 7, CH₂—CH₂N), 3.60 (2H, t, J 6.6, CH₂—CH₂OH), 1.85 (2H, m, J 7.2, CH₂—CH₂—CH₂OH), 1.53, 1.38, 1.23 (16H, m, N—CH₂—(CH₂)₈—CH₂—CH₂OH). IR: (KBr, cm⁻¹) 3271, 3046, 2919, 2848, 1597, 1483, 1451, 1345, 1325, 1233, 1151, 1120, 1054, 748, 720.

Synthesis of 11-(*N*-carbazolyl)Undecylmethacrylate 2

N-(11-hydroxyundecyl)carbazole (3.38 g, 0.01 mol) and methacryloyl chloride (1.04 g, 0.011 mol) were dissolved in 100 mL dry THF. Triethylamine (1 g, 0.01 mol) was added dropwise to the solution. After stirring for 5 h at room temperature, THF was removed, and the crude reaction product dissolved in 100 mL diethylether, before being washed with 2 n sodium hydroxide, 0.1 n HCl, and water successively. The organic layer was dried over magnesium sulfate. Removal of the solvent yielded 3.84 g (95%) of 11-(*N*-carbazolyl)undecylmethacrylate. NMR: δ (ppm, CDCl₃) 8.07, 7.46, 7.37 and 7.21 (8 H, m, N(C₆H₄)₂), 6.08 (1H, s, CH₂=C—CO), 5.53 (1H, s, CH₂=C—CO), 4.27 (2H, t, J 7, CH₂—CH₂N), 4.13 (2H, t, J 6.8, CH₂—CH₂—O—CO), 1.93 (3H, s, CH₂=C(CH₃)—CO), 1.85 (2H, m, J 7.2, CH₂—CH₂—CH₂O), 1.53, 1.38, 1.23 (16H, m, N—CH₂—(CH₂)₈—CH₂—CH₂OH). IR: (KBr, cm⁻¹) 3050, 2926, 2853, 1717, 1677, 1628, 1597, 1484, 1453, 1325, 1165, 748, 723.

Synthesis of 2,5-Dimethyl-[(4-nitrophenyl)azo]-Phenol 6

p-Nitroaniline (4.14 g, 0.03 mol) was dissolved in a mixture of 30 mL concentrated hydrochloric acid, 40 mL water, and 30 mL ethanol. After complete dissolution, the solution was cooled down to 0 °C and potassium nitrite (2.58 g, 0.03 mol), previously dissolved in 10 mL water, was added dropwise. After 15 min stirring at this temperature, 2,5-dimethylphenol (3.66 g, 0.03 mol) dissolved in a 10 mL 2 n sodium hydroxide solution was slowly added, leading to a red precipitate. Temperature was allowed to increase up to room temperature and the reaction mixture was neutralized with a 0.1 n sodium hydroxide solution (pH 7). The insoluble compound was filtered off and dried overnight yielding 7 g (86%) of 2,5-

dimethyl-[(4-nitrophenyl)azo]-phenol. NMR: (ppm, CDCl₃) 8.35 (2H, d, J9, (CH)₂—C—NO₂), 7.95 (2H, d, J9, N—C—(CH)₂—(CH)₂—C—NO₂), 7.63 (1H, s, —C(CH₃)—CH—C—N) 6.76 (1H, s, —CH—C(CH₃)—C—N), 2.69 and 2.27 (6H, 2s, —C(CH₃)—CH—C—N and —CH—C(CH₃)—C—N), 2.04 (1H, s, —OH). IR: (KBr, cm⁻¹) 3293, 2922, 1590, 1546, 1512, 1443, 1339, 1251, 1166, 1085, 1014, 856.

General Procedure for the *O*-Alkylation of 2,5-Dimethyl-[(4-nitrophenyl)azo]-Phenol

In a single-necked flask equipped with a condenser, 2,5-dimethyl-[(4-nitrophenyl)azo]-phenol 6, alkyl (or *n*-hydroxyalkyl) halide, potassium carbonate, and potassium iodide were dissolved in methylethylketone (MEK) and heated at 80 °C for a well-defined period of time (see specific procedure). After cooling down to room temperature, the reaction mixture was hydrolyzed with water. The organic phase was washed with potassium hydrogenocarbonate and water, and dried over magnesium sulfate before the solvent was removed under reduced pressure. Crude product was further purified by chromatography through a silica gel column (eluent: *n*-hexane-ethylacetate, 1/1, v : v).

Synthesis of (4-methoxy-2,5-dimethylphenyl)-(4-nitrophenyl)Diazene (DMNPAA) 8c

According to the general procedure described above, 2,5-dimethyl-[(4-nitrophenyl)azo]-phenol (5.42 g, 0.02 mol) was dissolved in 100 mL MEK along with potassium carbonate (4.14 g, 0.03 mol) and potassium iodide (one crystal). It was then alkylated with iodomethane (4.32 g, 0.03 mol) under reflux for 2 h. This yielded 5.4 g (95%) of (4-methoxy-2,5-dimethylphenyl)(4-nitrophenyl)-diazene (DMNPAA). mp = 145 °C. NMR: δ (ppm, CDCl₃) 8.34 (2H, d, J 8.8, (CH)₂—C—NO₂), 7.95 (2H, d, J 8.8, N—C—(CH)₂—(CH)₂—C—NO₂), 7.64 (1H, s, —C(CH₃)—CH—C—N) 6.77 (1H, s, —CH—C(CH₃)—C—N), 3.93 (1H, s, —OCH₃), 2.69 and 2.27 (6H, 2s, —C(CH₃)—CH—C—N and —CH—C(CH₃)—C—N). IR: (KBr, cm⁻¹) 2924, 2850, 1608, 1575, 1521, 1469, 1342, 1276, 1246, 1101, 1020, 857, 752, 722.

Synthesis of [4-(6-hydroxyhexyloxy)-2,5-dimethylphenyl](4-nitrophenyl)diazene

According to the general procedure described above, 2,5-dimethyl-[(4-nitrophenyl)azo]-phenol

(1.17 g, 0.0043 mol) was dissolved in 25 mL MEK, along with potassium carbonate (1.38 g, 0.01 mol) and potassium iodide (one crystal). It was then alkylated with 6-chloro-1-hexanol (1.36 g, 0.01 mol) under reflux for 5 n days. 1.0 g (63%) of [4-(6-hydroxyhexyloxy)-2,5-dimethylphenyl](4-nitrophenyl)diazene was recovered as a red oil. NMR: δ (ppm, CDCl_3) 8.34 (2H, d, J 8.8, $(\text{CH})_2\text{—C—NO}_2$), 7.95 (2H, d, J 8.8, $\text{N—C—}(\text{CH})_2\text{—}(\text{CH})_2\text{—C—NO}_2$), 7.64 (1H, s, $\text{—C(CH}_3\text{)—CH—C—N}$) 6.74 (1H, s, $\text{—CH—C(CH}_3\text{)—C—N}$), 4.06 (3H, t, J 6.4, $\text{CH}_2\text{—CH}_2\text{—O—Ph}$), 3.68 (3H, t, J 6.4, $\text{HO—CH}_2\text{—CH}_2$), 3.6 (1H, s, —OH), 2.75 and 2.22 (6H, 2s, $\text{—C(CH}_3\text{)—CH—C—N}$ and $\text{—CH—C(CH}_3\text{)—C—N}$), 1.95 to 1.25 (8H, m, $\text{CH}_2\text{—(CH}_2\text{)}_4\text{—CH}_2\text{—O}$). IR: (NaCl , cm^{-1}) 3339, 2935, 2860, 1606, 1521, 1461, 1340, 1245, 1089, 1054, 860.

Synthesis of [4-(11-hydroxyundecyloxy)-2,5-Dimethylphenyl](4-nitrophenyl)Diazene

According to the general procedure described above, 2,5-dimethyl-[(4-nitrophenyl)azo]-phenol (0.54 g, 0.002 mol) was dissolved in 20 mL MEK, along with potassium carbonate (0.276 g, 0.002 mol) and potassium iodide (one crystal). It was then alkylated with 11-bromo-1-undecanol (0.5 g, 0.002 mol) under reflux for 2 days. 0.5 g (57%) of [4-(11-hydroxyundecyloxy)-2,5-dimethylphenyl](4-nitrophenyl)diazene was isolated as a red oil. NMR: δ (ppm, CDCl_3) 8.34 (2H, d, J 9, $(\text{CH})_2\text{—C—NO}_2$), 7.95 (2H, d, J 9, $\text{N—C—}(\text{CH})_2\text{—}(\text{CH})_2\text{—C—NO}_2$), 7.63 (1H, s, $\text{—C(CH}_3\text{)—CH—C—N}$) 6.74 (1H, s, $\text{—CH—C(CH}_3\text{)—C—N}$), 4.05 (3H, t, J 6.4, $\text{CH}_2\text{—CH}_2\text{—O—Ph}$), 3.68 (3H, t, J 6.4, $\text{HO—CH}_2\text{—CH}_2$), 3.6 (1H, s, —OH), 2.73 and 2.24 (6H, 2s, $\text{—C(CH}_3\text{)—CH—C—N}$ and $\text{—CH—C(CH}_3\text{)—C—N}$), 1.7 to 1.2 (18H, m, $\text{CH}_2\text{—(CH}_2\text{)}_9\text{—CH}_2\text{—O}$). IR: (NaCl , cm^{-1}) 3339, 2935, 2860, 1606, 1521, 1461, 1340, 1245, 1089, 1054, 860.

Synthesis of [4-(6-methacryloylhexyloxy)-2,5-dimethylphenyl](4-nitrophenyl)Diazene 8a

According to the procedure reported for the synthesis of monomer **2**, [4-(6-hydroxyhexyloxy)-2,5-dimethylphenyl](4-nitrophenyl)diazene (1.17 g, 0.0043 mol), methacryloyl chloride (0.624 g, 0.006 mol) and triethylamine (0.60 g, 0.006 mol) were reacted in 100 mL THF for 5 h at room temperature. After the previously described treatment and chromatography over a silica gel column (eluent = *n*-hexane/ethylacetate, 1/1, v :

v), 1.2 g of [4-(6-methacryloylhexyloxy)-2,5-dimethylphenyl](4-nitrophenyl)diazene (90%) were isolated as a red oil. NMR: δ (ppm, CDCl_3) 8.34 (2H, d, J 8.8, $(\text{CH})_2\text{—C—NO}_2$), 7.95 (2H, d, J 8.8, $\text{N—C—}(\text{CH})_2\text{—}(\text{CH})_2\text{—C—NO}_2$), 7.64 (1H, s, $\text{—C(CH}_3\text{)—CH—C—N}$) 6.74 (1H, s, $\text{—CH—C(CH}_3\text{)—C—N}$), 6.08 (1H, s, $\text{CH}_2\text{=C—CO}$), 5.53 (1H, s, $\text{CH}_2\text{=C—CO}$), 4.06 (3H, t, J 6.4, $\text{CH}_2\text{—CH}_2\text{—O—Ph}$), 4.13 (2H, t, J 6.8, $\text{CH}_2\text{—CH}_2\text{—O—CO}$), 2.75 and 2.22 (6H, 2s, $\text{—C(CH}_3\text{)—CH—C—N=}$ and $\text{—CH—C(CH}_3\text{)—C—N=}$), 1.93 (3H, s, $\text{CH}_2\text{=C(CH}_3\text{)—CO}$), 1.95 to 1.25 (8H, m, $\text{CH}_2\text{—(CH}_2\text{)}_4\text{—CH}_2\text{—O}$). IR: (NaCl , cm^{-1}) 2936, 2860, 1718, 1677, 1606, 1523, 1451, 1341, 1246, 1163, 1091, 860, 841.

Synthesis of [4-(11-methacryloylundecyloxy)-2,5-Dimethylphenyl](4-nitrophenyl)Diazene 8b

According to the procedure reported for the synthesis of monomer **2**, [4-(11-hydroxyundecyloxy)-2,5-dimethylphenyl](4-nitrophenyl)diazene (0.9 g, 0.002 mol), methacryloylchloride (0.2 g, 0.0022 mol) and triethylamine (0.2 g, 0.0022 mol) were reacted in 20 mL THF for 5 h at room temperature. After the previously described treatment and chromatography over a silica gel column (eluent = *n*-hexane/ethylacetate, 1/1, v : v), 0.9 g [4-(11-methacryloylundecyloxy)-2,5-dimethylphenyl](4-nitrophenyl)diazene (90%) was isolated as a red oil. NMR: δ (ppm, CDCl_3) 8.34 (2H, d, J 8.8, $(\text{CH})_2\text{—C—NO}_2$), 7.95 (2H, d, J 8.8, $\text{N—C—}(\text{CH})_2\text{—}(\text{CH})_2\text{—C—NO}_2$), 7.64 (1H, s, $\text{—C(CH}_3\text{)—CH—C—N}$) 6.74 (1H, s, $\text{—CH—C(CH}_3\text{)—C—N}$), 6.08 (1H, s, $\text{CH}_2\text{=C—CO}$), 5.53 (1H, s, $\text{CH}_2\text{=C—CO}$), 4.06 (3H, t, J 6.4, $\text{CH}_2\text{—CH}_2\text{—O—Ph}$), 4.13 (2H, t, J 6.8, $\text{CH}_2\text{—CH}_2\text{—O—CO}$), 2.75 and 2.22 (6H, 2s, $\text{—C(CH}_3\text{)—CH—C—N=}$ and $\text{—CH—C(CH}_3\text{)—C—N=}$), 1.93 (3H, s, $\text{CH}_2\text{=C(CH}_3\text{)—CO}$), 1.95 to 1.25 (18H, m, $\text{CH}_2\text{—(CH}_2\text{)}_9\text{—CH}_2\text{—O}$). IR: (NaCl , cm^{-1}) 2926, 2854, 1720, 1606, 1524, 1447, 1342, 1296, 1245, 1160, 1096, 1037, 838, 850, 815.

Polymerization

Methacrylic monomers were polymerized in dry DMF in the presence of azobisisobutyronitrile (AIBN, 2 wt %) as an initiator. The polymerization medium was outgassed twice before heating and stirring overnight at 65 °C. Reaction was stopped by pouring the polymerization mixture into methanol cooled down to -78 °C. The isolated polymer was redissolved in THF and precip-

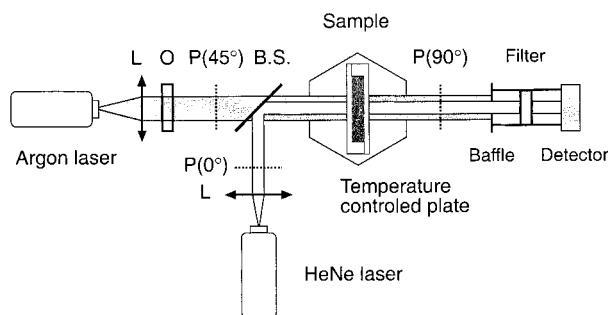


Figure 2. Experimental setup used for the analysis for the photoinduced birefringence. L: lens, O: obturator, B.S.: beam splitter, P(x°): polarizer with axis at x° .

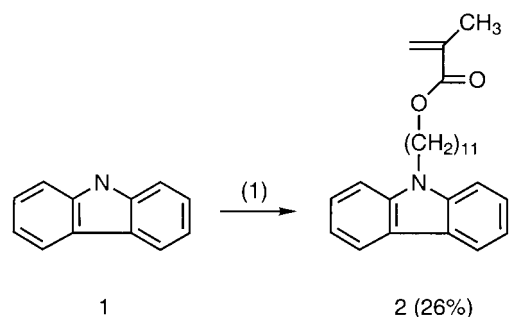
itated again in cold methanol, filtered and finally dried under vacuum overnight.

Birefringence Measurement

The experimental setup, used to measure the polarized light-induced birefringence is presented in Figure 2. A linearly polarized argon laser beam ($\lambda = 514$ nm, 5.0 mW/cm²) was filtered and expanded before being strongly absorbed by the sample, so generating birefringence. A second beam, coming from an helium–neon laser ($\lambda = 633$ nm, 36.5 μ W) and propagating parallel to that of the argon, is collimated to an analysis diameter of 8 mm. Its polarization was also linear but rotated by 45° with respect to that of the argon beam. After the crossing of the sample, the helium–neon beam was analyzed by a polarizer rotated at 90° with respect to the incident helium–neon polarization. A narrow bandpass filter, whose transmission peak was centered at 633 nm, was placed before the detector in order to stop any diffuse or direct light coming from the argon laser. The transmitted efficiency was defined as the detected intensity divided by the incident helium–neon light. The sample was placed on a temperature-controlled plate such that the measurements were carried out at constant deduced temperature relative to T_g of the polymeric matrix ($T - T_g = 10^\circ\text{C}$).

Sample and Film Preparation

Copolymers (or polymer blends) were dissolved in THF, and the solutions were filtered through a 0.45 μm filter. The solvent was removed under reduced pressure. The isolated material was dried overnight at room temperature under vacuum



- (1) i) NaH, THF, reflux
ii) 11-bromoundecanol, reflux
iii) NEt_3 , THF, methacryloylchloride

Figure 3. Reaction pathway for the synthesis of the carbazolyl–methacrylic monomer **2**.

(0.1 mmHg). The polymer was then crushed into a fine powder that was spread on a clean glass slide heated much above T_g and covered by a second slide. Under pressure, the polymer forms a film whose thickness is controlled by 70 μm glass spacers between the slides. Homogeneous films of a good optical quality were accordingly prepared.

RESULTS AND DISCUSSION

Monomer Synthesis

The monomers **2** and **8** have been prepared according to the general reaction scheme shown in Figures 3 and 4. The previously reported synthesis of *N*-(11-(methacryloyloxy)undecyl)carbazole

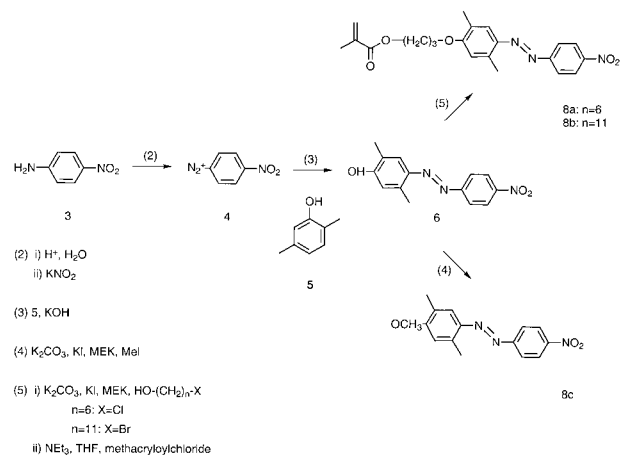


Figure 4. Reaction pathway for the synthesis of the azo-dye methacrylic monomer **8**.

Table I. Homo- and Copolymer Molecular Characterization

Polymer	Initial Comonomer Feed Wt % 8	Copolymer Comp. ^a		M_n^b (*10 ⁻⁴)	M_w/M_n	T_g^c °C
		Wt % 8	Mol % 8			
P2	—	—	—	0.73	1.5	-5
P2-co-8a	25	13	10	1.1	1.6	-23
P2-co-8b(5)	9	5	4	1.4	1.9	2
P2-co-8b(15)	25	15	11	1.2	1.7	-11
P2-co-8b(45)	50	45	40	1.2	1.9	-20
P2-disp-8c	—	15 ^d	—	—	—	-10

^a ¹H NMR analysis.^b SEC analysis in CHCl₃ (calibration with polystyrene standards).^c DSC (heating rate = 20 °C/min).^d Corresponding to 15 wt % of DMNPAA, **8c** dispersed in homo **P2**.

2¹⁴ was changed so as to avoid the hydroboration step of the intermediate ω -olefin. Carbazole **1** was directly alkylated by 11-bromo-undecanol and further esterified with methacryloyl chloride (Fig. 3). Methacrylic monomers containing the 2,5-dimethyl-[(4-nitrophenyl)azo]-phenol **6** (DMNPAA) group have been synthesized by alkylation and esterification as shown in Figure 4.

Polymer Characterization

The main characteristic features of homo- and copolymers are listed in Table I. The copolymer composition has been analyzed by ¹H NMR, by comparison with the ¹H NMR spectrum of the parent homopolymer **P2**. The azo-dye content of the copolymer is systematically smaller than that one of the original comonomer feed. Polymers with molecular weights up to 14 K have been synthesized by free radical polymerization. In contrast to the observations made by Stohriegl,¹⁴ the use of DMF instead of toluene as the polymerization solvent reduced the polydispersity because of increased solubility of both the monomer and the polymer in this solvent.

The physical dispersion of 15 wt % of azo-dye **8c** in the **P2** matrix decreases T_g from -5 °C to -10 °C. Quite the same T_g (-11 °C) is observed for the copolymer in which the azo-dye has been grafted on the methacrylic backbone with a long undecyl spacer. Surprisingly, reducing the length of this spacer from 11 to 6 carbon atoms decreases further the T_g [compare **P2-co-8a** and **P2-co-8b(15)**, which have the same chromophore concentration].

Increasing the concentration of the azo-dye **8b** from 5 wt % to 45 wt % lowers the T_g [**P2-co-**

8b(5), **P2-co-8b(15)**, **P2-co-8b(45)**]. So, the chromophore acts as a plasticizer.

Photoinduced Birefringence

Figure 5 shows the time dependence of the photoinduced birefringence, expressed in terms of transmitted efficiency, for the six polymers under consideration. Because of the major influence of the temperature on the orientational behavior of the azo-dyes,¹⁵ all the experiments discussed below have been performed at the same deduced temperature relative to T_g ($T - T_g = 10$ °C). One could see the large behavior discrepancies in the

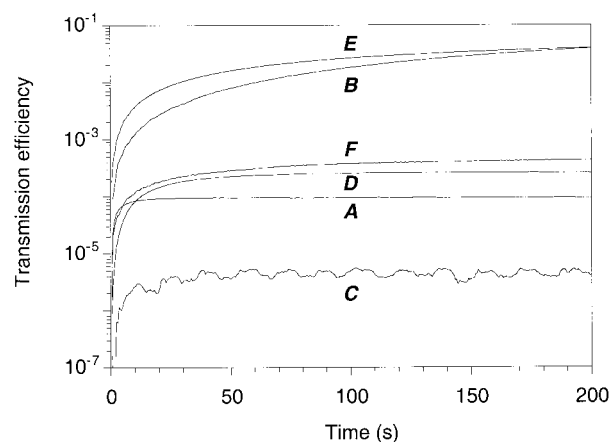


Figure 5. Experimental writing birefringence curves for doped or grafted copolymers versus time. Measurements have been done at constant deduced temperature relative to T_g ($T - T_g = 10$ °C). **P2-disp-8c** (A), **P2-co-8a** (B), **P2-co-8b(5)** (C), **P2-co-8b(15)** (D), **P2-co-8b(45)** (E), and **PVK + ECZ-disp-8c** (F).

Table II. Parameters Obtained by Fitting the Curves of the Photoinduced Birefringence vs Time by the Biexponential Equation (eq 1)

Curve	Polymer	A	B	τ_A [s]	τ_B [s]	R	$\eta(\infty)$	$d\eta/dt _{t=0}$
A	P2-disp-8c	6.310^{-5}	3.110^{-5}	2.46	8.34	0.994	9.410^{-5}	2.910^{-5}
B	P2-co-8a	0.5	—	2220	—	0.99979	0.5	2.210^{-4}
C	P2-co-8b(5)	4.410^{-6}	—	15.8	—	0.816	4.410^{-6}	2.810^{-7}
D	P2-co-8b(15)	2.610^{-4}	—	25.1	—	0.9989	2.610^{-4}	$1 \cdot 10^{-5}$
E	P2-co-8b(45)	2.610^{-2}	6.310^{-2}	86.6	670	0.99999	8.910^{-2}	3.910^{-4}
F	PVK + ECZ-disp-8c	1.510^{-4}	3.110^{-4}	13.6	83.5	0.9988	4.610^{-4}	1.510^{-5}

properties of the various polymers. The use of a semi-logarithmic scale emphasizes the difference.

As made by several authors,^{16–20} the experimental data of transmission efficiency measured versus time have been by a phenomenological biexponential:

$$\eta(t) = A[1 - \exp(-t/\tau_A)] + B[1 - \exp(-t/\tau_B)] \quad (1)$$

where A , B , τ_A and τ_b are parameters fixed by least square fitting.

A similar biexponential function has been used by Hwang et al.²¹ in their study of the photoinduced anisotropy of methylorange dispersed in polyvinyl alcohol in the glass-transition temperature region, and by Eisenbach³ in the case of methacrylic copolymers of 4-[4-(methacryloyloxy)-butyryl-amino]azobenzene and methylmethacrylate below T_g .

The fitting parameters are listed in Table II. Three samples can be fitted using a single exponential. The regression coefficient R given by the fit program is also included in order to show the good agreement between the (bi)exponential function and the experimental data.

It must be clear that eq 1 does not rely on any theoretical model, but it is merely phenomenological. Therefore, it should be hazardous to discuss the experimental data directly on the basis of the biexponential coefficients. Although some mathematical models can describe the dynamics of the photo-orientation of azo-dyes in polymer matrices,²² their complexity has prompted us to restrict ourselves to the biexponential fitting.

The first part of the discussion will be devoted to the effect that the grafting of the azo-dye onto carbazolyl-methacrylate copolymers can have on the kinetics and the magnitude of the photoinduced orientation. Attention will then be paid to the transmission efficiency in relation to the dye

concentration (Fig. 6). Since the chromophores are quite the same in all the samples, only the influence of the environment on their properties behavior is observed.

In Table II, we give the maximum of transmission efficiency: $\eta(\infty) = A + B$, and its slope at the origin that has been calculated as the first derivative of the equation 1 at $t = 0$:

$$\left. \frac{d\eta}{dt} \right|_{t=0} = \frac{A}{\tau_A} + \frac{B}{\tau_B}. \quad (2)$$

The transmission efficiency strongly depends on the polymer matrix. Even in the case of the two doped polymers (**P2-disp-8c** and **PVK + ECZ-disp-8c**), the transmission is changed by a factor of more than five, so emphasizing the major role that the surroundings have on the photoreorientation ability of the dye.

The grafting of the chromophore on the polymer backbone has a significant effect on the pho-

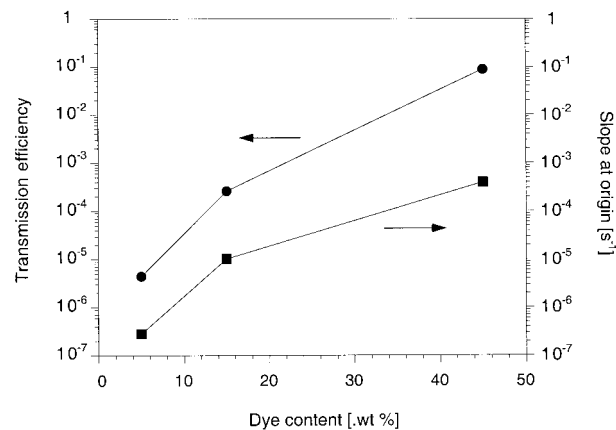


Figure 6. Influence of the azo-dye content on the maximum of transmission efficiency and the slope at the origin for the polymer **P2-co-8b**.

toanisotropy, because the maximum of transmission efficiency is increased when **P2-co-8a** or **P2-co-8b(15)** is substituted for **P2-disp-8c**, which indicates an improved alignment of the chromophores. One possible explanation is that the grafting of the dye makes its orientation by the polarized light less perturbed by the thermal agitation.²³ The photoinduced orientation is remarkably increased by more than three orders of magnitude when the dye is grafted (**P2-co-8a**) rather than dispersed in the polymer matrix.

The slope at the origin gives information on the efficiency of the system, that is, the ability for the chromophores to reorient themselves in the medium. Surprisingly, the grafting of the chromophore might, at least in some cases (**P2-co-8a** compared to **P2-disp-8c**), enhance its mobility.

Although the grafting of the chromophore greatly changes the optical properties of the polymer, no systematic modification can be attributed to this chemical linking. A possible reason for the variations from one grafted sample to another one might be found in the T_g of the polymer matrix. Some explanations have been posited in some of our other papers.^{23,24} One of the lessons drawn from this work is that the measurements done at constant deducted temperature do not correct the T_g variations.

Data of polarized light-induced birefringence for three copolymers of increasing content of grafted azo-dye [**P2-co-8b(5;15;45)**] are shown in Figure 6. Expectedly, the transmission efficiency increases with the dye content; because there is more chromophore, the phenomenon is amplified. The law followed is not a linear relationship, but rather an exponential one. Additional samples and measurements are, however, needed to draw a more accurate conclusion. It may indeed be, anticipated that the dependence of the transmission efficiency on the dye content is complex as a result of the interplay of the chromophore-polymer and chromophore-chromophore interactions, so that a single exponential dependence is not very likely.

As shown in Figure 6, the slope at the origin is also dependent on the dye content, once more emphasizing the influence of the chromophore-polymer and the chromophore-chromophore interactions on the dynamics of the system. Because the dye acts as a plasticizer (see Table I), modification of the T_g could account for the experimental observation.

CONCLUSION

This work has focused on the grafting of an azo-dye onto a carbazole-containing polymethacrylate. The azo-dye has also been dispersed in the polymer matrix for the sake of comparison. The effect of the dye grafting, the length of the alkyl spacer, the azo-dye content, and the type of polymer matrix have been investigated.

Experimental data have shown that the writing process is dependent on the way the azo-dye is incorporated into the polymer matrix, whose nature has also an influence on the chromophore behavior. However, no final conclusion can be drawn about the optical properties of the azo-dye containing polymer depending on whether the dye is grafted to or merely dispersed in the polymer matrix. T_g of the polymer seems to have an predominant role although all the measurements have been carried out at the same relative temperature ($T - T_g = 10$ °C).

As expected, the transmission efficiency is strongly amplified when the dye content is increased (nearly exponential). The dynamics of the molecular orientation is also influenced by this content in proportion to the polymer matrix plasticization by the dye.

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