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Preparation and Characterization of PVC-based Photoresponsive Polymers Containing Azo-chromophores

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New strategy was developed for the preparation of the photoresponsive polymers containing azo-chromophores as side-groups from the active chlorine atoms of polyvinyl chloride (PVC). The anilinated polyvinyl chloride precursors, anilinated polyvinyl chloride (PVC-An) and o-chloroanilinated polyvinyl chloride (PVC-oClAn), synthesized chemically by reacting PVC with sodium aniline (o-chloroaniline) salt. Then the two novel PVC-based polymers functionalized with azo-chromophores (PVC-AZ-An and PVC-o-AZ-NP) were synthesized via the azo-coupling reactions of the anilinated polyvinyl chloride precursors (PVC-An and PVC-oClAn) with the diazonium salts of aniline and alpha naphthylamine, respectively. The structures of polymers were confirmed by FTIR and ^{1}H–NMR. The UV-Vis spectra of the obtained polymer in THF solution showed that the $\pi - \pi^*$ absorption band of PVC-o-AZ-NP shifted to longer wavelength (red-shifted) due to the influence of auxochrome (-Cl) compared to the $\pi - \pi^*$ absorption band of PVC-AZ-An.

Keywords: Photoresponsive polymer, azo-chromophore, polyvinyl chloride, azo-coupling reaction

1 Introduction

Recently, some chromophores such as azobenzene (1), spiropyran, fulguid and their derivatives have been introduced into the polymers as photoresponsive groups (2, 3). Irradiation of a linearly polarized light on the above chromophores induces changes in their optical birefringence and absorbance. Among various chromophores, azo-chromophores respond to light much more rapidly than any other photoresponsive groups (4). Therefore, polymers containing azo-chromophores have been the subject of intensive research because of their potential applications in various fields, such as optical data storage (5,6), real-time optical holography (7), optical switching (8), integrated optics (9), liquid crystal alignment (9, 10), and optical memory media (4,11).

Generally speaking, the azo-functionalized polymers are mainly divided into azo side-chain liquid crystalline polymers (12–14) and main-chain azo-polymer (15–18). Main-chain azo-polymers are relatively less due to the complexity of their preparation and the steric hindrance of conversion from the *trans* isomer to *cis* isomer at the photostationary state compared to the azo side-chain liquid crystalline polymers, the latter have been designed and prepared recently by different methods, such as post-polymerization approaches via azo-coupling (19–21) or ester-interchange reaction (22), and the controlled/"living" radical polymerization (CLRP) of azo-monomers via atom transfer radical polymerization (ATRP) (23–25), reversible addition-fragmentation chain transfer (RAFT) (26) and nitroxide-mediated radical polymerization (NMP) (27) technique. In particular, post-polymerization azo-coupling methods have been extensively used to prepare azo-polymer in recent years because it is convenient compared to the CLRP methods because the vinyl monomers containing azo-chromophores can scarcely be polymerized via the conventional radical polymerization and the polymerizing conditions of the CLRP are rigorous. By far, the preparation of azo-polymer based on the ready-made polymers is scarce by azo-coupling reaction.

In this work, we have designed and prepared two novel PVC-based polymer containing photoresponsive azo-chromophores by the azo-coupling method using precursor polymers, which were synthesized by the reactions between polyvinyl chloride (PVC) and aniline or o-chloroaniline from the active chlorine atoms of PVC, respectively. Poly(vinyl chloride) (PVC) was chosen for the backbone polymer because it is a cheap and familiar

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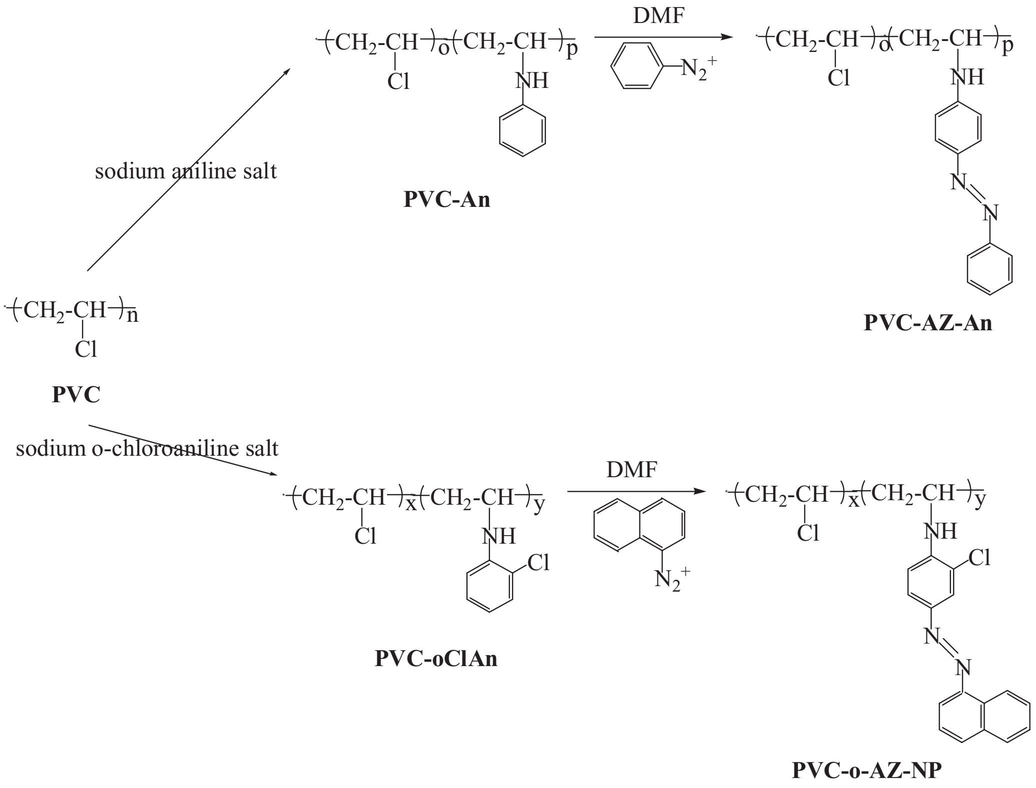

Sch. 1. Synthetic route of the PVC-based azo polymers.

thermoplastic plastic due to its unique properties, such as superior mechanical and physical properties, high chemical and abrasion resistance (28). It especially has reactive chlorine atoms for graft sites even though the reactivity of chlorine in PVC is relatively low (29).

2 Experimental

2.1 Materials and Reagents

Poly(vinyl chloride) (PVC) powers used were commercial products from Yanguoxia Chemical Factory, Gansu, China, and were used after being washed with ethanol for removal of the surface contamination and then dried under vacuum at room temperature.

Aniline, o-chloroanilinate and N, N-dimethylformamide (DMF) were purified by vacuum distillation. Other chemicals were used without further purification.

2.2 Preparation of Anilinated Polyvinyl Chloride (PVC-An and PVC-oClAn)

The preparation of PVC-An and PVC-oClAn were completed by the reactions between polyvinyl chloride (PVC) and aniline or o-chloroaniline through a procedure similar to the reference previously (29). The synthesis of PVC-An is illustrated here as a typical example. Sodium aniline salt was prepared by aniline with sodium hydride in DMF for 12 h at room temperature under N_2 atmosphere. DMF solution of PVC was added into a flask that contained sodium aniline salt prepared. The reaction was continued for 8 h at 60°C under the protection of N_2 atmosphere. The above reactant solution was poured into ethanol in order to obtain the precipitation of anilinate polyvinyl chloride (PVC-An), which was filtered and washed with ethanol, and then dried under vacuum at 40°C for 24 h.

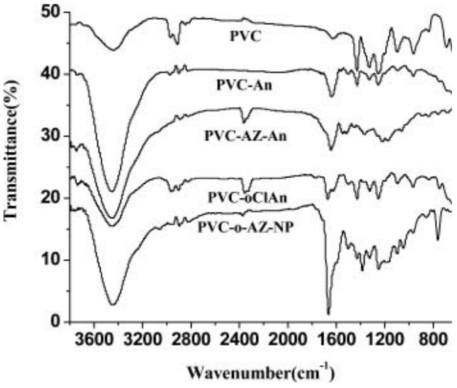

Fig. 1. FT-IR spectra of PVC, PVC-An, PVC-AZ-An, PVC-oClAn, and PVC-o-AZ-NP.

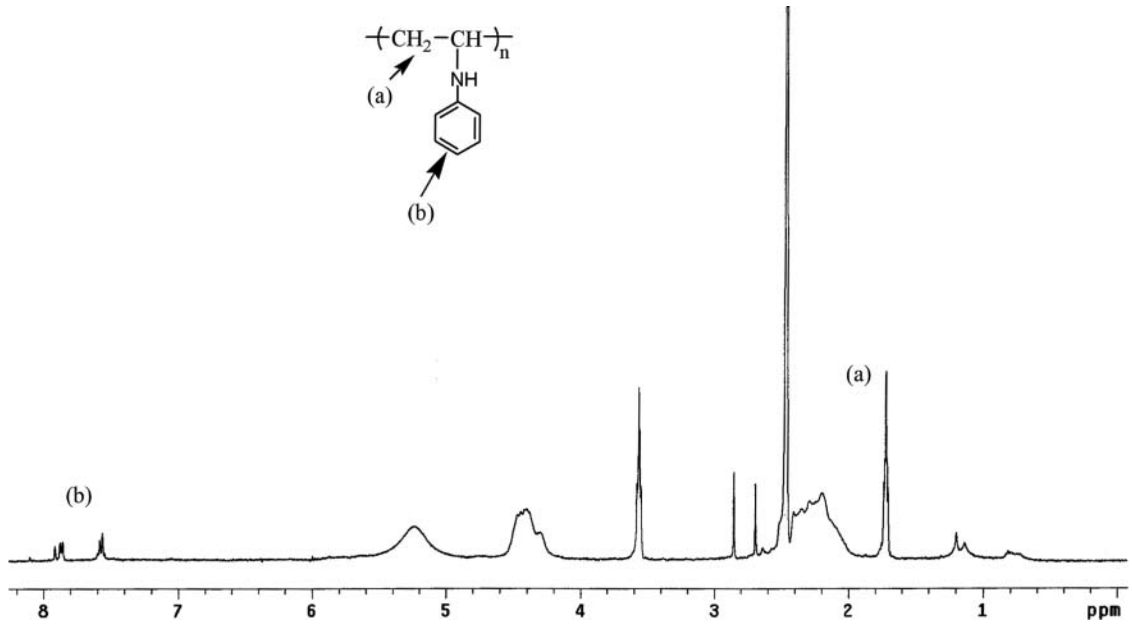

Fig. 2. ^{1}H-NMR of PVC-An.

2.3 Preparation of Azo-Polymers

The azo-polymers were synthesized by the azo-coupling reactions of the above modified PVC (PVC-An and PVC-oClAn) with diazonium salts of aniline and alpha naphthylamine, respectively. The synthesis of PVC-AZ-An is illustrated here as a typical example. PAC-An (0.6 g, 4.6 mmol) was dissolved in 40 mL N, N- dimethylformamide (DMF) and the solution was kept in an ice bath. Sodium nitrite (0.38 g, 5.5 mmol) was dissolved in 1.0 mL water with ice bath cooling. Diazonium salt of aniline was prepared by

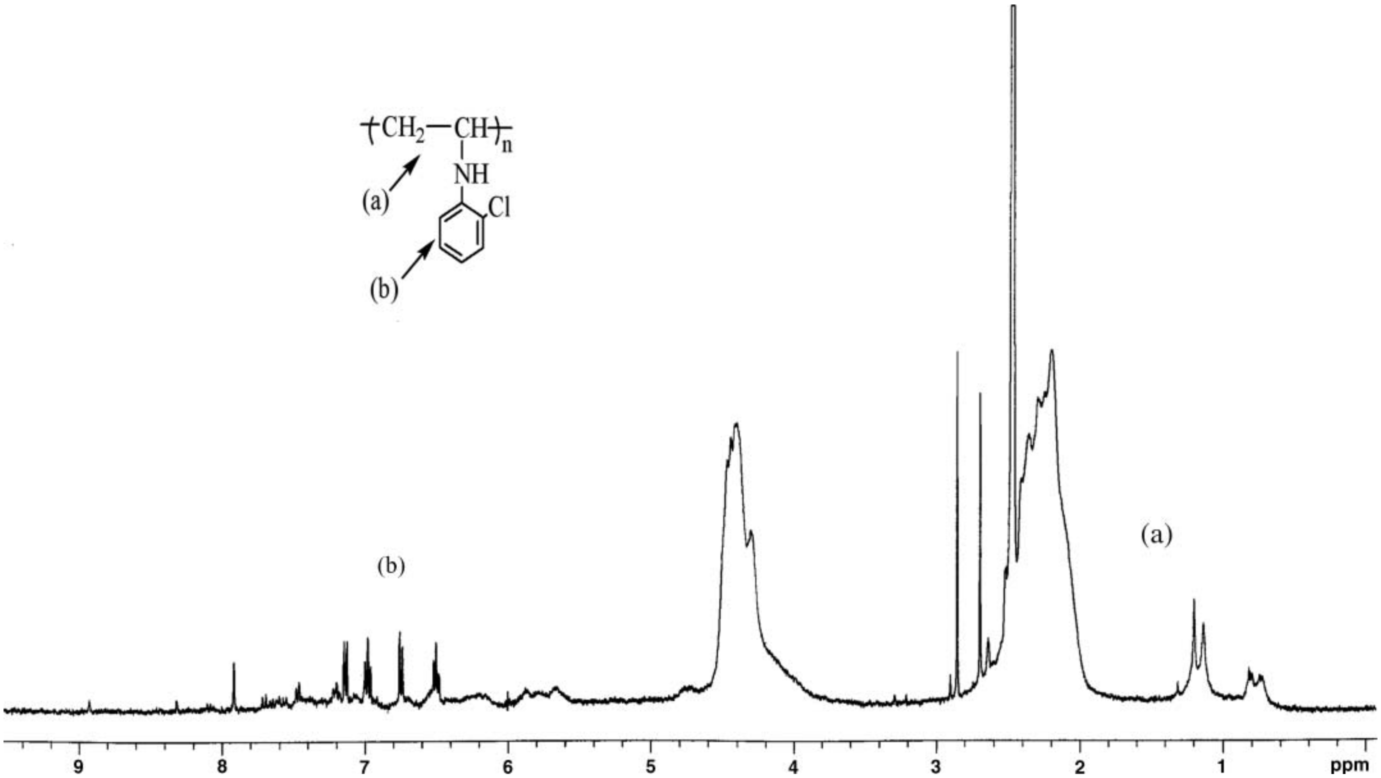

Fig. 3. ^{1}H-NMR of PVC-oClAn.

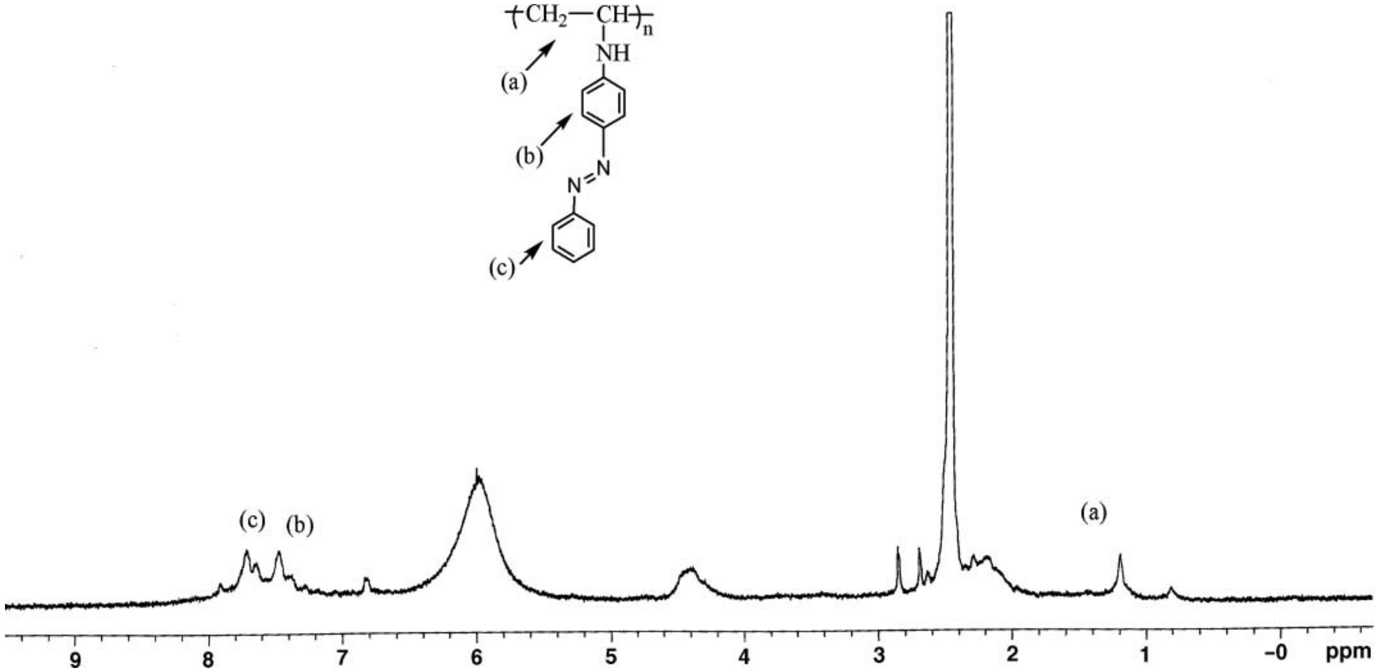

Fig. 4. ^{1}H-NMR of PVC-AZ-An.

adding the above aqueous solution of sodium nitrite into aniline (0.465 g, 5 mmol) in a homogeneous mixture of 1.5 mL of sulfuric acid and 12 mL glacial acetic acid. The mixture was stirred at 0°C for 30 min and then was added dropwise into the PAC-An solution, and the solution was stirred for 12 h. The production of PVC-AZ-An was obtained by precipitation of the above solution into plenty of water. The polymer was further purified by dissolving THF and precipitating into petroleum ether. The final production was filtrated, washed and dried under vacuum at 40°C for 48 h.

The other azo-polymer PVC-o-AZ-NP was synthesized via the similar procedure with PVC-oClAn and the diazonium salts of alpha naphthylamine. The synthetic routes of the two azo-polymers were shown schematically as Scheme 1.

2.4 Characterization

Elemental analysis (EA) of C, N and H was performed on a Elementar vario EL instrument (Elementar Analysensysteme GmbH, Munich, German). Bruker IFS 66 v/s infrared spectrometer (Bruker, Karlsruhe, Germany) was used for the Fourier transform infrared (FT-IR) spectroscopy analysis in the range of 400–4000 cm^{-1} with the resolution of 4 cm^{-1}. The KBr pellet technique was adopted to prepare the sample for recording the IR spectra. The polymers were dissolved in DMSO-d^6 and then characterized with ^{1}H-NMR using a Varian UNITY INOVA-500 FT-NMR (400 MHz) spectrometer (Palo Alto, CA). Thermogravimetric analysis (TGA) was performed with a Perkin-Elmer TGA-7 system (Norwalk, CT, USA) at a scan rate of 20°C min^{-1} to 700°C in N_2 atmosphere. The UV-Vis spectra of the THF solution of polymers were followed by a Perkin-Elmer Lambda 35 UV/vis Spectrometer (Perkin-Elmer Instruments, USA) at room temperature.

3 Results and Discussion

Two novel PVC-based polymers containing photoresponsive azo-chromophores were prepared by the azo-coupling method using precursor polymers, which were synthesized by the reactions between polyvinyl chloride (PVC) and aniline, o-chloroaniline as shown in Sscheme 1. The FT-IR spectra of PVC, PVC-An, PVC-AZ-An, PVC-oClAn, PVC-o-AZ-NP are shown in Figure 1. It can be seen that all spectra show the $\delta_{(C-Cl)}$ of PVC at 1328 cm^{-1}, 1253 cm^{-1}. In comparison of all spectra, two new peaks appear at about 1610 cm^{-1}, 1500 ~1510 cm^{-1}due to C=C stretch of aromatic rings which do not exit in that of pure PVC. It indicated that the aniline and azobeneze structures had been introduced to the side-groups of PVC. However, it does not clearly indicate the peak of –N=N- of azobeneze chromophores at about 1500 cm^{-1}in Figure 1 (PVC-AZ-An and PVC-o-AZ-NP). It may be attributed to the following reasons: 1) it is relatively weak, 2) it may overlap between the C=C stretch of aromatic and the peak of –N=N- of azobeneze chromophores each other at 1500 cm^{-1}.

According to the elemental analysis, about 1.46 mmol aniline or 1.81 mmol o-chloroaniline groups have been introduced to 1 g PVC, respectively. It is noteworthy that

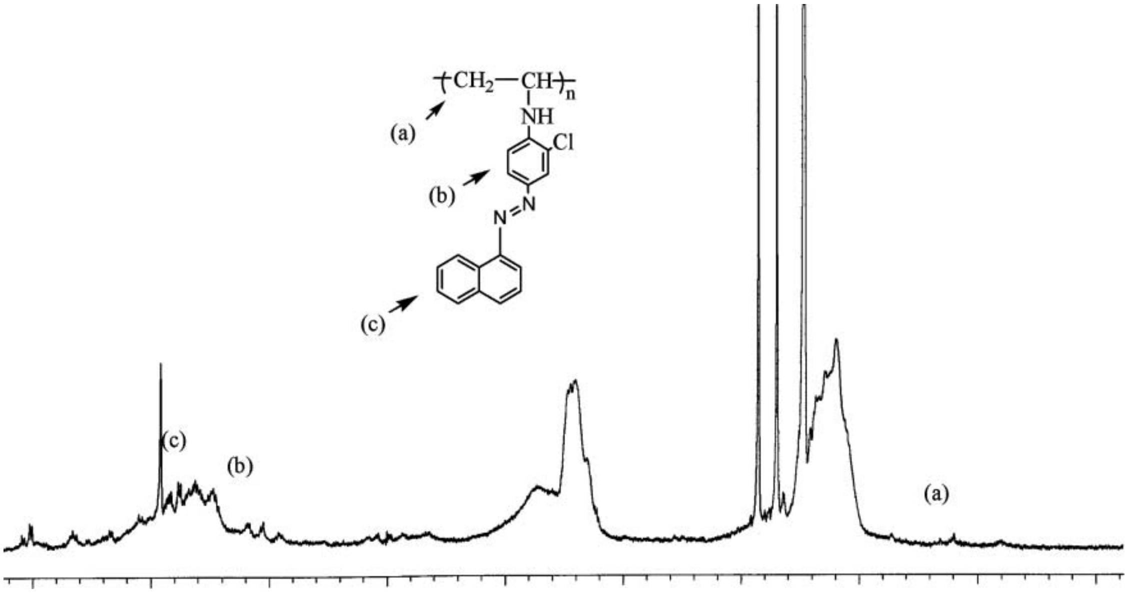

Fig. 5. ^{1}H-NMR of PVC-o-AZ-NP.

about 9% and 11% chlorine atom of PVC had been substituted by aniline and o-chloroaniline, respectively; this may be the result of the reactivity of chlorine in PVC being relatively low. After azo-coupling reaction, the aniline and o-chloroaniline groups almost completely react with corresponding diazonium salts of aniline and alpha naphthylamine, according to the element analysis.

^{1}H-NMR spectra of PVC-An and PVC-oClAn are shown in Figures 2 and 3. The occurrence of the peaks at $\delta = 7.57$ and 7.87 (Fig. 2) and $\delta = 6.48$-7.19 (Fig. 3) indicate that aniline and o-chloroaniline groups have been successfully bound to PVC. Figures 4 and 5 show the ^{1}H-NMR spectra of PVC-AZ-An and PVC-o-AZ-NP, respectively. It can be seen that the spectral line intensity and width of aromatic proton intensify compared to PVC-An and PVC-oClAn. It also proves that the azo-coupling reaction took place between anilinate polyvinyl chloride (PVC-An, PVC-oClAn) and corresponding diazonium salts.

The TGA curves of PVC, PVC-An, PVC-AZ-An, PVC-oClAn and PVC-o-AZ-NP are shown in Figures 6 and 7, respectively. The weight loss of PVC starts at 265°C. Between 265 and 360°C, a rapid weight loss occurs and PVC loses 60% of its weight. It can be attributed to the dehydrochlorination. The dehydrochlorination reaction ended at around 400°C (30). The weight loss above 400°C can be attributed to the polymer decomposition. In the case of PVC-An, the weight loss occurs before 150°C, which can be attributed to the expulsion of loosely bound water and solvent molecule from the polymer chain. Between 150 and 330°C, the weight loss reaches about 50%; this can be attributed mainly to the beginning of chain degradation. Above this temperature range, the polymer presents relatively slow weight loss process assigned to main chain degradation. For PVC-AZ-An, the weight loss occurs before 150°C, which can be attributed to the expulsion of loosely bound water and solvent molecule from the polymer chain. However, a slower weight loss than in the cases of PVC and PVC-An occurs between 150 and 325°C, which may be the result of the beginning of chain degradation. The weight loss above this temperature range can be attributed to the polymer decomposition. The thermal degradation behavior of the PVC-oClAn and PVC-o-AZ-NP are similar to the PVC-An and PVC-AZ-An within corresponding temperature range.

The azo-functionalized polymer, as well as the corresponding azo-monomer, can change their conformation in response to light because of the *trans*-to-*cis*

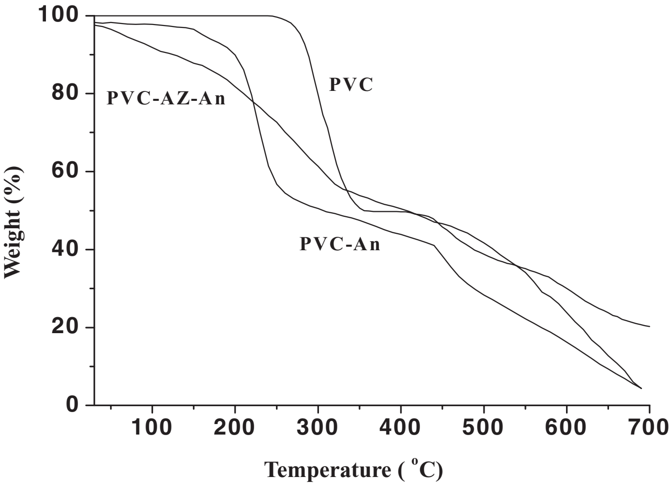

Fig. 6. TGA curves of PVC, PVC-An, and PVC-AZ-An.

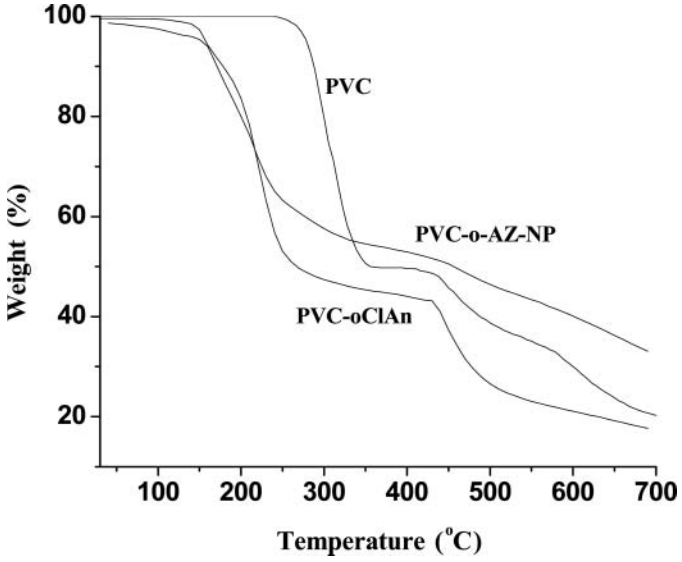

Fig. 7. TGA curves of PVC, PVC-oClAn, and PVC-o-AZ-NP.

photoisomerization and *cis*-to-*trans* thermal or light isomerization. They show the spectroscopic characteristics of donor-acceptor type azo-chromophores (i.e., pseudo-stilbene type chromophores), in which the high-intensity $\pi - \pi^*$ absorption band appears at long wavelength in a visible region. The UV-Vis spectra of the PVC-AZ-An and PVC-o-AZ-NP in THF solution are shown in Figure 8. The $\lambda_{\max}$ are strongly affected by the functional groups of azobenzene units due to their inductive conjugative effect on both the ground and excited states. The $\lambda_{\max}$ values of PVC-AZ-An and PVC-o-AZ-NP in THF solution are 389 nm and 441 nm, respectively. The $\pi - \pi^*$ absorption band of PVC-o-AZ-NP shifts to longer wavelength (red-shifted) due to the influence of auxochrome (-Cl) compared to the $\pi - \pi^*$ absorption band of PVC-AZ-An.

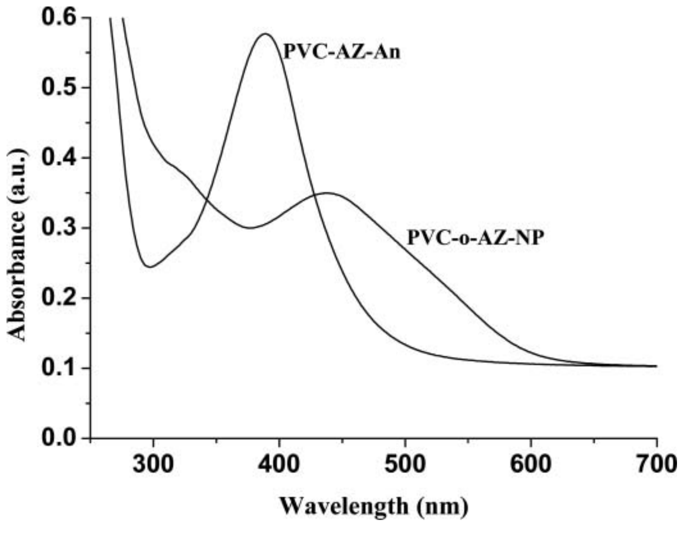

Fig. 8. UV-Vis spectra of PVC-AZ-An, PVC-o-AZ-NP in THF solution.

4 Conclusions

Two novel PVC-based polymers functionalized with azo-chromophores have been designed and prepared by the azo-coupling method using precursors, which were synthesized chemically by reacting PVC with sodium aniline (o-chloroaniline) salt. More photoresponsive polymers containing azo-chromophores as side-groups are expected to be prepared via the versatile strategy developed here by extending to other polymers.

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