e-Polymers **2006**, no. 063 http://www.e-polymers.org
ISSN 1618-7229

Preparation and characterization of post-derivatives from functional polystyrene (ATRP) with p-nitroaniline-azomethine phenol and their thermal and optical study

Xifei Yu,[a,b] Guo Zhang,[b] Tongfei Shi,[a] P.K.Dutta,[a#] Lijia An[a]*

[a] State Key laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences (CAS), Jilin Province , Changchun 130022, P.R.China. Email: ljan@ciac.jl.cn
[b] College of Chemistry, Ministry of Education Key Laboratory of Atutomobile Materials, Jilin University, Changchun 130023, P.R. China.
[#*] CAS-TWAS Visiting Fellow, Department of Chemistry, M.N.National Institute of Technology, Allahabad-211 004, India. Email: pkd_437@yahoo.com.

(Received: 11 February, 2006; published: 13 September, 2006)

Abstract: The functional polystyrene, $(Cl\text{-}PS)_2\text{-}CHCOOCH_2CH_2OH$ (designated as XPSt and coded P2) was prepared by ATRP at 130^0C using CuCl and bipyridine as catalysts, 2,2-dichloro acetate-ethylene glycol (DCAG) as multifunctional initiator and THF as solvent. 4-Nitoroaniline azomethine-4' phenol (P1) as chromophores were covalently linked to the functional end groups of the polymer by using simple displacement reaction. The functional polystyrenes, namely XPSt (P2) and $(PS)_2\text{-}CHCOOCH_2CH_2OH$, designated as X^-PSt and coded P3 and their post-derivatives, namely, DXPSt (P4) and DX^-PSt (P5) respectively were characterized by IR, NMR and UV spectroscopies, gel permeation chromatography (GPC) and thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), polarising optical microscopy (POM) and XRD studies. DSC showed that incorporation of chromophores in the side chains of polymers towards the polystyrene moiety increases the rigidity of the polymer and subsequently, its glass transition temperature; however the incorporation of side chain towards the alcoholic functional group decreases the glass transition temperature. The post derivatives do not play any significant role to increase the thermal stability (TGA). There was evidence for liquid crystalline properties in the resulting polymer derivative DXPSt (P4) as observed from POM study, which defines the alignment of chromophores into the polymers. The XRD study shows crystalline behaviour of the polymer derivative, P4. The polymer derivative, DX^-PSt (P5) does not show such behaviour and this may be due to the bonding of azomethine towards the short chain alcoholic telechelic alcoholic sides of the copolymer.
Key words: Functional polystyrene, ATRP, post-derivatives, azo-methine, optical, thermal study.

Introduction

Polymers containing an azobenzene moiety in the side chain have been the most significant area of investigations over the past decade due to their potential utilities in information storage, optical memory, wave-guide switch and so many other fields of applications.[1-4] In recent years, attention on synthesis of the block copolymers with azobenzene moieties has been increasing. The groups of researchers have already reported the block copolymers with liquid crystalline azobenzene side-chain by different polymerization methods [5]. Since the pioneering work of Matyjaszewski [6]

and Sawamoto [7], this technique has been widely used to prepare polymers, co-polymers as well as star dendritic-polymers [8], functional polymers from a variety of new macroinitiators [10, 11] and metal catalysts [9]. However, the polymers containing azobenzene in the main chain or as side chain are rigid and difficult to process [12]. The contents of azobenzene in small quantities in copolymers of reasonable molecular weight may find multipurpose applications in industrial as well as biomedical fields of research like molecular devices for sensors, switchable and signal transducing, labeling effect in biomedical and pharmaceutical uses [4]. A new approach to well-defined homo copolymers with architectural control by living radical polymerization (ATRP) and thereafter incorporation of the azobenzene moiety as an end chain in the polymer may find good prospect. Moreover, the macroscopic material architectures are expected to implement exploiting new concepts in nanoscale architectural engineering. Multi-chromophore-containing dendrimers and dendronized polymers not only permit optimization of electro-optic activity but also of auxiliary properties including optical loss (both absorption and scattering), thermal and photochemical stability and processability [13].

Our group has recently reported several block copolymers of various functional sites by using ATRP and anionic polymerization [14]. The present study focused on azomethine benzene instead of azobenzene as end-side chains into the polymers because it has not been studied extensively as our knowledge. Furthermore, the compounds containing the azomethine groups (-CH=N-) are considered as Schiff bases. Among organic NLO molecules, the Schiff bases have been a special interest to many investigators because of their relatively large molecular hyperpolarizability β due to delocalization of the π-electronic clouds [15, 16]. In this paper, we report the use of ATRP method to synthesize the polystyrene with functional sites and their post-derivatizations with 4-nitoroaniline azomethine-4' phenol to obtain azomethine chromophores for thermal and optical study for nonlinear optical applications.

Results and Discussion

Preparation of azomethine, functional polystyrenes and its derivatives

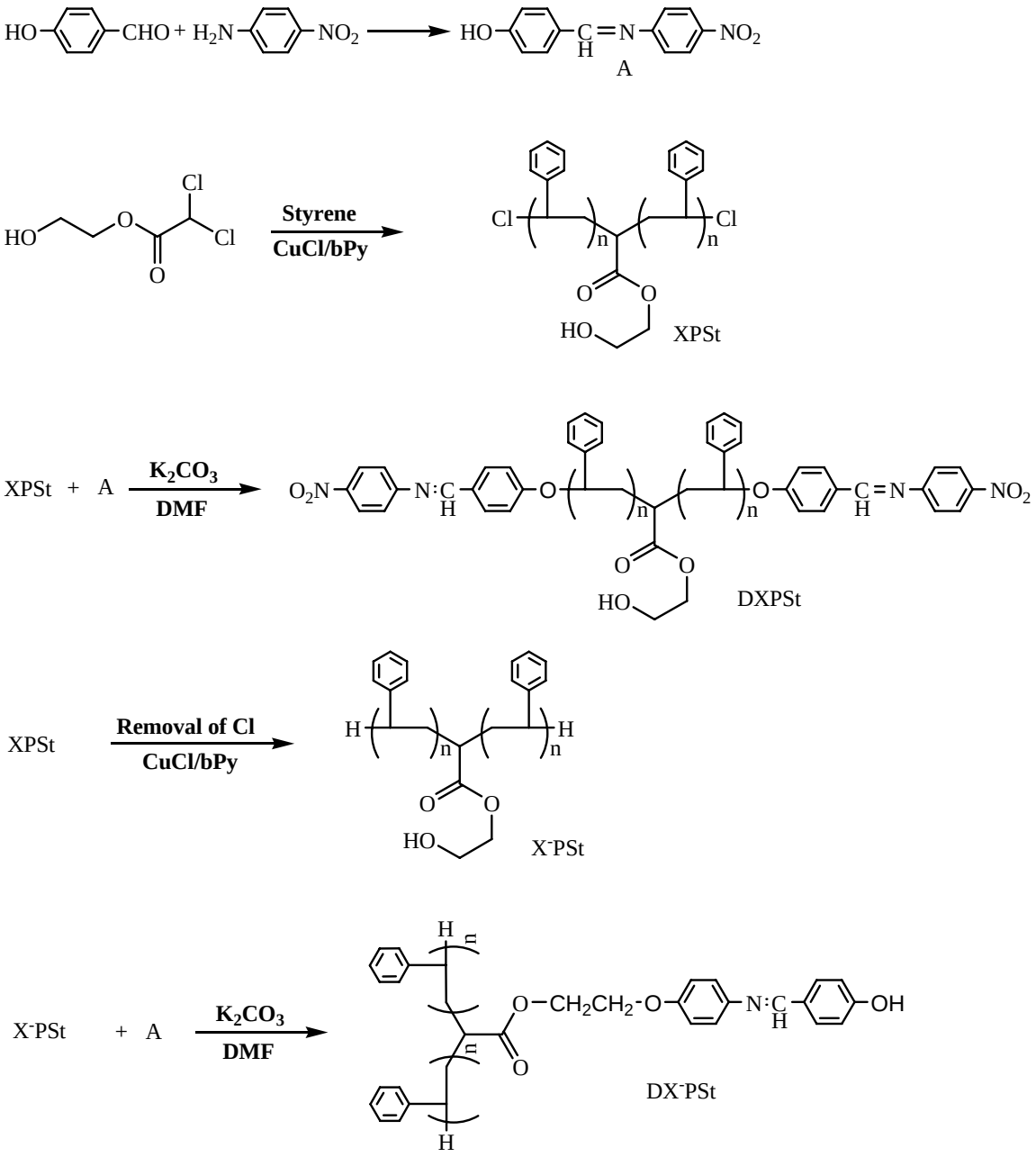
-Functional polystyrene: $(Cl\text{-}PS)_2$-$CHCOOCH_2CH_2OH$, XPSt (P2)

The ATRP was followed for the controlled polymerization of styrene using dichloroacetyl ethylene glycol (DCAG) as multifunctional initiator, CuCl and Bipy as catalyst system in THF [14]. Reaction of copper (I) with the chloro-based initiator generates the carbon-centered radicals and occurred as per the ATRP principle [6] and thus formed a short 2-branched polymer chain with a labile carbon-chlorine end group and the tail side - the telechelic alcoholic group.

Functional polystyrene: $(PS)_2$-$CHCOOCH_2CH_2OH$, *X^-PSt (P3)*

The removal of chloro group from functional polystyrene (XPSt) was made by ATRP. As per the understanding of the mechanism (Scheme 2) of ATRP and radical chain transfer reaction, iso-propylbenzene acted as chain transfer agent [17]. The abstraction of hydrogen atom from isopropylbenzene and its transfer into polystyrene chain radicals would result in the formation of polystyrene with stable end group and iso-propylbenzene radical as 1-chloro isopropylbenzene. Accordingly, in the ^{1}H-NMR spectrum of the chlorine free polystyrene X^-PSt, the apparent reduction in the intensity of the signal at chemical shift of 4.41-4.44 ppm corresponding to the

methane protons of the chloro end group proves that the labile carbon-chlorine bonds have been partially converted into much more stable carbon-hydrogen bonds. However, the trace peak appears at .473-4.75 [-CH (ph)Cl] indicates presence of small proportion of chloro-group in the polymer system.

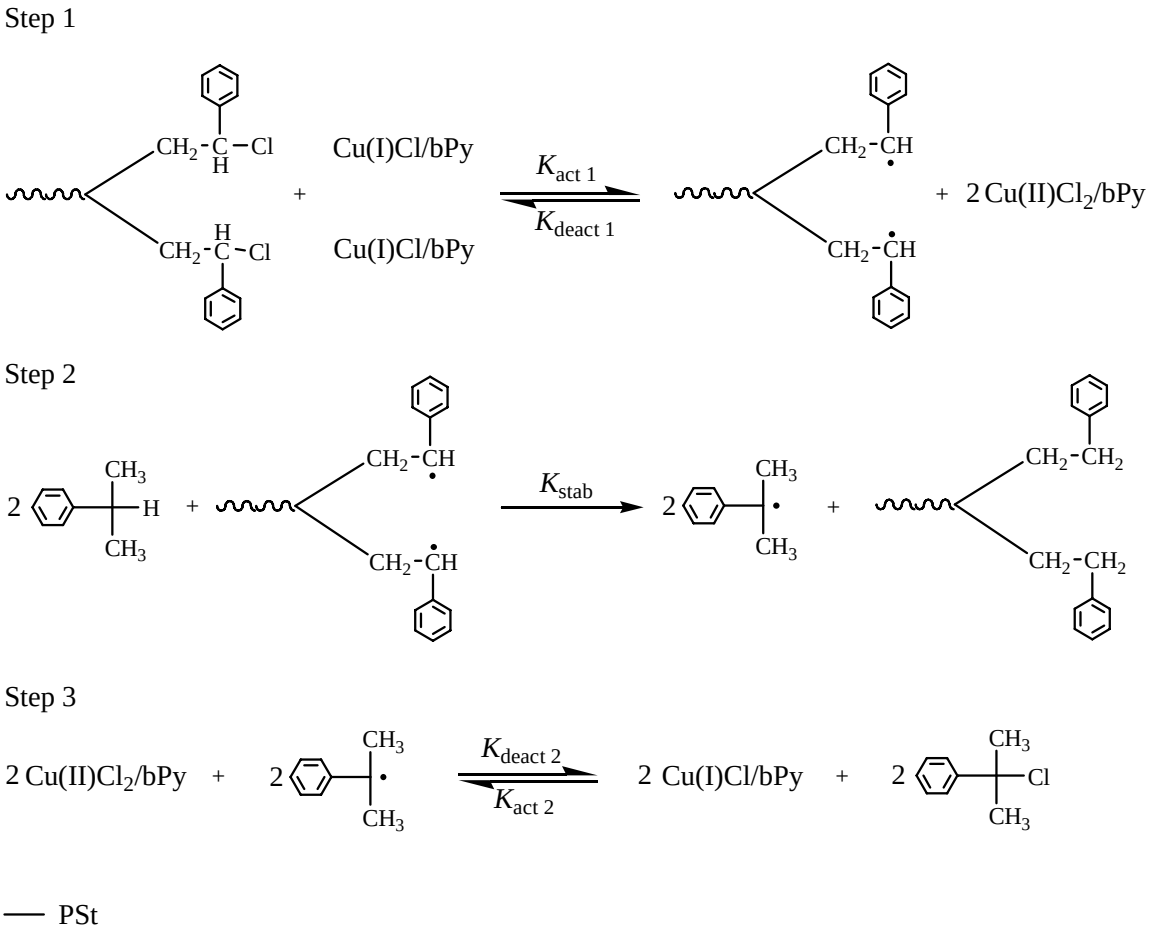


Scheme 1. Preparation of post-derivatives (DXPSt and DX$^-$PSt) (P4 and P5) from functional polystyrenes, namely, XPSt and X$^-$PSt with 4-nitroaniline azomethine-4' phenol.

Formation of C-O-C linkages in DXPSt (P4) and DX$^-$PSt (P5)

The oxygen in the nucleophile, being the kind of atom it is, donates a pair of its electrons to the C-Cl group of XPSt and C-NO_2 of azomethine respectively. Carbon can only share four pairs of electrons at once, so one pair has to go if it wants to take

the oxygen's pair. So it lets go of the electrons it has been sharing with chlorine (in case of XPSt) /nitro group (in case of azomethine), and sends the atom/groups of atoms on its way, expelling it from the molecule as KCl/KNO_2. The azomethine labels at the ends of the polymer (P4) and it is in the middle of polystyrene chains of polymer, P5 (Scheme 1). The synthetic strategy of those polymers (as described in experimental section) are different because of the attacking nature of respective nucleophiles, i.e., 4-nitoroaniline azomethine-4' phenoxy and telechelic oxy ions to C-Cl group of XPSt and C-NO_2 of azomethine are responsible for post derivatization of azomethine groups to the functional polystyrenes.



Scheme 2: Possible mechanism for chlorine free polystyrene.

UV Spectra

The electronic spectroscopy show the transition of both the polymer derivatives (P4 and P5) and 4-nitoroaniline azomethine-4' phenol at 363 nm (λ_{max}) which defines the $\pi \rightarrow \pi^*$ transition and the presence of chromophoric groups (Fig. 1). The chromophore containing compound dissolved in chlorinated solvents, alcohols and aliphatic ketones. All chromophores exhibit a strong absorption in UV range. Values of λ_{max} are in proximity for all polymers and the significant changes in absorption spectra of P4 and P5 were observed for different substituents with the reference to 4-Nitoroaniline azomethine-4' phenol (P1) as shown in Fig. 1. Utilizing experimental data it is possible to determine optimal working wavelength for the materials based on these chromophores. The basic theory of nonlinear- optical properties of π-

conjugated organic materials emphasizes that the conjugation length can enhance the electron delocalization in molecules and which are needed for large hyperpolarizabilities for non linear optical properties [18]. The post-derivatives of the polymers possess this kind of characteristics and further work towards the spectral changes of those polymers after UV-irradiation in this line is under progress.

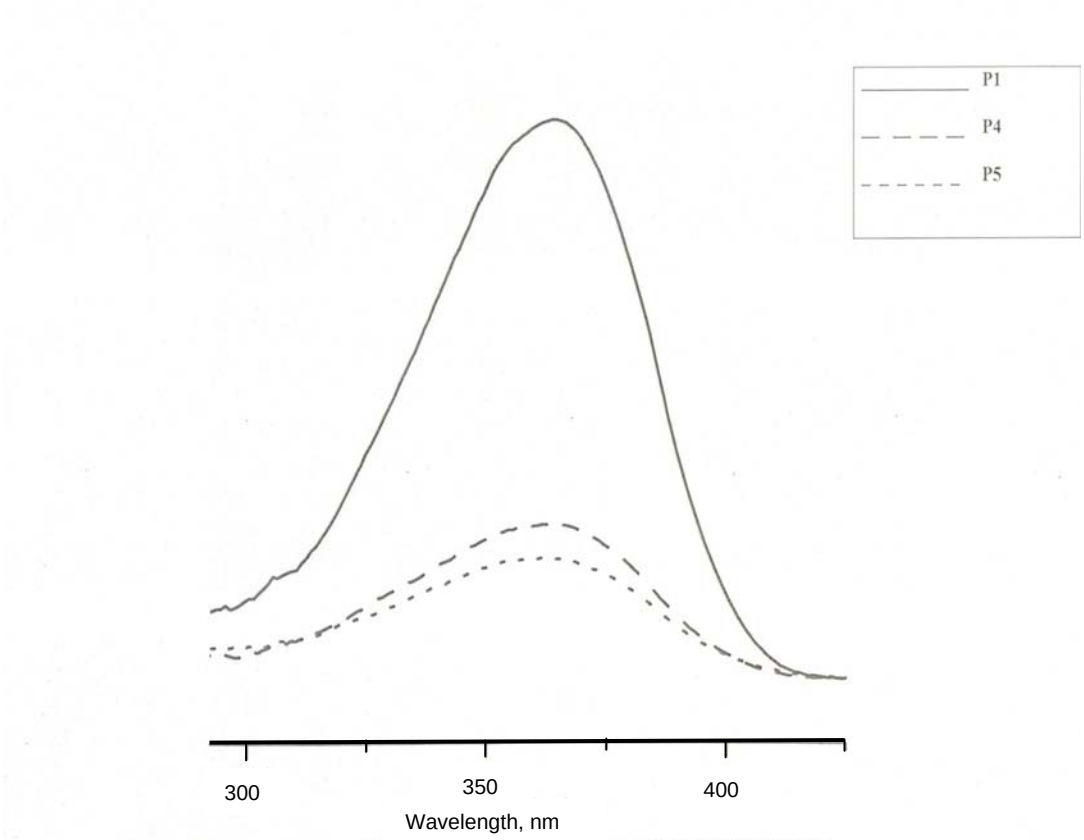


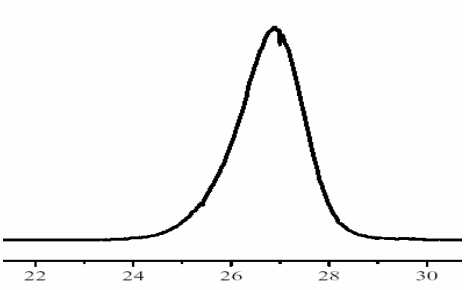
Fig. 1. UV Spectra of 4-nitroaniline azomethine-4'phenol (P1), DXPSt (P4) and DXPSt' (P5)

GPC

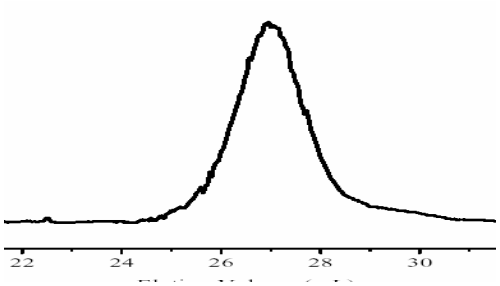
The number-average molecular weight of XPSt (P2) and X-PSt (P3) determined by GPC were 12400 and 9800 with polydispersity index of 1.15 and 1.18 respectively (Table 1). The obtained polymers have narrow dispersity index values and thus show controlled polymerization by ATRP. The number-average molecular weight of DXPSt (P4) and DX-PSt (P5) determined by GPC were 12700 and 10600 with polydispersity index of 1.15 and 1.19 respectively. There was no variation of polydispersity of the functional polymer and its respective derivative because the incorporation of side chains of the post derivatised polymers were almost uniform (Fig. 2).

Tab.1. Molecular weight of polymers from GPC.

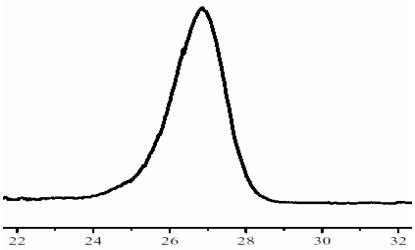
No.	Mw	Mn	Mw/Mn
P2	14200	12400	1.15
P3	11600	9800	1.18
P4	14600	12700	1.15
P5	12600	10600	1.19



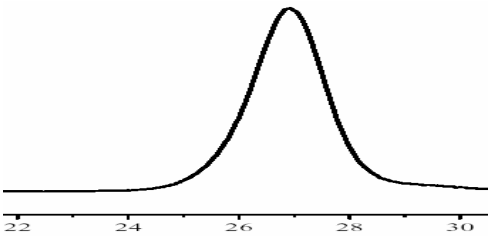
P2



P3



P4



P5

Fig. 2. GPC traces of Polymers.

TGA

TGA study of the polymers and their respective derivatives are shown in Table 2. It can be observed that side-chain azomethine copolymers exhibit lower thermal stability after post derivatization. The similar kind of observation was reported by Liu et. al [19] during post azo-coupling reaction of polyimides. This is because of the numbers of azomethine group in the polymer chains are less and their bonding in the polymer chains are also in different functional sites. Hence they cannot participate to the higher sides of the thermal stability. Obviously, the presence of chloro end group in XPSt would give the better thermal stability. However, from opto-electronic applications point of views, the presence of chloro as end groups is detrimental and not desirable.

Tab. 2. Thermal properties of Polymers and their Derivatives.

Polymer	T_g[a], ^{0}C	Degradation temperature[b] (^{0}C)				
		Initial loss	10% loss	20% loss	50% loss	Residue at 500^{0}C (%)
XPSt	90	250	350	375	400	2.00
X-PSt	87	240	345	375	400	0.00
DXPSt	120	162	240	325	380	8.00
DX-PSt	82	100	350	370	400	6.00

[a] Determined from DSC curves
[b] Determined from TGA curves

DSC

The functional polystyrene XPSt, possesses slightly higher T_g than X-PSt, this is because of the end chloro group enhances the steric-hindrence and bulkiness in the polymer moiety. Moreover, the introduction of azomethine group towards the chloro group further increases the bulkiness of the polymer moiety and hence enormous increase (of about 30^{0}C) of T_g. We get interesting result for DX-PSt. When the azomethine group is attached towards the alcoholic side, the T_g reduces a little bit than the X-PSt. This shows the attachment of azomethine towards the telechelic alcoholic group acts as alkyl spacer chain in the polymer backbone. The larger flexibility of the polymer may provide better processing and good aspects from applications point of views.

XRD

The X-ray diffraction (XRD) study shows that polymers, XPSt, X-PSt and DX-PSt are amorphous in nature; however, DXPSt shows highly crystalline behaviour in the span of 2θ from 10 to 30^0. This indicates the alignment of azomethine with –NO_2 group towards the polystyrene sides only (Table 3). The alignment of azomethine with –OH group towards the telechelic alcoholic sides was not found.

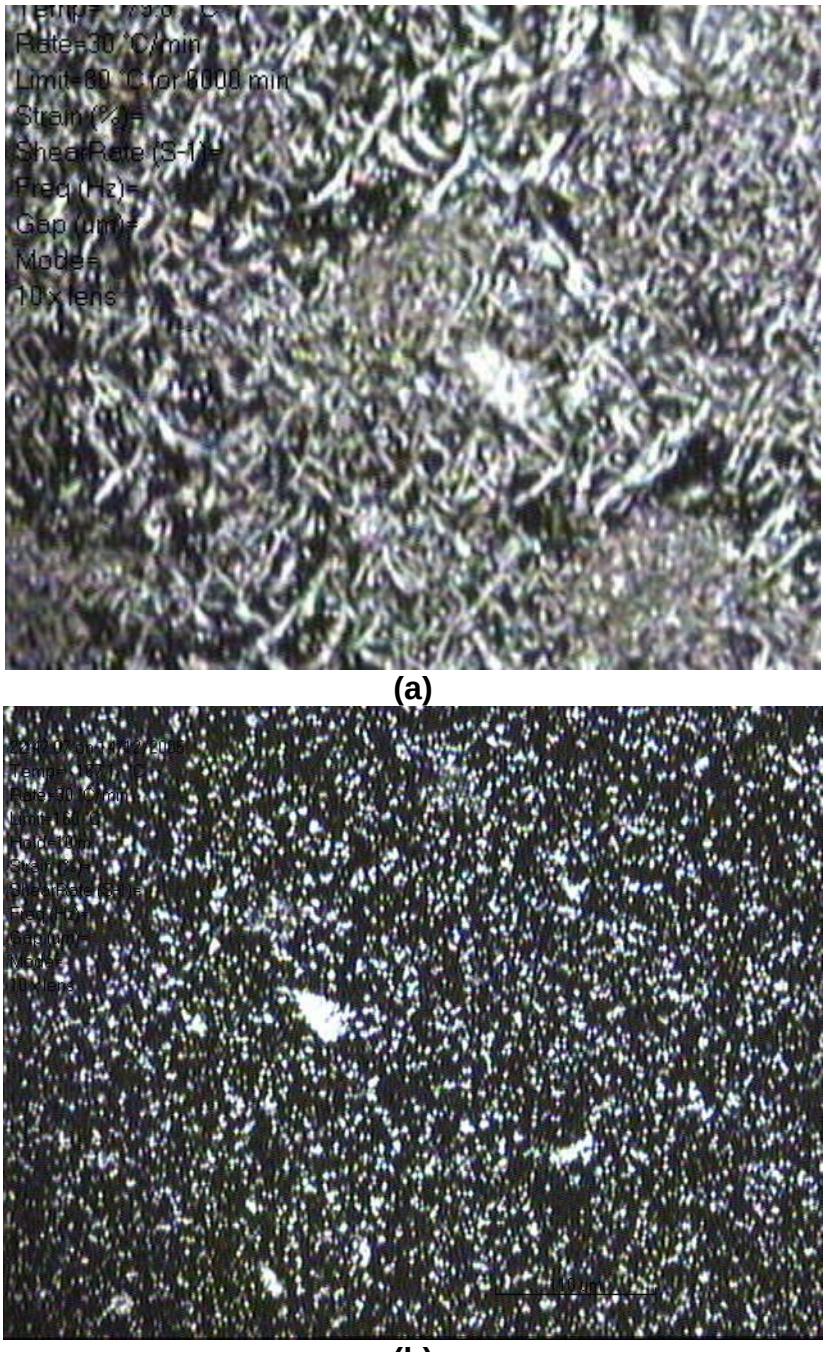
Tab. 3. XRD data of DXPSt.

2θ (degree)	d-value (Å)
12.32	7.18
14.26	6.21
16.24	5.45
17.84	4.97
19.18	4.62
23.10	3.85
25.46	3.50
28.32	3.15
29.34	3.04

The diffraction angles of the sharp peaks from 12 – 30 degrees were evaluated to be 7.18 – 3.04 Å. These values well correspond to an inter-chain distance between side chains [20].

POM

In order to reveal the thermal phase transition, investigation using polarizing optical microscope (POM) has been carried out for a range of 80–130 ^{0}C. Fig. 3 shows POM images of the polymer solid (P4) at 80 and 120 ^{0}C, respectively; they were taken under cross Nichols conditions. At 80 ^{0}C, the filament type (macroscopic level) arrangement was observed. After raising the temperature, the POM image became arranged (microscopic level) indicating that the side chain of polymer molecules can move above 120 ^{0}C to form a new solid phase where the polymer molecules form an aligned structure with a higher order of alignment.



(a)

(b)

Fig. 3. Polarizing Optical Micrograph of DXPSt at (a) 80^{0}C and (b) 120^{0}C.

Conclusions

Two novel chromophores, whose structures are shown in Scheme 1, have been synthesized and characterized. Functional polystyrenes are linked through azomethine side chains with the reasonable molecular weight structure. They exhibit fairly good optical property. Physico-chemical data indicate that they are perfect candidates to synthesize moderate thermo-stable polymers, which would display nonlinear-optical properties for various applications.

Experimental Procedure

Materials

Styrene (Sanghai First Chemical Reagent Co.) was used after purification and distillation, CuCl and bipyridine (China Medicine Group Sanghai Chemical Reagent Co.) were used after proper purification. Multifunctional initiator was synthesized in our laboratory and detail is described elsewhere[14]. 4-Nitroaniline and 4-hydroxy benzaldehyde (Sanghai First Chemical Reagent Co.) were re-crystallized in ethanol. K_2CO_3 anhydrous (Sanghai First Chemical Reagent Co.) and isopropylbenzene (Sanghai First Chemical Reagent Co.) were used as received. THF and DMF were distilled and stored properly. Ethanol absolute glacial acetic acid and dichloromethane (Sanghai First Chemical Reagent Co.) were used as received.

Measurements

^{1}H-NMR spectra were recorded on a Bruker AV-600, 400 MHz NMR-spectrometer in chloroform-d solution with TMS as internal standard. IR spectra were taken on a Perkin Elmer spectrometer. A Milton Roy Spectronic Genesis 5 UV spectrophotometer was used to record the UV spectral data.TGA was carried out in Universal V2.6D TA Instruments and DSC was performed in a Perkin Elmer Pyris DSC7 at heating rate of 10 ^{0}C/min under argon.Gel permeation chromatography (GPC) analysis was carried out on Waters GPC PL-GPC220 equipped with 3 PL gel 10 μm mixed columns and Walters RI detector at 30 ^{0}C which was calibrated with PL EasiCal PS-1 standards. THF was used as the eluent at a flow rate of 1.0 ml/min. The data were calculated by the PL Caliber GPC Software. XRD of the polymer samples was recorded on Phillips PW 1729 diffractometer using CuKα radiation. Polarizing optical microscopy (POM) was carried out with an Olympus Polarizing microscope.

Preparation of functional polystyrene: $(Cl\text{-}PS)_2\text{-}CHCOOCH_2CH_2OH$, *(XPSt, P2)*

The functional polymer was prepared by using styrene as monomer, THF as solvent, CuCl and bipyridine as catalysts and DCAG as initiator at 130 ^{0}C by atom transfer radical polymerization (ATRP) following the method as described elsewhere [14]. The initiator consists of at the end two chloro groups and other end alcoholic –OH group hence, the prepared polymer contained chloro group in each end of the polymer and other side contained telechalie alcoholic –OH group. (IR: $\nu_{C=O}$,1760cm^{-1}; ν_{OH},3380cm^{-1} and $\nu_{C\text{-}O\text{-}C}$, 1260cm^{-1}, and 854-765, 839-779 cm^{-1} ($\nu_{C\text{-}Cl,}$ Ar-Cl) were observed.

^{1}NMR: 6.30-7.25 [ar.protons], 4.73-4.75 [-CH (ph)Cl], 4.41-4.44 [$-COOCH_2CH_2OH$], 3.65 [OCH_2CH_2OH], 1.31-1.98 [methylene and methane protons],1.02-1.08 [$-CCH(CH_2\text{-})_2$], 0.953-0.954 [$-OOCCH(CH_2CH(ph)\text{-})_2$].

Removal of chloro group from functional polystyrene: $(PS)_2$-$CHCOOCH_2CH_2OH$ *(X-PSt, P3)*

$(Cl\text{-}PS)_2$-$CHCOOCH_2CH_2OH$, CuCl, bipyridine, isopropylbenzene,THF (1/6/18/100/50) was taken into a 20 ml polymerization tube and it was degassed oxygen by three or more freeze-vacuum –thaw cycles. The tube was sealed under vacuum and followed the same procedure and purification method as described for XPSt. (IR: $\nu_{C=O}$,1760cm^{-1}; ν_{OH},3380cm^{-1} and $\nu_{C\text{-}O\text{-}C}$, 1260$cm^{-1}$, 839-779 cm^{-1} ($\nu_{C\text{-}Cl,}$ Ar-Cl)**,** NMR: 6.30-7.25 [ar.protons], 4.41-4.44 [-$COOCH_2CH_2OH$], 3.65 [OCH_2CH_2OH], 1.31-1.98[methylene and methane protons],1.02-1.08[-$CCH(CH_2\text{-})_2$], 0.953-0.954 [-$OOCCH(CH_2CH(ph)\text{-})_2$]. The peak intensity at 4.73-4.75 [-CH (ph)Cl] was present in minor intensities.

Preparation of 4-nitoroaniline azomethine-4' phenol (P1)

2.76 g (0.02 mol) 4-Nitroaniline and 2.44 g (0.02 mol) 4-hydroxy benzaldehyde were dissolved in 50 ml ethanol and 2 ml acetic acid was used as catalyst and refluxed for 24 h. After cooling, the solution was precipitated out in cold water, filtered and washed with hot water. The precipitate was dried under vacuum at 50^0C for 24 h. Yield: 52 %, The vibrational bands of the compound was observed in the 686-3695 cm^{-1}. The vibration bands with the wave numbers of 3076 cm^{-1} ($\nu_{C\text{-}H,}$ Ar-H), 1628, 1627 cm^{-1}($\nu_{C=N}$), 1597-1578, 1614-1578 cm^{-1} ($\nu_{C=C}$), 1513-1494, 1526-1501 cm^{-1} ($\nu_{NO2,}$ Ar-NO_2), and 1375-1342, 1349-1313 cm^{-1} ($\nu_{C\text{-}N,}$ Ar-N) were observed in the compound. The absorbing bands at frequencies 1628 and 1627 cm^{-1} for the compound assignable to the stretching of C=N bond confirm the values reported in the IR spectrum for substituted aromatic schiff base which possesses the azomethine group[16]. The NMR spectrum shows the azomethine group at 8.086 ppm.

Preparation of derivative from XPSt with 4-nitoroaniline azomethine-4' phenol (DXPSt, P4)

2 mmol 4-Nitoroaniline azomethine-4' phenol was dissolved in 20 ml DMF and excess K_2CO_3 (15 mmol) was added into the solution and heated about 100 ^{0}C for 2 h. The solution of XPSt (1 mmol) in DMF was added through dropping funnel and continued for 20 h in argon atmosphere. After cooling the solution was added in ice cold water, washed thoroughly with hot water and dried under vacuum at 50^0C for 24 h. Yield: 90%, (IR $\nu_{C=O}$,1760cm^{-1}; ν_{OH},3380cm^{-1} and $\nu_{C\text{-}O\text{-}C}$, 1260$cm^{-1}$were observed. NMR: 8.09 for azomethine group , 6.30-7.25 [ar.protons], 4.41-4.44 [-$COOCH_2CH_2OH$], 3.65 [OCH_2CH_2OH], 1.31-1.98[methylene and methane protons],1.02-1.08[-$CCH(CH_2\text{-})_2$], 0.953-0.954 [-$OOCCH(CH_2CH(ph)\text{-})_2$].

Preparation of derivative from X-PSt with 4-nitoroaniline azomethine-4' phenol (DX-PSt, P5)

0.5 mmol X-PSt was dissolved in 10 ml DMF and excess K_2CO_3 (0.4 mmol) was added into the solution and heated about 100 ^{0}C for 2 h. The solution of 4-nitoroaniline azomethine-4' phenol (0.5 mmol) in 10 ml DMF was added through dropping funnel and refluxed for 24 h in argon atmosphere. After cooling the solution was added in ice cold water, washed thoroughly with hot water and dried under vacuum at 50^0C for 24 h. Yield: 87% (IR $\nu_{C=O}$,1760cm^{-1}; ν_{OH},3380cm^{-1} and $\nu_{C\text{-}O\text{-}C}$, 1260$cm^{-1}$, 839-779 cm^{-1} ($\nu_{C\text{-}Cl,}$ Ar-Cl)

NMR: 8.02 azomethine group, 6.30-7.25 [ar.protons], 4.73-4.75 [-CH (ph)Cl], 3.65 [OCH_2CH_2OH], 1.31-1.98[methylene and methane protons],1.02-1.08 [ ))CCH(CH_2-)$_2$], 0.953-0.954 [-OOCCH(CH_2CH(ph)-)$_2$]. The peak intensity at 4.73-4.75 [-CH (ph)Cl] was present in minor intensities.

Acknowledgements

One of the authors (PKD) gratefully acknowledges the visiting scholar fellowship award-2004 provided by the Chinese Academy of Sciences (CAS) and Academy of Sciences for Developing World (TWAS) to Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun.

References

[1] Natansohn A.; Rochon P. C*hem.Rev.* **2000**, 102, 4139.
[2] Ikeda T. *J.Mater.Chem.***2003**, 13, 2037.
[3] Tong X.; Cui L.; Zhao Y. *Macromolecules* **2004**, 37, 3101.
[4] Cui L.; Zhao Y. *Macromolecules* **2003**, 36, 8246.
[5] Chen J.; Zhang H. L.; Wang X.;Wang X. *Polym.Bull.***2005**, 53, 223.
[6] (a) Wang J.S.; Matyjaszewski K. *J. Am. Chem. Soc.* **1995**, 117, 5614; (b) Matyjaszewski K.; Xia J. *Chem. Rev.* **2001,** 101, 2921.
[7] (a) Kato M.; Kamigaito M.; Sawamoto M.; Higashimura T. *Macromolecules* **1995,** 28, 1721; (b) Ando T.; Kato M.; Kamigaito M.; Sawamoto M. *Macromolecules* **1996,** 29, 1070.
[8] Heise A.; Hedrick J.L.; Trollsas M.; Miller R.D.; Frank C.W. *Macromolecules* **1999**, 32, 231.
[9] (a) Viau L.; Even M.; Maury O.; Haddleton D.M.; Bozec H.L. *C. R. Chimie* **2005**, 8,12987; (b) Peter K.; Thelakkat M. *Macromolecules* **2003**, 36,1779.
[10] (a) Edmondson S.; Vicky L.; Borne O.S.; Huck W.T. *Chem.Soc.Rev.* **2004**, 33,14; (b) Lecolley F.; Waterson C.; Carmichael A.J.; Mantovani G.; Harrisson S.; Chappel H.; Limer A.; William P.; Ohno K.; Haddelton D. M. *J Mater Chem.* **2003**, 13, 2689.
[11] (a) Opsteen J.A.; van Hest C.M.J. *Chem. Commun*. **2005**, p.57; (b) Shemper B.S.; Mathias L. J. *Eur.Polym J.* **2004**, 40, 651.
[12] Dutta P.K.; Jain P.; Trivedi R.; Sen P.; Sen P.K.; Dutta J. *Eur.Polym.J.* **2003**, 39, 1007.
[13] Dalton L.R. *J.Phys.Condens Matter* **2003,** 15, 897.
[14] Yu X.; Shi T.; Zhang G.; An L.J. *Polymer*, **2006**, 47,1538.
[15] Lambert C.; Schmalzlin E.; Meerholz K.; Brauchle C. *Chem.Eur.J.* **1998**, 4, 512.
[16] Karakas A.; Elmali A.; Unver H.; Svoboda I. *Spectro Chim Acta Part A* **2005,** 61, 2979.
[17] Bibial J.; Jianbo F.; Yang Y.; Qiang R.; Wenyun W.; Jianjun H. *Eur.Polym.J.* **2005**, in press.
[18] Zadrozna I., Kaczorowska E. *Dyes and Pigments* **2006,** 71, 164.
[19] Liu Y-G, Sui , in J, Gao J, Zhu Z-K, Huang D-Y and Wang Z-G, *J.Appl.Polym.Sci*. **2000**, 76, 290
[20] Akagi K.; Oguma J.; Shibata S.;Toyoshima R.; Osaka I.; Shirakawa H. *Synthetic Metals* **1999,** 102, 1287.