Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

SYNTHESIS AND CHARACTERIZATION OF NEW POLYMETHACRYLATES BEARING AN AZO-DYE IN THE SIDE CHAIN

Eleftherios V. Tourasanidis[a]; George P. Karayannidis[a]
[a] Laboratory of Organic Chemical Technology, Department of Chemistry, Aristotle University of Thessaloniki, Thessaloniki, Macedonia, Greece

To cite this Article Tourasanidis, Eleftherios V. and Karayannidis, George P.(1999) 'SYNTHESIS AND CHARACTERIZATION OF NEW POLYMETHACRYLATES BEARING AN AZO-DYE IN THE SIDE CHAIN', Journal of Macromolecular Science, Part A, 36: 9, 1241 — 1258
To link to this Article: DOI: 10.1081/MA-100101595
URL: http://dx.doi.org/10.1081/MA-100101595

J.M.S.—PURE APPL. CHEM., A36(9), pp. 1241–1258 (1999)

SYNTHESIS AND CHARACTERIZATION OF NEW POLYMETHACRYLATES BEARING AN AZO-DYE IN THE SIDE CHAIN

Eleftherios V. Tourasanidis and George P. Karayannidis*

Laboratory of Organic Chemical Technology
Department of Chemistry
Aristotle University of Thessaloniki
Thessaloniki 540 06, Macedonia, Greece

Key Words: Polymethacrylates, Comb-Like Polymers, Non-Linear Optics, Side Chain Crystallization, Azo-Dye

ABSTRACT

4-(4′-Nitrophenylazo)-1-naphthol, a commercial azo-dye, was used as a side chain moiety for the preparation of six members of a new series of polymethacrylates, the poly(ω-[4-(4′-nitrophenylazo)-naphthalene-1-yloxy]alkyl methacrylate)s with 2, 4, 5, 6, 10, and 11 methylene units as spacer. A two-step synthesis gave the corresponding monomeric methacrylates, which were polymerized by a free radical polymerization using AIBN as initiator. The above polymethacrylates did not show any liquid crystallinity, however a side chain crystallization was observed for the last member of the polymer series. The UV/Vis spectroscopy showed that all polymers retained the optical properties of the azo-dye with a small hypsichromic shift and a decrease in intensity when moving from monomer to polymer. A copolymer of

---

* Author to whom correspondence should be addressed.

Tel: (3031) 997814; Fax: (3031) 997769; E-mail: karayan@chem.auth.gr

6-methylene spacer monomeric ester with methyl methacrylate was also prepared, in order to study how copolymerization affected the properties of the corresponding homopolymer.

INTRODUCTION

Optically non-linear materials possess many potential applications in opto-electronic systems, primarily in telecommunications where the need for high-bandwidth optical switching and processing devices is high [1, 2]. Especially polymeric non-linear optical materials have recent growth in interest because they combine the non-linear optical properties with the unique properties of polymers [3, 4]. There are two main approaches to prepare polymeric non-linear optics (NLO). The first one is the ‘Guest/Host’ systems [5] and the second one involves the incorporation of non-linear optical organic molecules in the main chain [6] or in the side chain of a polymer [3, 7-10].

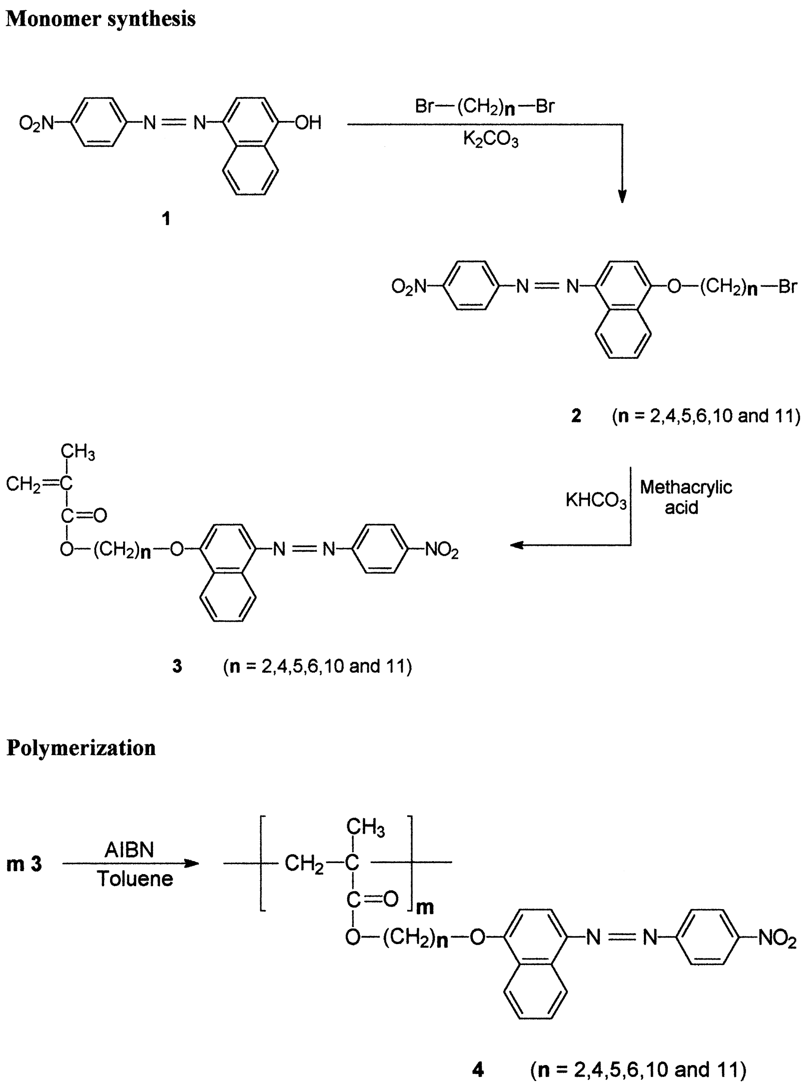
Organic molecules which possess large values of the second order hyperpolarizability, β, must contain delocalized π electronic system and asymmetry in their response to an applied electric field [11]. The largest values are obtained when these molecules occupy charge-transfer resonance, which can be achieved with an electron donating and electron withdrawing group connecting together by an extended conjugated system [11, 12]. Another condition that has to be fulfilled for macroscopic nonlinear effects is the centrosymmetric behavior of the molecule [13, 14].

In this work, the synthesis and the thermal and spectroscopic characterization of a new series of poly(methacrylate)s (six homopolymers and one copolymer) is described (Scheme 1 and 2). These polymers have an azo-dye, the 4-(4′-nitrophenylazo)-1-naphthol, in the side chain, and it is expected to have non-linear optical properties because the azo-dye covers the main features of a NLO molecule, i.e. it is a highly conjugated molecule with an electron donating group (aromatic system) and an electron withdrawing group (NO_2).

EXPERIMENTAL

Materials

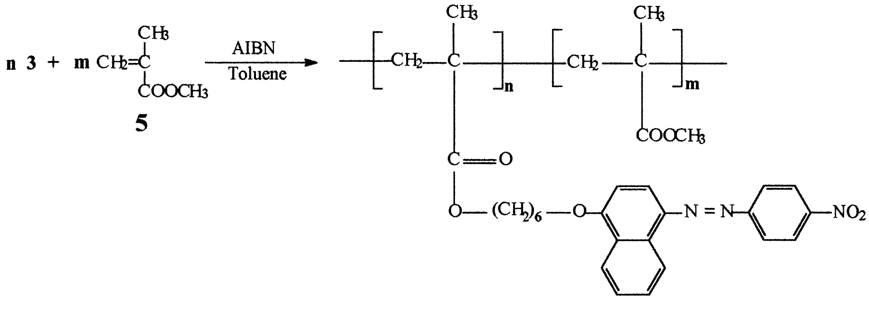
4-(4′-Nitrophenylazo)-1-naphthol, α,ω-dibromoalkanes and methacrylic acid were purchased from Aldrich and were used as received. Methyl methacry-



Scheme 1.

late (Merck) stabilized with hydroquinone monomethylether was used after passing through an Aldrich inhibitor remover column. 2,2′-azoisobutyronitrile (AIBN) (Aldrich) was used after two recrystallizations from methanol. All organic solvents, which are commercially available, were used as received.

Copolymerization



Scheme 2.

Measurements

^{1}H-NMR spectra were measured on a Bruker 300 MHz spectrometer and TMS was used as an internal standard. Infrafed spectra were recorded on a Perkin-Elmer 281 B spectrophotometer. UV/Vis spectra were taken from a Shimadzu UV-2101PC UV/VIS Scanning Spectrophotometer. Elemental analyses were taken on a Perkin-Elmer Series II CHNS/O analyzer.

The molecular weights of the polymers were measured by gel permeation chromatography (GPC) using a Rigas Labs Marathon Series III HPLC pump equipped with a Polymer Laboratories 5 μm Mixed D column and a Polymer Laboratories PL-EMD 950 Evaporative Mass Detecror. GPC was controlled by Polymer Laboratories PL LogiCal GPC/SEC software. THF was used as the eluent. A calibration curve was obtained using polystyrene standards. The homopolymers were dissolved in THF (0.2% w/v concetration) using an ultrasonic bath.

The thermal properties of the compounds were determined by differential scanning calorimetry (DSC) using a Perkin-Elmer DSC-2 differential scanning calorimeter. Heating rates were 20°C/min and cooling rates 10°C/min in all cases. First-order transitions were read at the maximum or minimum of the endothermic or exothermic peaks. Glass transition temperatures (T_g's) were read at the middle of the change of the heat capacity and were obtained from quenched samples. Inherent viscosities were measured using an I-Ubbeholde-type viscometer in N-methyl-2-pyrrolidone (NMP), at 25°C, and concentration

0.25%, in a constant-temperature bath. Phase identification was performed by polarized light microscopy using a Nikon Optiphot-2 polarizing microscope equipped with a Linkam THMS 600 heating stage and a TP 91 control unit. Heating rates were 10ºC/min and cooling rates were 0.2 or 0.4°C/min.

The X-ray diffraction pattern was taken on powder speciment, using a Siemens D500 diffractometer (CuK_α radiation, λ = 1,54 Å).

Monomer Synthesis

Only one method of preparation is given below for the monomer synthesis, because this experimental procedure was used as a general process to prepare all other methacrylic esters (Scheme 1).

1-Bromo-10-[4-(4'-nitrophenylazo)-naphthalen-1-yloxy]-decane (2)

1-Bromo-10-[4-(4'-nitrophenylazo)-naphthalen-1-yloxy]-decane was prepared using the procedure described by Craig *et al.* [15]. 4 g (13.64 mmol) 4-(4'-nitrophenylazo)-1-naphthol (**1**), 30.66 mL (136.4 mmol) 1,10-dibromode-cane, and 14.14 g (102.3 mmol) K_2CO_3 were refluxed with stirring in acetone (210 mL) for 24 hours. The reaction mixture was filtered hot, and the residue washed with hot acetone. The acetone was then removed under reduced pressure, and petroleum benzin (40-60°C) was added for the ether's precipitation. The resulting precipitate was dried under reduced pressure at 40°C, and recrystallized twice from ethanol (EtOH). Brown-red powder. Yield: 4.20 g (60%); m.p. 90-92°C.

$C_{26}H_{30}N_3O_3Br$ (512.45)	Calc.	C 60.94	H 5.90	N 8.23
	Found	C 61.65	H 5.99	N 7.45

IR (KBr, cm^{-1}): 2960 (m, CH_2), 1580 (vs, NO_2), 1525 (s, N=N) and 1280 (w, CH_2-Br).

^{1}H NMR ($CDCl_3$): δ (ppm) = 1.34-1.58 (m, $CH_2(CH_2)_4CH_2$, 12H), 1.85 (m, CH_2CH_2Br, 2H), 1.97 (m, OCH_2CH_2, 2H), 3.41 (t, CH_2Br, 2H), 4.25 (t, OCH_2, 2H), 6.90-8.90 (m, aromatic, 10H).

10-[4-(4'-Nitrophenylazo)-naphthalen-1-yloxy]decyl methacrylate (3)

The methacrylic ester **3** was prepared using the procedure described by Nakano *et al.* [16]. Methacrylic acid (0.75 mL, 8.84 mmol) and potassium hydrogen carbonate (1.01 g, 10.10 mmol) were stirred for 5 minutes at room temperature to form potassium methacrylate. This salt was added to a mixture of compound **2** (3.50 g, 6.83 mmol), hydroquinone (0.10 g, 0.92 mmol) in 90 mL N,N-dimethylformamide (DMF) and the reaction mixture was stirred at 100°C for 12 hours. The solvent was then removed under vacuum and the organic extract was dissolved in dichloromethane (DCM). This solution was washed with 100 mL water and the organic layer was dried over magnesium sulfate. DCM was removed and the organic product was recrystallized twice from EtOH. Red crystals. Yield: 1.90 g (54%); m.p. 78°C.

$C_{30}H_{35}N_3O_5$ (517.63)	Calc.	C 69.60	H 6.82	N 8.12
	Found	C 69.78	H 6.99	N 7.41

IR (KBr, cm^{-1}): 2940 (m, CH_2), 1710 (vs, C=O), 1635 (w, C=C), 1580 (vs, NO_2) and 1520 (s, N=N).

^1H NMR ($CDCl_3$): δ (ppm) = 1.35 (m, $CH_2(CH_2)_4CH_2$, 12H), 1.59-1.65 (m, $CH_2CH_2OC(O)$, OCH_2CH_2, 4H), 1.94 (s, CH_3, 3H), 4.14 (t, OCH_2, 2H), 4.25 (t, $CH_2OC(O)$, 2H), 5.54 (s, CH=C, 1H), 6.10 (s, CH=C, 1H), 6.90-8.95 (m, aromatic, 10H).

UV/Vis (NMP): $\lambda_{max} = 443.5$ nm, $\varepsilon = 9090\ L \cdot mol^{-1} \cdot cm^{-1}$

Polymerization

Radical Polymerization of 10-[4-(4′-nitrophenylazo)-naphthalen-1-yloxy]decyl methacrylate

Ester **3** (0.75 g, 1.45 mmol) was dissolved in 10 mL of toluene and 5 mol% AIBN (0.012 g) was added as initiator. The polymerization mixture was flushed with argon for 10 minutes and heated at 60°C for 24 hours. The resulting viscous solution was cooled and poured into 100 mL of agitated methanol (MeOH) to precipitate the polymer as an amorphous red solid. The polymer was then reprecipitated twice from NMP into MeOH, and dried under reduced pressure. Yield: 0.45 g (60%).

IR (KBr, cm^{-1}): 2935 (m, CH_2), 1720 (vs, C=O), 1575 (vs, NO_2) and 1520 (s, N=N).

UV/Vis (NMP): $\lambda_{max} = 435.5$ nm, $E^{1\%} = 8160\ L \cdot g^{-1} \cdot cm^{-1}$

Copolymerization

Copolymerization of 6-[4-(4′-nitrophenylazo)-naphthalen-1-yloxy]hexyl Methacrylate with Methyl Methacrylate

The copolymer was prepared using the method described for the homopolymers employing a **1:1 feed ratio** of the monomers. Thus, a mixture 6-[4-(4′-nitrophenylazo)-naphthalen-1-yloxy]hexyl methacrylate (0.35 g, 0.77 mmol), methyl methacrylate (0.23 mL, 0.77 mmol) and AIBN (0.012 g, 5 mol%) in 10 mL of toluene, was degassed with argon for 10 minutes and heated at 60°C for 24 hours. The resulting viscous solution was cooled and poured into 100 mL of agitated MeOH. The copolymer was reprecipitated twice from NMP into MeOH, and dried *in vacuo*. Yield: 0.31 g (75%).

IR (KBr, cm^{-1}): 2940 (m, CH_2), 1730 (vs, C=O), 1580 (vs, NO_2) and 1515 (s, N=N).

^{1}H NMR ($CDCl_3$, δ ppm): 0.9-1.44, 1.84-2.07 (m, 12H, CH_2), 1.60 (s, 6H, CH_3), 2.85 (s, 3H, OCH_3), 3.56-3.97 (m, 4H, OCH_2, $CH_2OC(O)$), 6.71-8.95 (m, 10H, aromatic).

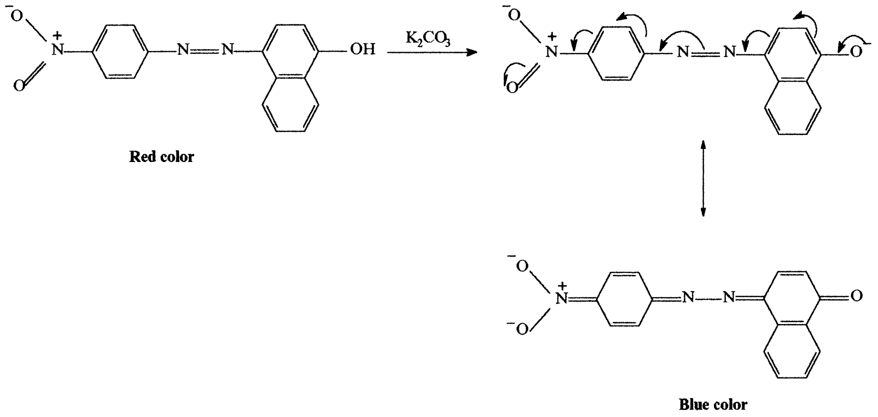
UV/Vis (NMP): λ_{max} = 439.5 nm, $E^{1\%}$ = 9980 $L \cdot mol^{-1} \cdot cm^{-1}$

RESULTS AND DISCUSSION

Monomer Synthesis

The first step of the methacrylic monomer synthesis is the most difficult one because the reaction is very slow, probably due to stabilization of the naphthoxide ion by resonance effect [10] (Scheme 3).

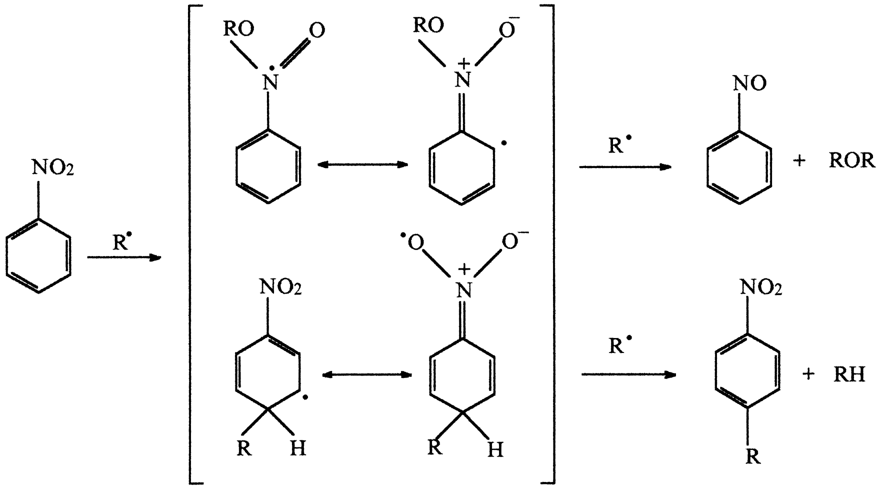
During this step, there was also a change in the color of the reaction mixture and this color change can be used as indication of the reaction's completion. Thus, while the azo-dye is red, the starting reaction mixture (azo-dye, dibromoalkane, K_2CO_3 and acetone) had a blue color due to the bathychromic shift caused by the resonance shown in Scheme 3. The azo-dye's conversion to the 1-bromo-derivative **2** (Scheme 1) caused a hypsichromic shift due to the disruption of the resonance, and this was the indicator that the reaction was nearly completed.



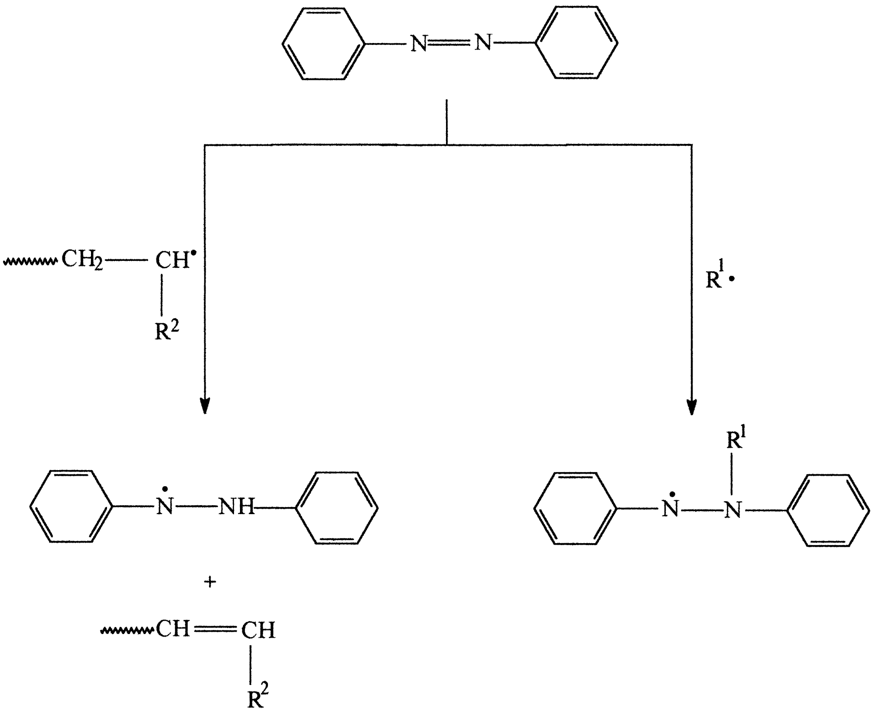
Scheme 3.

Polymerization

Free radical polymerization of the monomeric esters was carried out in toluene solution at 60°C using AIBN initiator for 24 hours to form the corresponding homopolymers and the copolymer with methyl methacrylate. Poly(methacrylate)s with pendant azobenzene groups which contain also polar groups such as -NO_2, are difficult to be prepared by free radical polymerization because either the azobenzene or the nitrobenzene group in the monomeric esters **3** can react as retarders [17]. Nitrobenzene is able to react with two radicals and retard the polymerization (Scheme 4).



Scheme 4.



Scheme 5.

Azobenzene group reacts about the same way as nitrobenzene group in free-radical polymerizations. During the polymerization azo-groups can sustain chain transfer reactions to form stable hydrazyl radicals [17] (Scheme 5).

As a consequence, a large amount (5 mol%) AIBN was used for the preparation of the homopolymers and the copolymer, resulting in relatively low molecular weight polymers as shown in Table 1.

The general accepted trend concerning the influence of molecular mass on phase transition temperatures of comb-like polymers, is that an increase of the polymer molecular mass increases the transition temperatures up to a certain degree of polymerization, approximately equal to 10 according to Finkelmann *et al.* [18] or 12 according to Percec *et al.* [19, 20], above which they become independent of molecular mass. Finkelmann suggested that the increased phase transition temperatures are due to the increased packing density of the side groups of the higher molecular weight polymer. As the packing of the side groups is becoming denser, the specific volume at the phase transformation decreases, and

TABLE 1. Molecular Weights, and Polydispersities (*PD*) and Number Average Degree of Polymerization ($\overline{DP}_n$) for the Polymethacrylate Polymer Series Prepared

Polymer	$\overline{M}_n$[a]	$\overline{M}_w$[a]	*PD*[a]	$\overline{DP}_n$[b]
P2	9000	11800	1,31	22
P4	8800	11000	1,25	21
P5	9300	12400	1,33	20
P6	20000	52600	2,63	43
P10	6000	8200	1,36	12
P11	12000	16900	1,40	23
CP6	10500	14700	1,40	—

[a] Molecular weights ($\overline{M}_n$, $\overline{M}_w$) and polydispersities determined by GPC.

[b] Number average degree of polymerization calculated from $\overline{M}_n$.

higher transition temperatures are observed [18]. The number average degree of polymerization of the homopolymers prepared were varied between 12 to 43, number sufficient enough to suggest molecular weight independence.

Thermal Characterization

Homopolymers

The glass transition temperatures, the inherent viscosities (η_{inh}), the λ_{max} and extinction coefficients ($E^{1\%}$) of the poly(ω-[4-(4'-nitrophenylazo)-naphthalene-1-yloxy]alkyl methacrylate)s, **4**, are listed in Table 2. All polymers exhibited a glass transition temperature, except P11 which exhibited also an endothermic peak at 90°C.

Figure 1 shows the influence of the number of methylene units of the alkyl spacer on the glass transition temperatures. The glass transition temperatures decrease with increasing spacer length from 2 to 10 methylene units, as a consequence of two factors: first of a decrease in the packing density of the chains [21] and second of an internal softening effect of the alkyl spacer [22, 23].

Polymer P11 showed a partial crystallization of the side chains (side chain crystallization), as detected by DSC (Figure 2). Side chain crystallization usually occurs in comb-like polymers with long spacer lengths and this phenomenon is attributed to a regular packing of the side chains when the spacer length reaches a certain critical value of *n* for a certain polymer series [24-27].

TABLE 2. Transition Temperatures, Inherent Viscosities, λ_{max} and Extinction Coefficients, $E^{1\%}$, for the Homopolymers and the Copolymer Prepared

Polymer	n	T_g in [°C]	T_m in [°C]	η_{inh} in [dL/g]	λ_{max} in [nm]	$E^{1\%}$ in [$L \cdot mol^{-1} \cdot cm^{-1}$]
P2	2	53	-	0.118	435.5	10380
P4	4	35	-	0.088	435.5	13480
P5	5	32	-	0.111	444.0	4080
P6	6	38	-	0.157	439.0	9520
P10	10	26	-	0.109	440.5	8160
P11	11	57	90	0.225	440.5	11030
CP6	6	75	-	0.150	439.5	9980

Although the x-ray diffraction pattern of P11 sample showed two very weak reflections at 31° and 34° angles probably due to side chain crystallization, a typical pattern of an amorphous polymer was revealed (Figure 3). This indicates a small part of crystallinity in the polymer sample, overlaped by the amorphous one.

P11 sample exhibited also an abnormally high glass transition temperature, which may be a reflection of a move towards the ordering of the side chains [25-27].

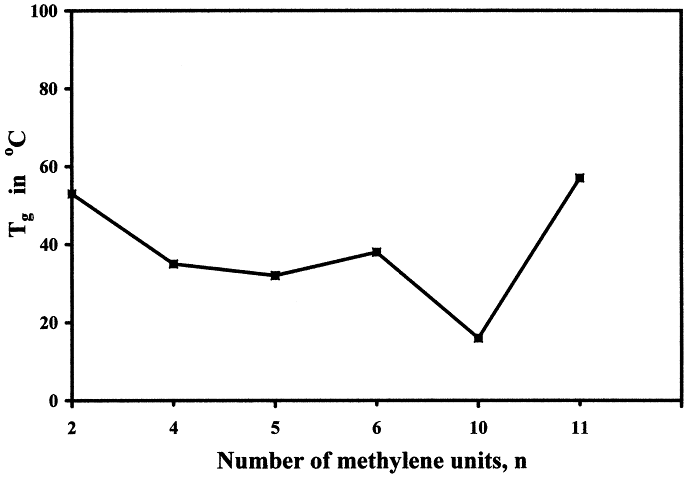


Figure 1. Dependence of the glass transition temperatures of the polymer series, on varying length of the alkyl spacer, **n**.

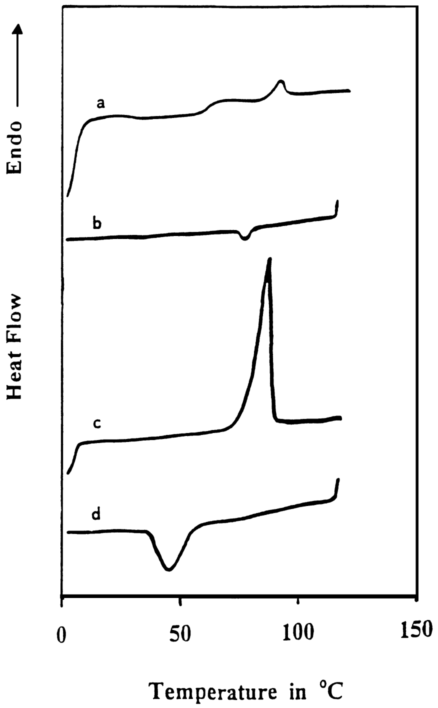


Figure 2. DSC traces for P11: obtained on heating after quenching (a) and on cooling (b) for M11: obtained on heating (c) and on cooling (d). Heating rate 20°C/min, cooling rate 10°C/min.

None of the homopolymers exhibited liquid crystalline behavior when examined by polarized microscopy. A possible explanation can be given if the second aromatic core of the 1,4-naphthylene moiety is considered as a lateral substituent (with respect to the longitudinal molecular axis). The introduction of lateral substituents into aromatic rings of a liquid crystalline compound lowers the transition temperatures. Thus according to Gray [28, 29] and Dewar [30] as the size of the substituent increases, a decrease in the transition temperatures is observed, due to a regular decrease in the intermolecular forces leading to corresponding increase in the mean intermolecular separations. This phenomenon was also observed in side-chain liquid crystalline polymers (SCLCPs). The introduction of lateral substituents into the mesogenic moieties of SCLCPs considerably lowers the stability of the liquid crystalline phase [31], while linear substituents are, in general, necessary for the existence of the liquid crystalline state [32].

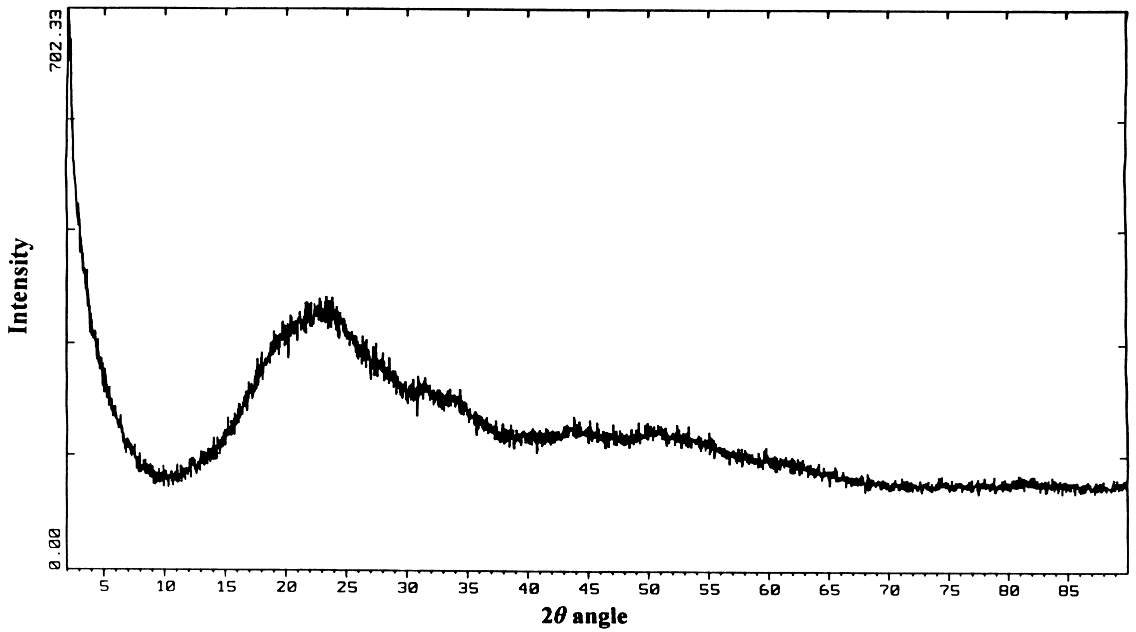
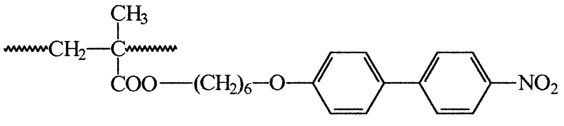
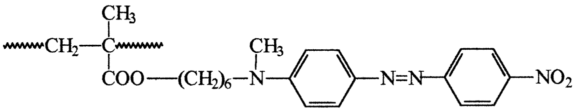
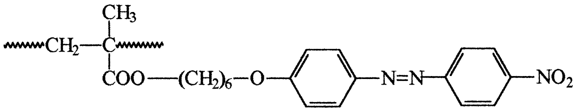
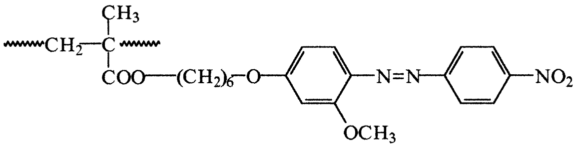
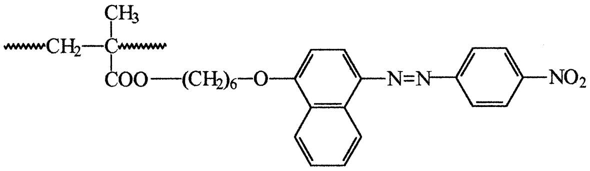


Figure 3. X-ray diffraction pattern of the P11 polymer sample.

TABLE 3. Comparison of the Physical Properties of Polymethacrylates with Stucture Similar to the Structure of Polymer **4**

No	Polymer structure	Transition temperatures in [°C]	Ref.
I		g40n64i	7
II		g78s180i	34
III		g55s173	13
IV		g88lc255dec.	10
V		g38i	

g=glassy, n=nematic, s=smectic, lc=liquid crystalline phase and i=isotropic

Table 3 gives a comparison of the physical properties of polymethacrylates, with stucture similar to the structure of polymer **4** (Scheme 1). Polymers I, II, and III which have no lateral substituents, had a pronounced liquid crystalline behavior. Liquid crystallinity in the polymer with the lateral methoxy group (polymer IV) was observed only on the polarizing microscope, and the DSC curve had no clear peak for an isotropic-liquid crystal transition. Polymer V, which is the polymer of this article, did not show mesomorphic behavior probably due to a major decrease of the stability of the liquid crystalline state, which was a consequence of the presence of the bigger in size lateral phenyl group.

TABLE 4. Melting Temperatures, λ_{max} and Molecular Extinction Coefficients, ε, for the Azo-Dye and the Monomers Prepared

Monomer	n	m.p. in [°C]	λ_{max} in [nm]	ε in [L mol^{-1} cm^{-1}]
azo-dye	-	270	473.0	21270
M2	2	135	442.5	7690
M4	4	88	442.0	15390
M5	5	103	449.0	8730
M6	6	68	444.0	12450
M10	10	77	443.5	9090
M11	11	89	442.0	20520

Spectroscopic Characterization of the Polymers

Table 4 shows the λ_{max} and the molecular extinction coefficients (ε) for the monomers prepared with the corresponding values of the azo-dye. UV/Vis spectroscopy indicated that the azo-dye retained its optical properties in homopolymers and the copolymer [33]. However, the attachment of the chromophores to the polymer backbone caused some interactions which could be detected by the UV/Vis spectroscopy as a small but significant hypsichromic shift and an attenuation in intensity of the absorption bands, as the concentration of the chromophores increases from the copolymer to homopolymer (Figure 4) [34].

Copolymer with Methyl Methacrylate

The copolymerization of M6 with methyl methacrylate gave the copolymer **6**. The composition of the copolymer was estimated by integration of the ^{1}H NMR signals and was found to be 41% of the monomeric dye and 59% of methyl methacrylate. As found by polarized microscopy and DSC the copolymer had no mesomorphic behavior. The DSC curve of copolymer **6** exhibited only a glass transition temperature at 75°C, i.e. 30°C higher comparatively to the glass transition temperature of the corresponding homopolymer (M6). This higher glass transition temperature makes the copolymer a better candidate for NLO applications, because a high glass transition temperature (T_g > 50°C) is one of the main requirements for NLO materials [3, 4, 35].

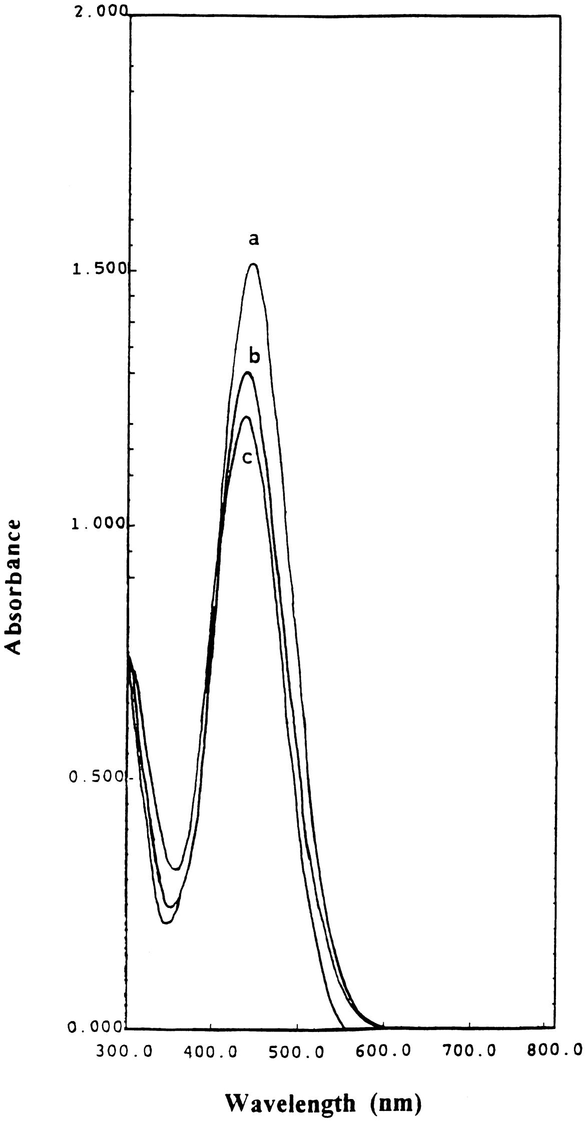


Figure 4. UV/Vis spectra of M6 (a), CP6 (b) and P6 (c), measured in NMP.

CONCLUSION

All homopolymers and the copolymer prepared were glassy at nature except P11 which exhibited side chain crystallization. The polymers prepared did not show liquid crystalline behavior, probably due to the lateral substitution of the mesogenic moiety. The T_g's of the homopolymers decrease with increasing spacer length, except that of P11 which was abnormally high. UV/Vis spectra showed that all polymers retain the optical properties of the azo-dye with a small hypsichromic shift and an attenuation in intensity. Finally copolymerization increased the T_g value with respect to the corresponding homopolymer.

REFERENCES

[1] D. J. Williams, *Angew. Chem. Int. Ed. Engl.*, *23,* 690 (1984).

[2] J. M. G. Cowie, in *Polymers: Chemistry and Physics of Modern Materials*, 2nd edition, Blackie, Glasgow, 1991, p. 422.

[3] V. Mohlmann, in *Side Chain Liquid Crystal Polymers*, C. B. McArdle, Ed., Blackie, Glasgow 1989, p. 330.

[4] G. R. Mohlmann, in *Organic Materials for Photonics: Science and technology*, G. Zerbi, Ed., 1993, p. 253.

[5] M. A. Mortazavi, A. Knoesen, S. T. Kowel, B. G. Higgins, and A. Dienes, *J. Opt. Soc. Am. B*, *6,* 733 (1898).

[6] J. D. Stenger-Smith, J. W. Fischer, R. Henry, J. M. Hoover, M. P. Nadler, R. A. Nissan, and G. A. Lindsay, *J. Polym. Sci., Part A: Polym. Chem.*, *29,* 1623 (1991).

[7] T. M. Leslie, R. N. Demartino, E. Won Choe, G. Khanarian, D. Haas, G. Nelson, J. B. Stamatoff, D. Stuetz, C. Teng, and H. Yoon, *Mol. Cryst. Liq. Cryst.*, *153,* 451 (1987).

[8] B. K. Mandal, T. Takahashi, M. Maeda, S. Kumar, A. Blumstein, and S. Tripathy, *Makromol. Chem.*, *192,* 1009 (1991).

[9] M. Yoshida, M. Asana, M. Tamada, and M. Kumakura, *Makromol. Chem., Rapid Commun.*, *10,* 517 (1989).

[10] H. K. Hall, T. Kuo, and T. M. Leslie, *Macromolecules*, *22,* 3525 (1989).

[11] P. N. Prasad, and D. J. Williams, in *Introduction to Nonlinear Effects in Molecules and Polymers*, J. Wiley & Sons, New York, 1991, p. 132.

[12] H. E. Katz, K. D. Singer, J. E. Sohn, C. W. Dirk, L. A. King, and H. M. Gordon, *Jr. Am. Chem. Soc.*, *109*, 6561 (1987).

[13] R. Lorenz, *Liquid Crystals*, *9,* 127 (1991).

[14] J. L. Qudar, *J. Chem. Phys.*, *67,* 446 (1977).

[15] A. A. Craig and C. T. Imrie, *J. Mater. Chem.*, *4,* 1705 (1994).

[16] T. Nakano, T. Hasegawa, and Y. Okamoto, *Macromolecules*, *26, 5494* (1993).

[17] P. Strohriegl, *Makromol. Chem.*, *194*, 363 (1993).

[18] H. Stevens, G. Rehage, and H. Finkelmann, *Macromolecules, 17,* 851 (1984).

[19] V. Percec and B. Hahn, *Macromolecules*, *22*, 1588 (1989).

[20] V. Percec, D. Tomazos, and C. Pugh, *Macromolecules, 22,* 3259 (1989).

[21] Z. Komiya, C. Pugh, and R. R. Schrock, *Macromolecules*, *25,* 3609 (1992).

[22] B. Messner and H. Finkelmann, *Makromol. Chem.*, *192,* 2383 (1991).

[23] V. Percec and C. Pugh, in *Side Chain Liquid Crystal Polymers*, C. B. McArdle, Ed., Blackie, Glasgow, 1989, p. 30.

[24] N. A. Plate and V. P. Shibaev, *J. Polym. Sci.: Macromol. Rev.*, *8*, 117 (1974).

[25] J. M. G. Cowie, Z. Haq, I. J. McEwen, and J. Velickovic, *Polymer*, *22,* 327 (1981).

[26] G. Decobert, J. C. Dubois, S. Esselin, and C. Noël, *Liquid Crystals*, ***1,*** 307 (1986).

[27] S. Esselin, L. Bosio, C. Noël, G. Decobert, and J. C. Dubois, *Liquid Crystals*, *2*, 505 (1987).

[28] G. W. Gray, *The Molecular Physics of Liquid Crystals*, G. R. Luckhurst, and G. W. Gray, Eds., Academic Press, London, 1979, p. 14.

[29] W. G. Gray, *Phil. Trans. R. Soc. Lond. A*, *309*, 77 (1983).

[30] M. J. S. Dewar, and A. C. Anselm, *J. Am. Chem. Soc.*, *97,* 6662 (1975).

[31] W. Weisflog, A. Wiegleben, and D. Demus, *Mater. Chem. Phys.*, *12**,*** 875 (1981).

[32] H. Finkelmann, *Angew. Chem. Int. Ed. Engl.*, *26*, 816 (1987).

[33] C. Combellas, M. A. Petit, A. Thiébault, G. Froyer, and D. Bosc, *Makromol. Chem., 193,* 2445 (1992).

[34] D. R. Robello, *J. Polym. Sci., Part A: Polym. Chem.*, *28,* 1 (1990).

[35] C. Hsu, *Prog. Polym. Sci.*, *22*, 829 (1997).

Received December 30, 1998
Revision received April 14, 1999