

Synthesis and Characterization of Photoactive Chiral Copolymers of (S)-N-(1-Phenyl ethyl) Methacrylamide and Disperse Red 1 Methacrylate

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ABSTRACT: In this article, we report the synthesis and characterization of chiral copolymers containing a photoactive azobenzene pendant group. The chiral copolymers of (S)-N-(1-phenyl ethyl) methacrylamide (S-NPEMAM) and disperse red 1 methacrylate (DR1MA) with two different feed compositions were synthesized by free-radical polymerization with 2,2'-azobisisobutyronitrile as an initiator. The purified chiral copolymers, poly[(S)-N-(1-phenyl ethyl) methacrylamide-co-disperse red 1 methacrylate], were characterized by Fourier transform infrared spectroscopy, NMR, ultraviolet-visible spectroscopy, and gel permeation chromatography analyses. The photoluminescence and

chiroptical properties of the copolymers were evaluated. Induced circular dichroism (CD) was observed in the CD spectra, which arose because of the exciton splitting originated by the cooperative interactions between the pendant azobenzene chromophore of DR1MA and the benzene ring of the chiral monomer. The glass-transition temperatures of the chiral copolymers were observed to be above 117°C, and the chiral copolymers were thermally stable up to 250°C. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 2595–2603, 2012

Key words: chiral; copolymerization; photophysics

INTRODUCTION

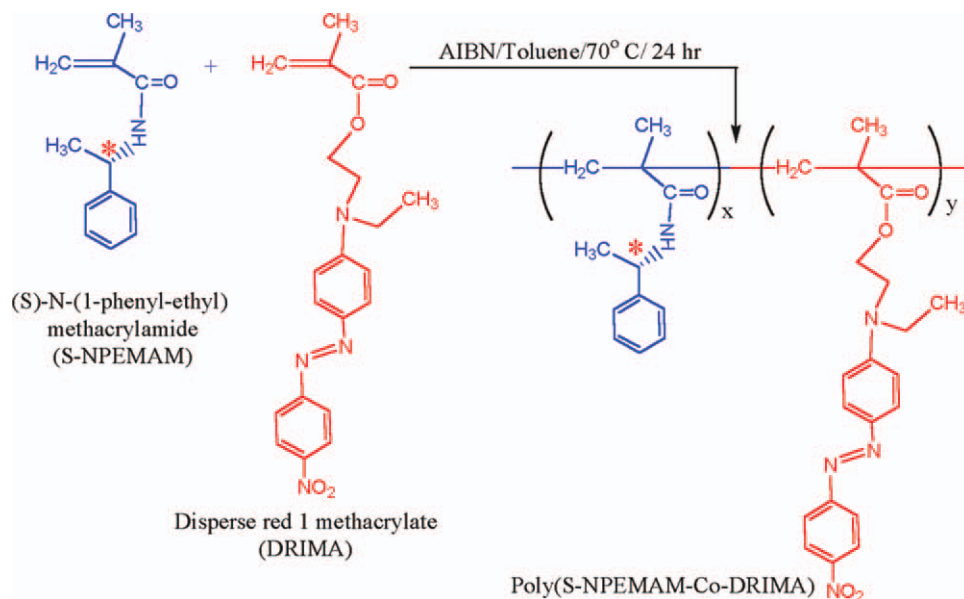
The synthesis of chiral and/or helical polymers is a topic of current interest.^{1–3} The amalgamation of photonic susceptibility, electrical conductivity, and biological activity into such chiral polymeric materials produces an array of high-tech applications, such as in artificial neurons and muscles, smart robotics and intelligent devices, scaffold matrices in tissue engineering, and photoresponsive antennas in photosynthesis cells, in addition to their usual potential use as chiral stationary phases in chromatographic enantioseparation, asymmetric electrodes in electrochemical processes, chiral polymeric catalysts and reagents in asymmetric organic synthesis. In addition to these aspects, the ability of chiral polymers for optical polarization has opened up their potential application as optical and chiroptical molecular switches and devices, optical shutters, optical wave guides, and in optical information storage and telecommunication devices.^{3–8}

On the other hand, polymers containing azobenzene chromophores (azopolymers) are promising materials for optical switching and optical storage because of the possible change of the orientation of

the azobenzene chromophores by irradiation with polarized light.^{9,10} Large numbers of azobenzene-containing side-chain and main-chain polymers have been reported to exhibit nonlinear optical properties and light-induced dichroism and birefringence.^{10–23}

When azobenzene molecules are attached to ordered chiral macromolecules, the trans-to-cis isomerization of the azobenzene chromophores can induce large changes in the chiroptical properties of the macromolecules. Polymers exhibit induced chirality because of the presence of an asymmetric center in the side group. Such polymer systems also offer the possibility of chain helicity. The helical structure of the polymer chain can be induced by the use of chiral azobenzene photoisomerizable side chains, for example, in poly(α -amino acids)²⁴ and helical polysocyanates.^{25–27} The chiroptical properties of chiral methacrylate polymers containing azobenzene have also been reported.^{28–35} In this investigation, chiral copolymers of (S)-N-(1-phenyl ethyl) methacrylamide (S-NPEMAM; synthesized at our laboratory as per a reported procedure⁸) and disperse red 1 methacrylate (DR1MA) were synthesized by free-radical polymerization in toluene at 70°C for 24 h with 2,2'-azobisisobutyronitrile (AIBN) as an initiator. The chiral copolymers, poly[(S)-N-(1-phenyl ethyl) methacrylamide-co-disperse red 1 methacrylate], were characterized with Fourier transform infrared (FTIR) spectroscopy, NMR, ultraviolet-visible (UV-vis)

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Scheme 1 Copolymerization of S-NPEMAM and DR1MA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

spectroscopy, and gel permeation chromatography (GPC) analyses. The photoluminescence (PL) and chiroptical properties, and the thermal properties of such photoactive chiral copolymers were examined.

EXPERIMENTAL

Materials

The chemicals, (S)-1-phenyl ethyl amine and methacryloyl chloride (Alfa Aesar, UK), ethanol, methanol, hexane, and NaOH (Samir Tech Chem Pvt. Ltd., India) were used as received. Disperse red1 methacrylate (DR1MA) (Aldrich, USA) was purified by crystallization from acetone/petroleum ether (bp = 60–90°C) and stored at 5°C in a refrigerator before use. It was red in color. Toluene (Ranbaxy) was dried over calcium chloride for 24 h, refluxed with sodium metal and finally distilled before use. AIBN (Aldrich, USA) was recrystallized twice from cold methanol, dried in a vacuum desiccator at room temperature, and stored in the dark at 5°C in a refrigerator before use.

The chiral vinyl monomer S-NPEMAM was synthesized by the condensation reaction of (S)-1-phenyl ethyl amine and methacryloyl chloride according to a reported method.⁸

Synthesis of the photoactive chiral copolymers

The copolymerization of the synthesized chiral monomer (S-NPEMAM) and DR1MA was carried out by free-radical polymerization with two different molar feed compositions (viz., 1 : 1 and 2 : 1 molar ratios). Both of the monomers in appropriate feed compositions and the AIBN initiator (5 wt %) were

placed, along with toluene, in a three-necked flask assembled with a nitrogen inlet and a condenser. The reactor was kept in an oil bath placed on a hot plate with a magnetic stirring arrangement. The copolymerization was carried out at 70°C under an N₂ atmosphere for 24 h. The copolymers were isolated by precipitation into methanol and purified by reprecipitation from tetrahydrofuran (THF) into methanol.

Characterization

The copolymers were characterized by FTIR and ¹H-NMR spectroscopy. The FTIR spectra of the samples were measured with KBr pellets in a Perkin Elmer RX-1 spectrophotometer (USA). The NMR spectra of the copolymers were recorded on a 400-MHz Bruker Fourier transform NMR spectrometer (Switzerland) by dissolution of the samples in CDCl₃. The chiral copolymers were characterized for their elements on a Vario-EL Elementar (CHNSO) analyzer (Germany). The molecular weights of the copolymers were measured by with a GPC instrument (Merck Hitachi LaChrom, Germany, Refractive-index detector L-7490, Pump L-7100, Styragel columns, and with THF as the mobile phase). The column was calibrated with PS standards.

The UV-vis spectra were recorded on a Varian Cary 500 UV-vis-near infrared spectrophotometer (USA) with solutions of the samples in THF. The circular dichroism (CD) was studied on a Jasco J-810L CD spectropolarimeter (JASCO, Japan) in THF solvent. The PL properties were studied for the copolymers in their THF solutions with a Varian Cary Eclipse fluorescence spectrophotometer (USA). Thermal analyses of the samples were carried out with a

TABLE I
Results of the Elemental (CHNSO)^a Analysis of the Chiral Copolymers

Copolymer sample	Molar ratio in the feed (S-NPEMAM:DR1MA)	C (%)	N (%)	H (%)	O (%)	N/C	O/C
PSMD-1	1 : 1	55.74	10.10	6.89	27.27	0.181	0.489
PSMD-2	2 : 1	68.42	10.56	6.80	14.22	0.154	0.208

^a Average of three measurements.

Mettler-Toledo TGA/SDTA 851 and a TA Instruments DSC Q200 under an N₂ atmosphere at a heating rate of 10°C/min.

RESULTS AND DISCUSSION

Synthesis of the photoactive chiral copolymers

Chiral copolymers of two different compositions of chiral monomer (S-NPEMAM) and DR1MA, were synthesized by a free-radical polymerization process with AIBN as an initiator at 70°C for 24 h under N₂ atmosphere (Scheme 1). The copolymers [PSMD-1 (obtained from a 1 : 1 molar ratio in the feed) and PSMD-2 (obtained from a 2 : 1 molar ratio in the feed)] were isolated by precipitation in methanol and purified by reprecipitation from THF into methanol. The chiral copolymers containing photoactive comonomer were obtained as a dark brown powder. However, their solutions in organic solvents appeared as orange in color.

Structural characterization

The purified copolymer samples were used for different analyses for their structural characterization. The results of the elemental analysis are given in Table I.

As the molar concentration of chiral monomer was increased in the feed, the N-to-C ratio decreased in the copolymer. This was obvious because of the fact that only one nitrogen element was present in the chiral monomer (S-NPEMAM), whereas four such nitrogens were present in the photoactive DR1MA comonomer. A similar trend was also observed for the oxygen element because of a similar reason (Scheme 1).

FTIR analysis

The FTIR spectra of the photoactive chiral copolymers are shown in Figure 1. The wide absorption band at 3440 cm⁻¹ was due to the NH trans-stretching vibration for the secondary amide. The narrow band at 1654 cm⁻¹ was due to the C=O stretching vibrations of -CONH- of S-NPEMAM.⁸ On the other hand, the C=O of the ester group of DR1MA appeared at 1725 cm⁻¹. The asymmetric stretching of NO₂ groups appeared at 1515 cm⁻¹, whereas the symmetric stretching of it appeared at 1337 cm⁻¹. The characteristic -N=N- (azo) stretching was observed³⁶ at 1386 cm⁻¹. The other characteristic peak at 1386 cm⁻¹, due to -OC-N of -CONH- groups, merged into it. However, the -OC-O of the ester of DR1MA appeared at 1260 cm⁻¹. The C-N stretching of DR1MA resonated at 1132 cm⁻¹.

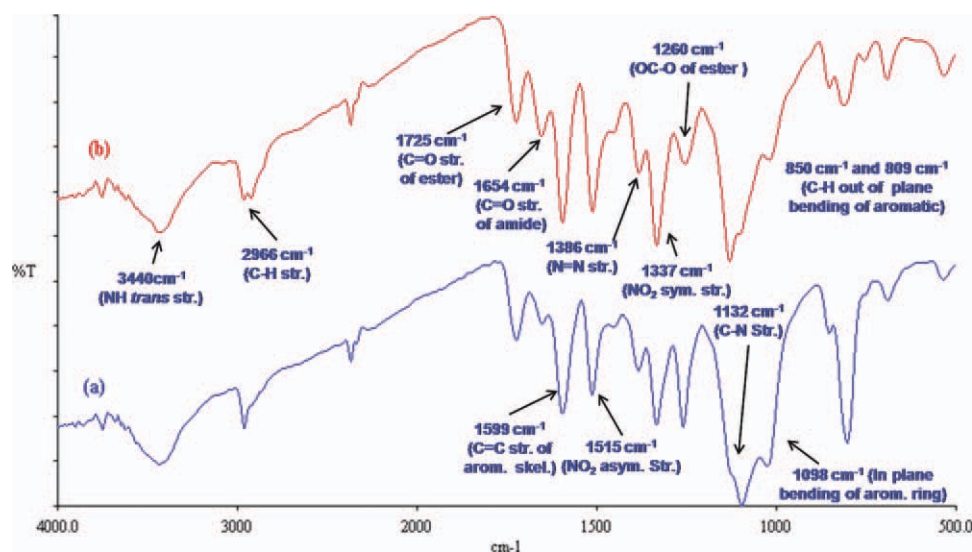


Figure 1 FTIR spectra of the chiral copolymers: (a) PSMD-1 and (b) PSMD-2. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

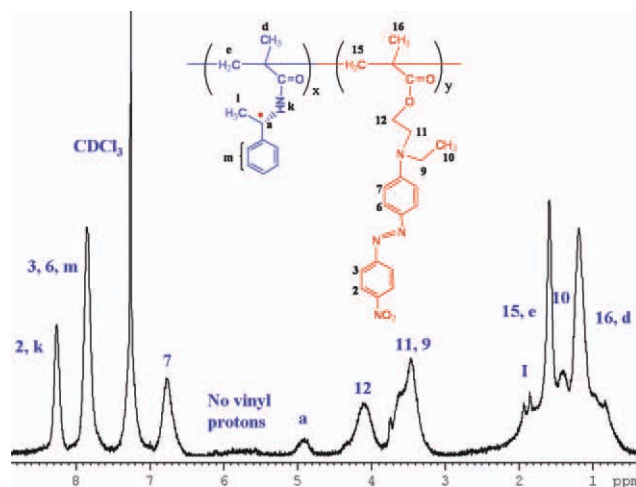


Figure 2 $^1\text{H-NMR}$ spectrum of the chiral copolymer PSMD-1 in CDCl_3 . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The C—H stretching of methyl group and also the alkyl chain ($-\text{CH}_2-$) all merged together and appeared at 2966 cm^{-1} . The aromatic C—H stretching around 3000 cm^{-1} could not be observed because of this merging. The aromatic ring stretching appeared at 1599 cm^{-1} . However, in-plane bending of the aromatic ring appeared at 1098 and 1018 cm^{-1} . The C—H (out-of-plane bending) of the aromatic and that of the aromatic nearby NO_2 resonated at 850 and 809 cm^{-1} , respectively.

On the other hand, the characteristic stretching frequency of double bonds ($\text{C}=\text{C}$) around 1614 cm^{-1} and the absorption band at 928 – 924 cm^{-1} , due to the C—H bending of vinyl groups ($=\text{CH}_2$), were absent in the spectra. This clearly indicated the formation of polymers by free-radical polymerization through the opening up of the π bonds of the comonomers.

NMR analysis

The $^1\text{H-NMR}$ spectrum of a photoactive chiral copolymer (along with the assignment^{8,37} of peaks) is shown in Figure 2. Different aromatic protons appeared in the range 6.8 – 8.3 ppm . The chemical shift value at 8.3 ppm was due to the NH protons of the chiral monomer merging there. The $\alpha\text{-CH}_3$ of both the comonomers exhibited two signals at 0.7 – 1.2 ppm . However, the methyl protons connected to $[-\text{CH}(\text{Ph})\text{CH}_3]$ appeared at 1.4 ppm . The proton of the aliphatic $-\text{CH}_2-$ of the polymeric chain appeared at 1.7 – 2.2 ppm . However, the absence of peaks at 5.3 – 5.7 ppm indicated the absence of vinyl protons. Hence, the disappearance of vinyl protons and the appearance of the alkyl chain clearly signified the formation of the copolymers.

A typical $^{13}\text{C-NMR}$ spectrum, along with the assignment^{8,38} of NMR signals of a copolymer, is shown in

Figure 3. The $\alpha\text{-CH}_3$ of both S-NPEMAM and DR1MA units in the copolymer appeared around 15 – 20 ppm . The methyl carbon of chiral unit exhibited a signal at 23 ppm . The aromatic carbons appeared as multiplets around 130 ppm . Two resonance signals of $\text{C}=\text{O}$ of the amide of S-NPEMAM and of the ester of DR1MA appeared around 178 ppm .

Composition and molecular weights of the photoactive chiral copolymers

The molecular weights of the polymers were measured with a GPC system. The number- and weight-average molecular weights of the photoactive chiral copolymers are given in Table II. The copolymer composition was readily obtained accurately from the $^1\text{H-NMR}$ spectrum. The composition of the chiral copolymers was calculated with consideration of the integral peak areas (I) of the CH of $\text{Ph}(\text{CH}_3)\text{CH}$ of the chiral monomer and the CH_2 of $-\text{COOCH}_2-$ of DR1MA with the following equation:

$$F_1 = \frac{I_a}{I_a + \left(\frac{I_{12}}{2}\right)}$$

where I represents integral peak area in the NMR spectrum and F_1 (molar fraction) is the composition of the chiral unit in the copolymer, and a and 12 denote the corresponding protons, as indicated in Figure 2. The results of copolymer composition obtained from NMR analysis are given in Table II. The chiral copolymer PSMD-1 contained more photoactive comonomer (DR1MA) than that of the copolymer PSMD-2.

Study of the electronic absorption

The UV-vis spectra of the chiral copolymers are shown in Figure 4. Two maximum electronic

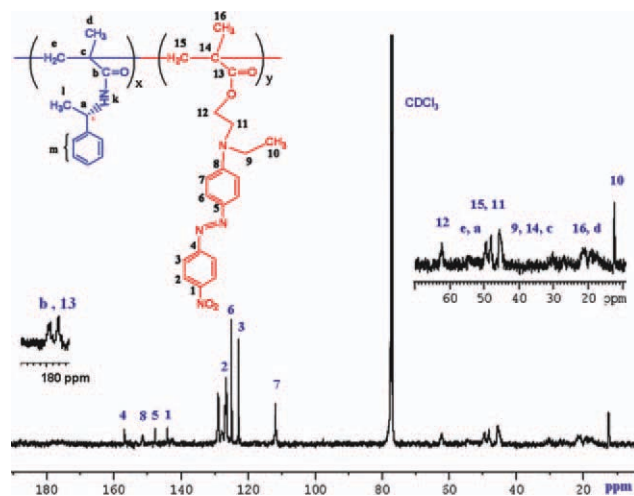


Figure 3 $^{13}\text{C-NMR}$ spectrum of the chiral copolymer PSMD-2 in CDCl_3 solvent. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE II
Copolymer Composition and Molecular Weights^a of the Chiral Copolymers

Copolymer sample	Monomer feed composition		Copolymer composition ^b		$M_n \times 10^{-3}$	$M_w \times 10^{-3}$
	S-NPEMAM	DR1MA	S-NPEMAM	DR1MA		
PSMD-1	0.500	0.500	0.414	0.586	1.40	4.45
PSMD-2	0.666	0.334	0.509	0.491	1.09	3.30

M_n , number-average molecular weight; M_w , weight-average molecular weight.

^a GPC analyses.

^b NMR analysis.

absorptions for the chiral copolymers appeared at 279 and at 469 nm. The first one was due to the $\pi-\pi^*$ transition associated with the aromatic ring present in the chiral and azobenzene moieties. On the other hand, the strong electronic absorption in the visible region at 469 nm corresponded to the combined contributions of the $n-\pi^*$, first $\pi-\pi^*$ and intermolecular charge transfer electronic transitions of the azobenzene chromophore of photoactive comonomer.³⁹ The characteristic value of λ_{max} for the DR1MA monomer in THF was 475 nm. Thus, a slight blueshift of about 6 nm was observed in the copolymers compared with those in the absorption of the comonomer (DR1MA). Azobenzene chromophores can easily $\pi-\pi$ stack in monomer solution, whereas in copolymer solution, the movement of azobenzene units is restricted, which may cause the difference. There was no change in the λ_{max} value for the two copolymers. The difference in absorption for the two copolymers was due to the difference in the concentration of DR1MA comonomer in the copolymers. The electronic absorption was higher for PSMD-1; this was a result of 58.6% DR1MA units in the copolymer versus 49.1% in the copolymer PSMD-2.

Study of the PL properties

The PL property was studied for the copolymers in their THF solutions (Figs. 5 and 6). This property

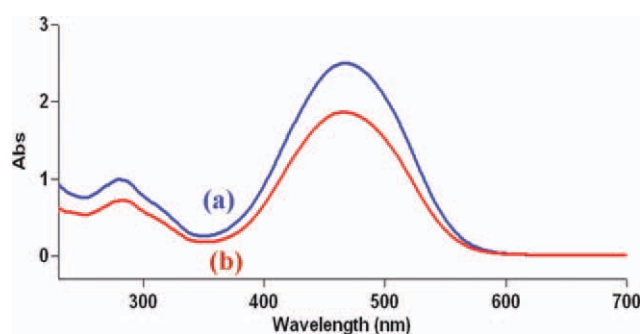


Figure 4 UV-vis spectra of the chiral copolymers, (a) PSMD-1 and (b) PSMD-2, in THF (0.06 mg/mL). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

was studied for the variation of concentration of the solution and with the variation of excitation energy from 250 to 300 nm. The optimum PL was observed at an excitation wavelength (λ_{ex}) of 270 nm, where the emitted wavelengths (λ_{em} 's) were observed as 310 and 307 nm for the copolymers PSMD-1 and PSMD-2, respectively (Table III). The PL spectra for both of the copolymers displayed a redshift of only 5 nm with increasing solution concentration [Fig. 6(b)], which resulted from excimer emission.

The effect of excitation energy (250–300 nm) on the fluorescence was not significantly observed in the PL spectra of the 6×10^{-4} mg/mL PSMD-2 solution [Fig. 5(b)]. The emission peaks appeared at 306–308 nm for the excitation from 250 to 290 nm. However, it appeared at 328 nm for λ_{ex} at 300 nm. Ding and Russell³⁷ observed a continuous blueshift (hypsochromic shift) in the PL spectra of the monomer DR1MA and its homopolymer with increasing λ_{ex} from 240 to 280 nm. The blueshift was explained as

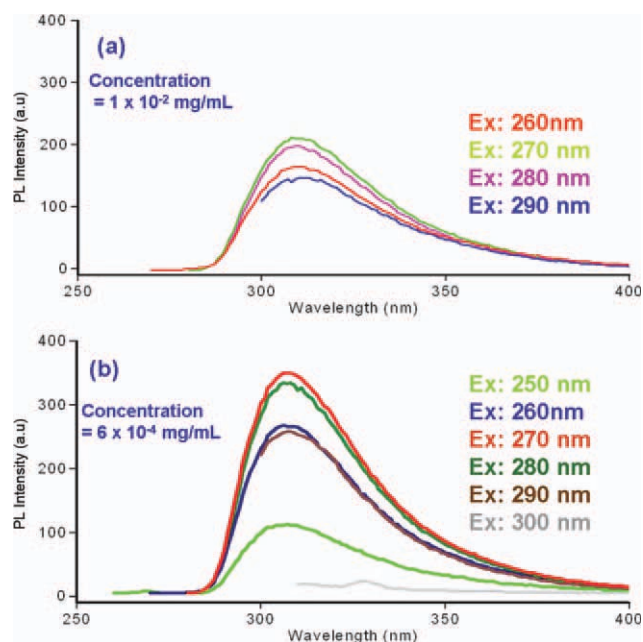


Figure 5 PL spectra of the photoactive chiral copolymers: (a) PSMD-1 and (b) PSMD-2 in THF at different excitation energies. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

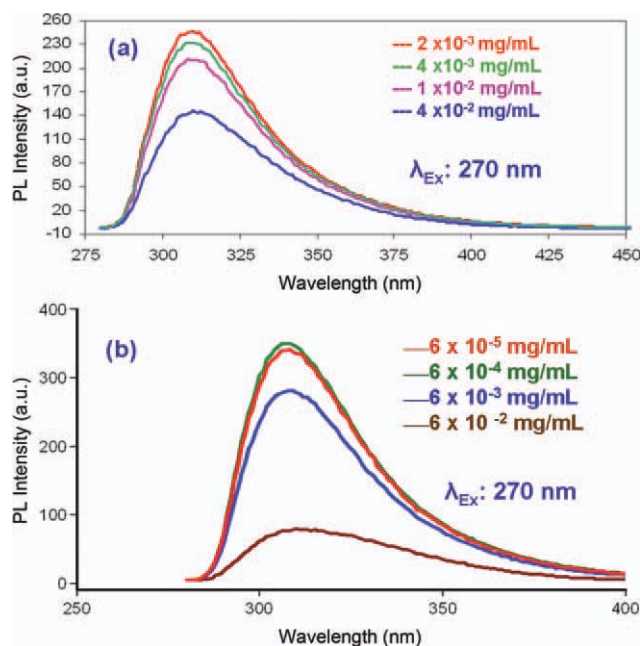


Figure 6 PL spectra of (a) PSMD-1 and (b) PSMD-2 in THF at various concentrations. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

possibly due to the increasing *trans-to-cis* photoisomerization at these wavelengths. The π -electron delocalization and conjugation were better in *trans*-azobenzene, where a bathochromic shift (redshift) was expected. The *cis*-azobenzene molecules obtained from the transformation of the planar *trans* form had a globular geometry with the phenyl rings twisted perpendicular to the plane determined^{40,41} by C=N=N=C. So the π -electron delocalization and conjugation were not favorable in *cis*-azobenzene. Hence, a hypsochromic shift (blueshift) should be expected in the *cis* form. The decrease in π - π stacking also caused a blueshift in the PL spectra of the polymer solutions in comparison to the monomer solution (DR1MA).³⁷

Here, in the chiral copolymers of DR1MA and S-NPEMAM, no such prominent blueshift was observed. Of course, it may not be true to say that the associated *trans-to-cis* transformation did not take place, as no such characteristic blueshift was observed. Again, it is also true that the π - π stacking arising out of two azobenzene moieties was also

TABLE III
Results of the PL Analysis of Photoactive Chiral Copolymers in THF Solution

Copolymer sample	$\lambda_{\text{ex}} = 270 \text{ nm}$		
	λ_{em} (nm)	PL intensity (au)	Concentration of solution (mg/mL)
PSMD-1	310	246.8	2×10^{-3}
PSMD-2	307	350.4	6×10^{-4}

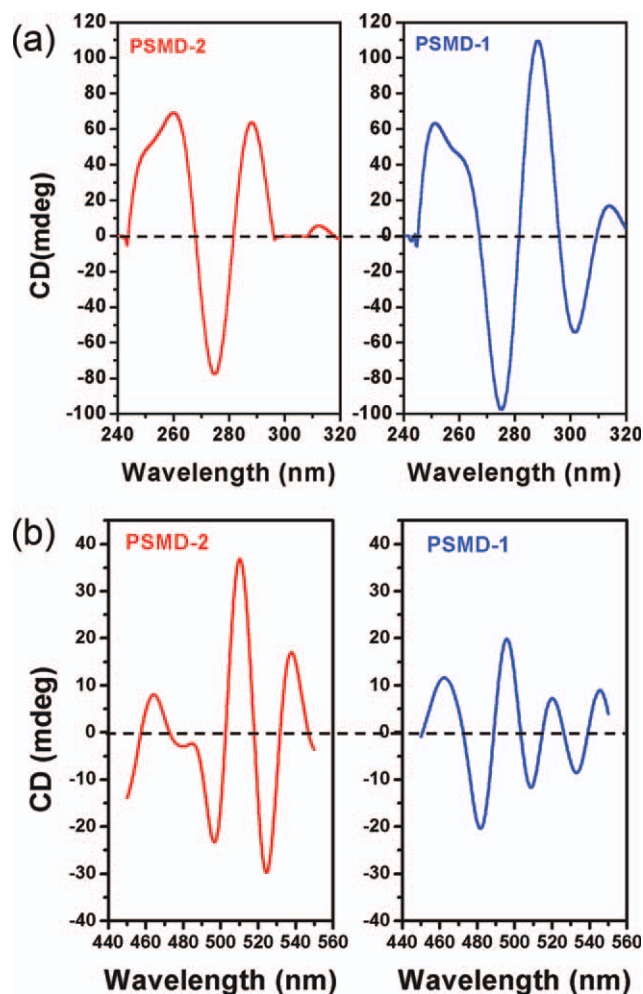


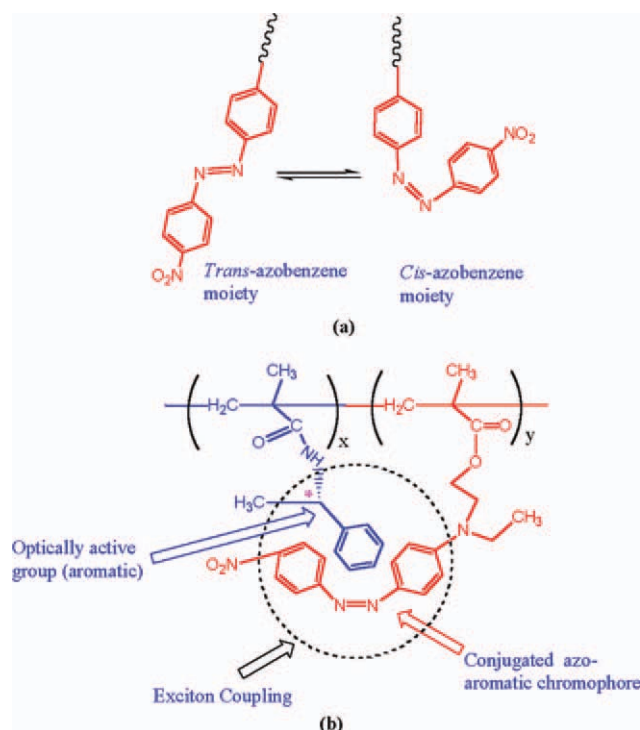
Figure 7 Deconvoluted CD spectra [(a) 240–320 and (b) 440–560 nm] of PSMD-1 (0.0108 w/v%) and PSMD-2 (0.0182 w/v%) in THF. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

minimized because of the introduction of the second monomer (chiral monomer) in the copolymer.

Again, when we compared the emission wavelengths in the PL spectra of the copolymers reported here with the homopolymer³⁷ of DR1MA, we observed a blueshift of 10–12 nm *wrt* from that of the homopolymer. This blueshift may not have only been due to π - π stacking of a similar kind of moiety, say, azobenzenes, but also to the π - π stacking of the randomly distributed aromatic and azobenzene chromophores. The π - π interaction of the benzene ring of the chiral unit and the azobenzene of DR1MA was also clearly observed in the CD spectra (see next section).

Study of the chiroptical properties

To investigate the chiroptical properties, the photoactive chiral copolymers were studied with CD spectroscopy in THF solution in the spectral region 220–700 nm (Fig. 7). Both samples displayed CD behavior in the two spectral regions: one corresponded to



Scheme 2 Representation of the (a) *cis* and *trans* forms of the azobenzene chromophores and (b) exciton coupling between the aromatic chiral moiety and azobenzene chromophore of the copolymer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the first UV-vis absorption ($\lambda_{\text{max}} = 279$ nm) band due to the aromatic ring, and the other was due to the second absorption ($\lambda_{\text{max}} = 469$ nm) associated with the azobenzene moiety. The first dichroic signal was obvious; this resulted because of the chiral monomeric unit. However, the observation of the CD band at the second absorption was certainly observed due to chiral induction onto the photoactive azobenzene chromophore. Again, the UV-vis absorption due to the azobenzene moiety was very pronounced and greater than the aromatic absorption. However, the intensity of CD signal was observed as the reverse trend. This might have been due to the fact that the induced CD signal was certainly weaker than the primary one because of the aromatic ring of the chiral monomer unit.

The first CD signal displayed two intense dichroic bands of opposite sign and slightly different intensity with a crossover point at 281.6 nm. Such behavior is typical of exciton splitting originated by cooperative interactions between side-chain azobenzene chromophores and the benzene ring of the chiral monomer, which are also disposed according to a mutual chiral geometry of one prevailing handedness.³² A similar behavior of exciton splitting was also observed for the second band. The multiple splitting may have been associated with both the *cis* and *trans* conformation of the azobenzene moiety.

Generally, azobenzene can be transformed between the more stable *trans* form and the less stable *cis* form upon exposure to UV or visible light. However, the composition of the photostationary state depends on the wavelength of irradiation and temperature.⁴² Therefore, the existence of the both forms caused multiple splitting in the spectra. Scheme 2 indicates the structural representation of exciton coupling. The amplitude in the case of PSMD-2 was more than that of PSMD-1; this might have been associated with the greater interaction in PSMD-2 than in PSMD-1 because of the greater chiral content in this copolymer.

Study of the thermal properties

The glass-transition temperature (T_g) of the homopolymer of a similar chiral monomer was reported⁸ to be 100.6°C. On the other hand, the homopolymer of DR1MA monomer was reported³⁷ to display a T_g of about 105.6°C. Here, the photoactive chiral copolymers exhibited T_g 's of 117 and 122°C for PSMD-1 and PSMD-2, respectively (Fig. 8). The higher T_g value was found for copolymer PSMD-2, which had the higher content of chiral unit (or in other words, a lower content of azoaromatic units) than the copolymer PSMD-1. The azoaromatic-containing comonomer may have had more flexibility because of its inherent nature associated with the *cis*-*trans* isomerization; this may have caused a lower T_g value of the copolymer containing a higher content of this unit in the copolymer.

Thermogravimetric analysis (TGA) thermograms of the copolymers are shown in Figure 9. The results indicate the three-staged thermal decomposition of the chiral copolymers at around 286°C, above 418°C,

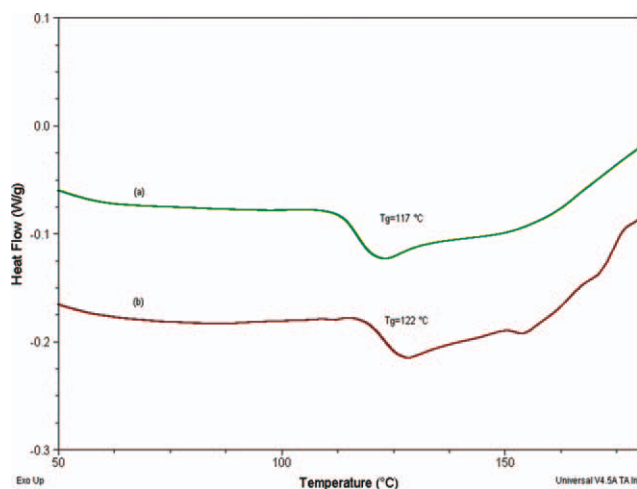


Figure 8 DSC thermograms of the chiral copolymers: (a) PSMD-1 and (b) PSMD-2. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

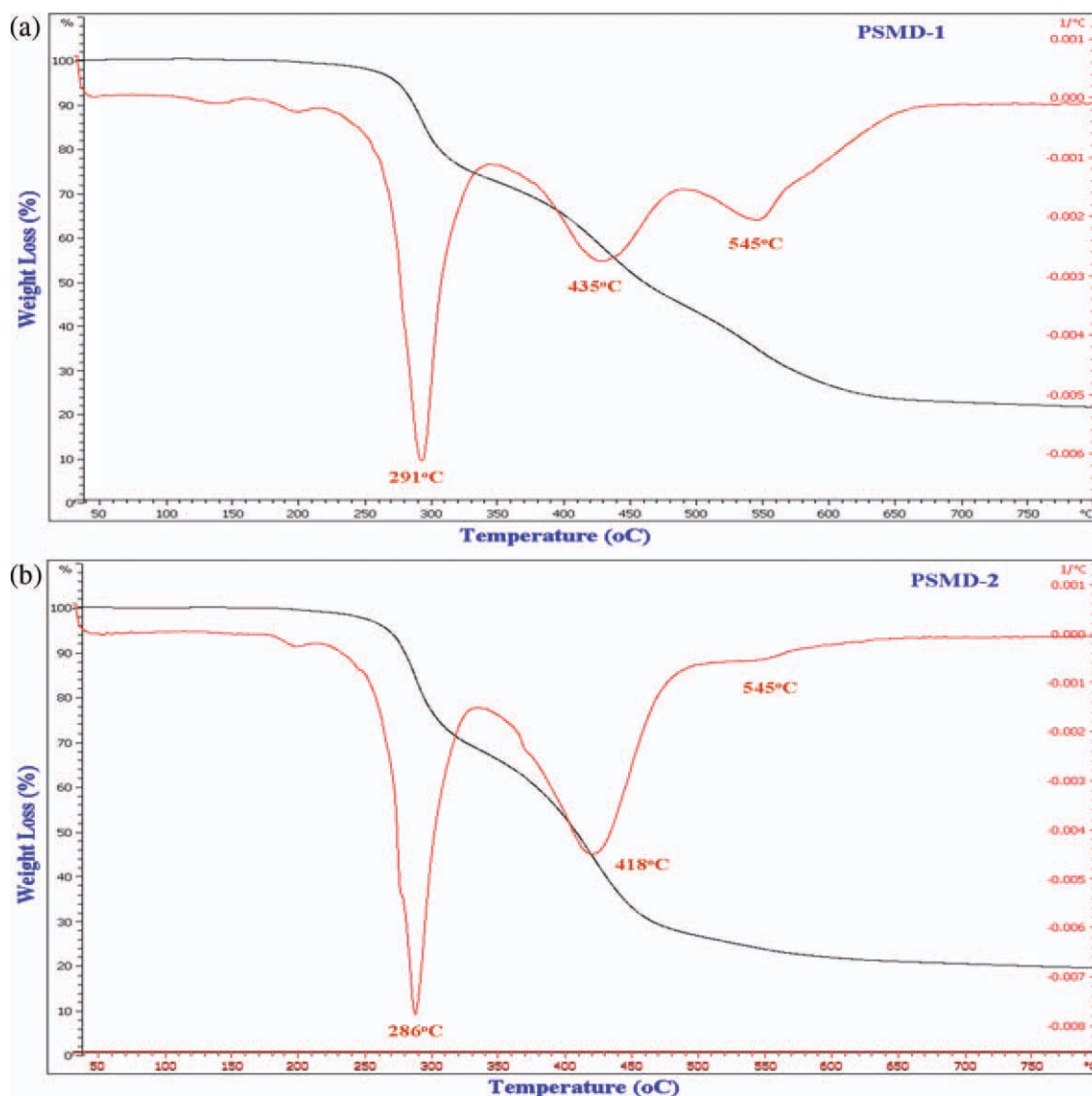


Figure 9 TGA thermograms of the chiral copolymers: (a) PSMD-1 and (b) PSMD-2. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE IV
Results of the Thermal Degradation of the Chiral Copolymers

Copolymer	First degradation temperature (°C)		Second degradation temperature (°C)		Third degradation temperature (°C)	
	Onset	Endset	Onset	Endset	Onset	Endset
PSDM-1	272.5	307.8	398.3	463.7	531.5	610.7
PSDM-2	269.7	303.9	377.7	452.9	Not so prominent	

TABLE V
Weight Loss and Char Residues of the Thermal Degradation of the Chiral Copolymers

Copolymer	Weight loss (%) at				Char residue (%) at	
	250°C	350°C	450°C	550°C	700°C	800°C
PSDM-1	1.8	27.5	47.8	66.0	22.8	21.7
PSDM-2	2.5	34.0	67.0	76.3	20.5	19.6

and at 545°C. A two-step decomposition process of the homopolymer of DR1MA was reported.³⁷ We also observed a two-step thermal degradation of a homopolymer of similar kind of chiral unit.⁸ Here, the mechanism and/or phenomenon associated with the third-stage decomposition for the copolymers reported was not clear. The results of TGA of the chiral copolymers are given in Table IV and V. Only a 1–2.5% weight loss at 250°C indicated very good thermal stability of these copolymers. Moreover, about 20% char residue at 800°C for both the copolymers indicated excellence in their thermal properties.

CONCLUSIONS

Chiral copolymers with photoactive comonomers were synthesized with S-NPEMAM and DR1MA by a free-radical polymerization process. The copolymers were characterized for their molecular weights by GPC analysis and elemental and copolymer composition with elemental, FTIR, and NMR analyses. The electronic absorption, photophysical, and chiroptical properties were studied. Both the chiral copolymers exhibited PL and chiroptical properties. The asymmetric induction to the azobenzene moiety was observed by the indication of induced CD in the CD spectra, where exciton splitting originated from the cooperative interactions between the pendant azobenzene chromophore of DR1MA and the benzene ring of the chiral monomer because of the statistical disposition of the azobenzene moiety in a mutual chiral geometry of one prevailing handedness.

The T_g values of the chiral copolymers were found to be 117 and 122°C. They were thermally stable up to 250°C and exhibited a three-stage degradation. This type of photoactive chiral copolymer may find optical and nonlinear optical applications.

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