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Synthesis, characterization, thermal and optical properties of styrene derivatives having pendant *p*-substituted benzylic ether groups

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Abstract The derivatives of styrene monomer, 4-chlorophenyl-4-vinylbenzyl ether (M1), 4-methoxyphenyl-4-vinylbenzyl ether (M2), 4-ethylphenyl-4-vinylbenzyl ether (M3) and 1-naphtylphenyl-4-vinylbenzyl ether (M4) were synthesized. The normal free radical polymerization of monomers in 1,4-dioxane were performed by using 2,2′-azobisisobutyronitrile as an initiator at 65 °C. The monomers and their homopolymers were characterized by FT-IR, NMR and elemental analyses measurements. The thermal stability of polymers was investigated by thermogravimetric and differential scanning calorimetric analysis. Thermal degradation activation energies of the polymers were calculated by the Ozawa and Kissinger methods. In addition, photo-stability tests of the polymers under near-UV irradiation were performed.

Keywords Styrene derivatives · Benzylic ether · Thermal properties · Activation energies · Photo-stability

Introduction

Styrene is widely used industrial monomer and its polymers are used in many different areas such as; plastics, latex paints and coatings, synthetic rubbers, polyesters and styrene alkyd coatings [1]. It is produced mainly by catalytic dehydrogenation of ethyl benzene and is used mainly for production of polystyrene (PST) and styrene copolymers. It is the second most widely used monomer for production of food-contact packaging polymers. Styrene and its derivatives are also polymerized via both cationic and radical routes and even with transition-metal complexes. It should be mentioned that living polymers of styrene and some of its derivatives can now be produced by living cationic and radical polymerizations progressed significantly in recent years.

4-Vinylbenzyl chloride (VBC), is one of the most important and interesting dual functional monomer. Due to presence of benzylic chlorine group in the structure, a great number of nucleophilic substitutions are made possible, leaving the double bond undamaged and providing new monomers that can be polymerized or copolymerized when the experimental conditions are well chosen [2, 3]. In addition, VBC can be easily polymerized or copolymerized with various initiators [4] and the obtained polymers are able to react with various nucleophilic reagents, giving fairly good yields in the process [5, 6].

A number of studies on thermal degradation kinetics of polymers have been investigated from thermogravimetric (TG) analysis and it is widely used as a method to investigate the thermal degradation of polymers and to determine the kinetic parameters [7, 8]. The Kissinger [9] and Ozawa's [10] methods are the most widely used methods for obtaining activation energy (Ea) values of polymers. The isoconversional methods require performing a series of experiments at different temperature programs and the yield values of effective activation energy as a function of conversion. More often than not, the activation energy is found to vary with the extent of conversion. The full potential of the isoconversional methods has been appreciated to Vyazovkin [11] brought analysis of the *E*a-dependences to the forefront and demonstrated that they can be used for exploring the mechanisms of processes and for predicting kinetics.

The general application areas of polymers are in outdoors and under sun light which includes ca. 5 % of near-UV radiation [12]. Therefore, it is important to synthesized

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photo-stabile polymers toward near-UV radiation. Moreover, photo-stability results could be used for determining application areas of polymers.

In the first part of this paper a synthetic approach, etheration of different alcohols with reactive VBC, was introduced and some general aspects of alcohol analogous reactions were discussed. Afterwards, the synthesis of the reactive prepolymers was described in more detail, followed by a number of examples for the preparation of PST's with simple polymers which be used in model studies and go step to step to more complex architectures with more than one functional group. Then the synthesized polymers were characterised and tested by thermal analysis and photo-stability experiments.

Experimental

Materials

4-Vinylbenzyl chloride, 4-methoxyphenol, 4-chlorophenol, 1-naphthol, 4-ethylphenol, 1,4-dioxane, potassium carbonate, acetonitrile and anhydrous magnesium sulphate were purchased from Sigma-Aldrich. 4-Vinylbenzyl chloride was purified from the inhibitor by distillation. 2,2′-Azobisisobutyronitrile was recrystallized from chloroform–methanol. All the other chemicals were analytical grade and used without any further purification.

The synthesis of monomers

A typical procedure for the etheration reaction of some alcohols with VBC was as follows: each alcohol and K_2CO_3 (1:1, mol:mol) were dissolved in 20 mL of anhydrous acetonitrile at 25 °C, and then VBC (1.1 mol) was added dropwise to the solution. The reaction mixture was stirred at 65 °C for 12 h. The organic layer was washed several times with diethyl ether and dried over $MgSO_4$. After removing diethyl ether, the monomers were crystallized by using ethanol (yields: ca. 80–85 %).

Polymerization of monomers

Appropriate amounts of each monomer, 1,4-dioxane and 2,2′-azobisisobutyronitrile (1 % of the weight of monomer) were placed in a reaction tube and purged with nitrogen for 10 min. The sealed tube was kept at 65 °C for 24 h. The reaction contents were poured dropwise into a large excess of ethanol. The polymers were purified by reprecipitation with ethanol from 1,4-dioxane solution and finally dried under vacuum (conversion is ca. 90 %).

Characterization techniques

Infrared spectra were measured by using a Perkin Elmer Spectrum BX FT-IR spectrometer. ^{1}H- and ^{13}C-NMR spectra were recorded in DMSO-d_6 with tetramethylsilane as the internal standard using on Bruker GmbH DPX-400 500 MHz spectrometer. Thermal data were obtained by using a Shimadzu DSC-60 instrument and TGA-60 thermobalance in nitrogen atmosphere. UV–Vis spectra were measured by Shimadzu UV 1700-Pharma spectrophotometer. Elemental analyses of polymers have been performed by using Vario EL III Elementar CHNOS Analyser.

Set-up and procedure of photo-stability experiments

A concentration of 85 mg L^{-1} in dimethyl formamide (DMF) of each polymer was prepared and used for photo-stability experiments. A quartz cuvette was used as a photo-reactor. The volume and thickness of the reactor were 3.5 mL and 1 cm, respectively. The irradiation source was 2 fluorescent black lamps (Philips, 8 W) which irradiate at 365 nm. The distances of between each lamp and from the lamp to the reactor were 2.0 and 4.5 cm, respectively. The radiation energy impinging on the sample had an average value of 2.5 mW cm^{-2}. It was measured at between 315 and 400 nm by using a radiometer (Delta Ohm, DO 9,721). The photo-stability experiments have been performed at room temperature, ca. 293 K. The results were followed by using UV–Vis measurements.

Results and discussion

As shown in Scheme 1, it was proposed a new route for styrene monomers having pendant ether moieties. The yields of the reactions in Scheme 1 are of medium quantity (80–85 %). The etheration reaction of VBC with various alcohols was also better examined using K_2CO_3 under the same conditions.

Structure characterization of the polymers

The FT-IR spectra of the monomer (M1) and its polymer (P1) are shown in Fig. 1. In the IR spectrum of P1 showed some characteristic absorption peaks at 1,600 cm^{-1} (C=C in aromatic ring) and 1,260 cm^{-1} (C–O–C). During the polymerization of the monomers, the IR band at 1,620 cm^{-1} (C=C) disappeared. The main evidence of polymer formation is certainly the disappearance of some characteristic signals of the double bond in the spectra and this fact was effectively observed in our case.

The ^{1}H- and ^{13}C-NMR spectra of P2 are shown in Fig. 2. From ^{1}H-NMR spectroscopy the formation of the

Scheme 1 Synthesis of monomers and their polymers

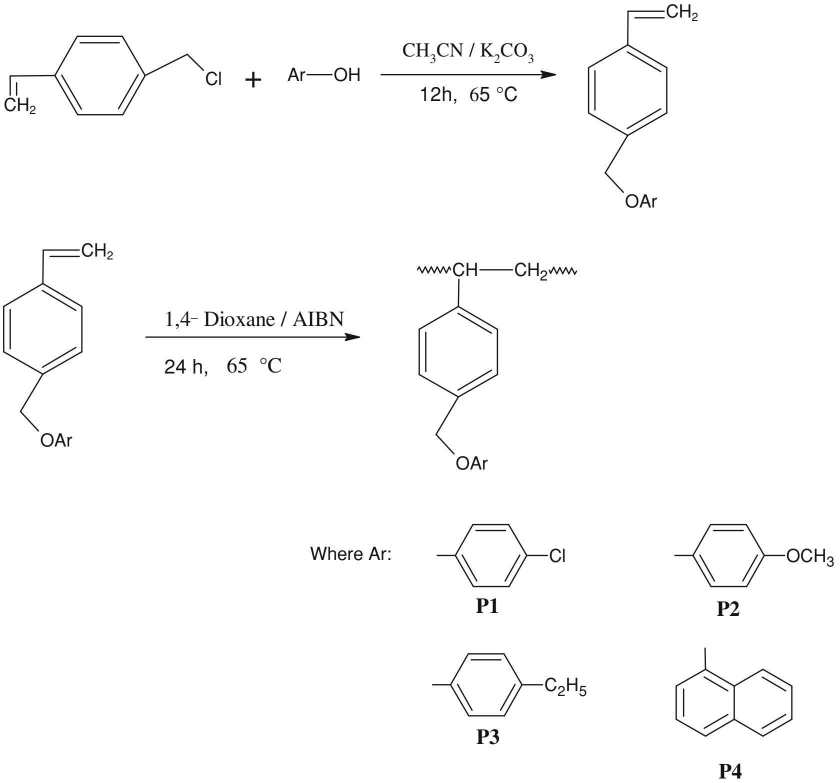
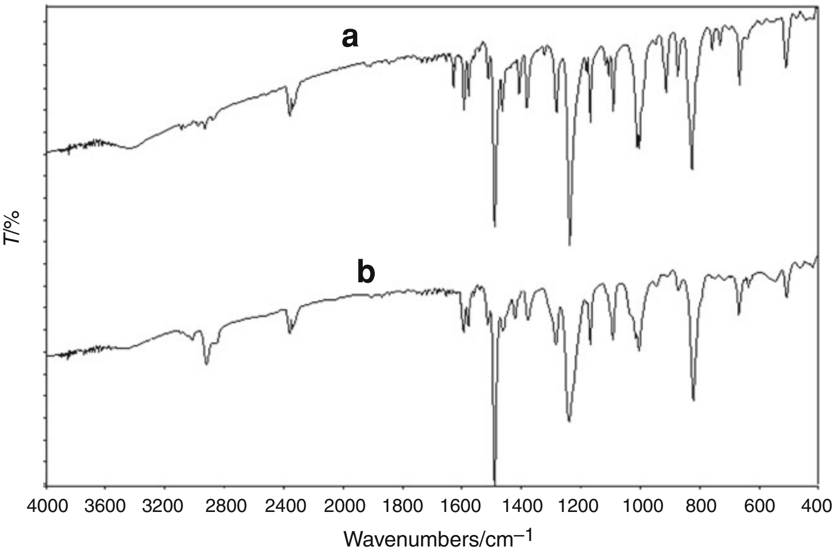


Fig. 1 FT-IR spectra of (*a*) M1 and (*b*) P1



polymer is also clearly evident from the vanishing of the two dublets at 5.24 and 5.65 ppm and one quartet at 6.72 of the vinyl protons and the appearance of the broad signals at 1.8 and 1.3 ppm assigned to an aliphatic –CH and $–CH_2$ groups. The signals of the aryl group are seen between 6.5 and 8.0 ppm. The methoxy protons appeared at 3.70 ppm. The peak at 4.9 ppm is attributed to the methyleneoxy protons. In the proton decoupled ^{13}C-NMR spectrum of P2, chemical shift assignments were made from the off-resonance decoupled spectra of the polymer. The signals due to carbons ($–CH_2–$ and –CH– in the polymeric chain) are observed at 40 and 42 ppm. The aromatic carbons are observed at 154.7–123.0 ppm. The methoxy carbons show signals at 63.0 ppm. The peak at 73 ppm is attributed to the methyleneoxy carbons. As summarized in Table 1, the structures of the obtained polymers were confirmed by IR,

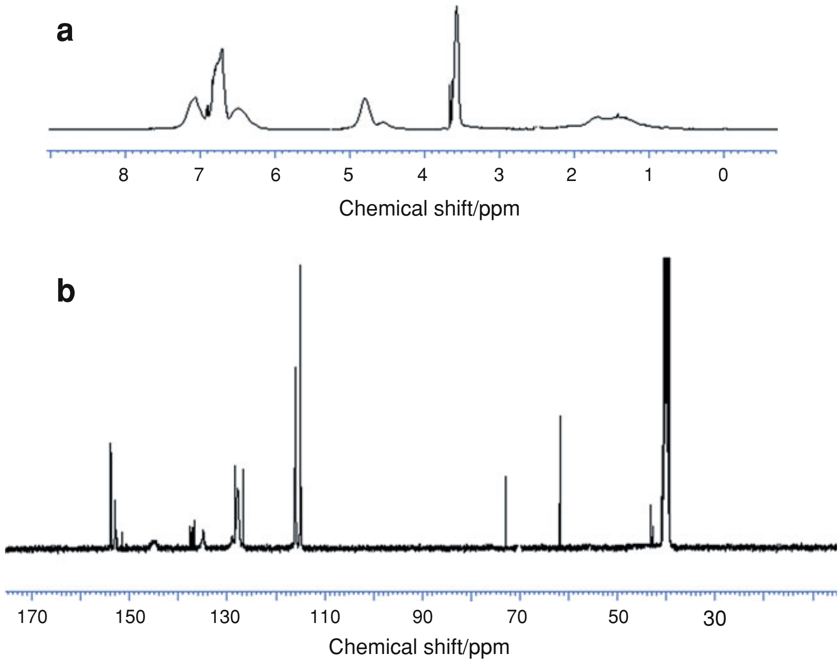


Fig. 2 (*a*) ^{1}H-NMR and (*b*) ^{13}C-NMR Spectra of P2

Table 1 FT-IR, ^{1}H-, ^{13}C-NMR spectral data and elemental analysis results of the polymers

Polymer	FT-IR spectral data (film/cm^{-1})	^{1}H-NMR spectral data (400 MHz, DMSO-d_6, TMS)	^{13}C-NMR spectral data (400 MHz, DMSO-d_6, TMS)	Elemental analysis results			
				C/%		H/%	
				Calc.	Found	Calc.	Found
P1	2960(CH), 3035(ArCH), 1600(ArC=C), 1250 (PhCH$_2$–O–Ph), 730(C–Cl).	δ/ppm: 1.7 (ArCH$_2$), 1.2(ArCH$_2$C$\underline{\text{H}}$), 4.8(ArOCH$_2$) 6.5–7.4 (Aromatic-H)	δ/ppm: 40, 42(CH$_2$– and CH– in the polymeric chain), 70 (ArOCH$_2$),110–135 (Aromatic-C), 158(C–Cl)	73.62	74.29	5.35	5.39
P2	2955(CH), 3070(ArCH), 1600(ArC=C), 1245 (PhCH$_2$–O–Ph and ArOCH$_3$).	δ/ppm: 1.7 (ArCH$_2$), 1.3(ArCH$_2$C$\underline{\text{H}}$), 4.9(ArOCH$_2$) 6.5–7.6 (Aromatic-H), 3.6(OCH$_3$)	δ/ppm: 41, 43(CH$_2$– and CH– in the polymeric chain), 71 (ArOCH$_2$),110–135 (Aromatic-C),158(ArOCH$_3$)	79.97	80.51	6.71	6.75
P3	2960(CH), 3065(ArCH), 1600(ArC=C), 1252 (PhCH$_2$–O–Ph).	δ/ppm: 0.8 and 1.2 (CH$_2$ and CH$_3$), 1.7 (ArCH$_2$), 1.2(ArCH$_2$C$\underline{\text{H}}$), 4.9(ArOCH$_2$) 6.5–7.4 (Aromatic-H)	δ/ppm: 18,23(CH$_3$ and CH$_2$), 40, 44(CH$_2$– and CH– in the polymeric chain), 73 (ArOCH$_2$),110–135 (Aromatic-C), 158(C–Cl)	85.68	86.62	7.61	7.67
P4	2962(CH), 3100(ArCH), 1600(ArC=C), 1250 (PhCH$_2$–O–Ph).	δ/ppm: 1.7 (ArCH$_2$), 1.2(ArCH$_2$C$\underline{\text{H}}$), 5.1(ArOCH$_2$) 6.5–8.2 (Aromatic-H)	δ/ppm: 42, 44(CH$_2$– and CH– in the polymeric chain), 71 (ArOCH$_2$),110–145 (Aromatic-C),	89.25	89.63	5.99	6.04

^{1}H- and ^{13}C-NMR spectra and elemental analyses results. All the other spectroscopic signals for the macromolecule appeared in a normal mode.

Solubility of the polymers

The solubility of the polymers was tested in various organic solvents at a concentration of 1 % (w/v). The new polymers are readily soluble in highly polar solvents such as DMF, EMK, DMSO, CH_2Cl_2 and 1,4-dioxane at room temperature or upon heating. The solubility of the resulting polymers is summarized in Table 2.

Physical parameters

Some physical parameters density, inherent viscosity (η_{inh}) and solubility parameter (δ) of the polymers were determined in the study. PST was used for comparison. The

Table 2 Solubility data of the resulting polymers

Solvent	P1	P2	P3	P4
DMF	++	++	++	++
DMSO	++	++	++	−
1,4-Dioxane	++	++	++	++
n-Hexane	−	−	−	−
Dichloromethane	++	++	++	++
Diethylether	−	−	−	−
Methanol	−	−	−	−
THF	++	++	++	++
EMK	++	++	++	+-
Acetonitrile	−	−+	−+	−
Ethanol	−	−	−	−

++, Soluble at room temperature; +−, swelling or party soluble at room temperature; −+, swelling or party soluble by heating; −, insoluble

Table 3 The physical parameters and glass transition temperatures of polymers

Polymer	d/g cm^{-3}	η_{inh}/dL g^{-1}	Δ/(cal cm^{-3})$^{1/2}$	*Tg*/°C
P1	1.12	0.67	10.52	64
P2	1.14	0.71	9.74	53
P3	1.13	0.70	10.05	56
P4	1.08	0.74	10.11	74
PST	1.05	0.71	9.35	105

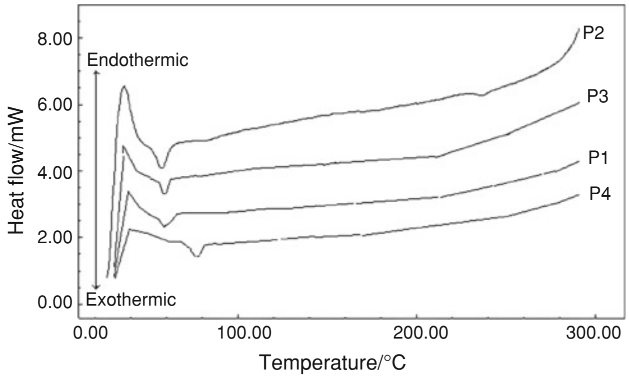


Fig. 3 DSC curves of the polymers

inherent viscosities of 1 % (w/v) solutions of the polymers in 1,4-dioxane were determined at 25 °C using an Ubbelohde viscometer. The densities of the polymers were determined experimentally by the flotation method at 25 °C using mixtures of methanol and formic acid as the floating agent, and many glass beads of known densities. The solubility parameters of the polymers were determined by using a titration method at 25 °C from a solubility test using CH_2Cl_2 as a solvent and n-hexane and ethanol as non-solvent. The results, shown in Table 3, inherent viscosity results of the synthesized polymers are similar to that of PST but their density and solubility results are a little higher than that of PST.

Thermal properties of the polymers

Tg's of the polymers

Tg is one of the most essential properties of polymers, dictating important features such as thermomechanical behavior and processing conditions. From differential scanning calorimetry measurements, the glass-transition temperatures were obtained as midpoints of the glass-transition region (see Fig. 3). The glass-transition temperatures of the polymers are listed in Table 3. It is to be expected, therefore, that the flexible benzylic ether functionality will cause a decrease in *Tg* compared to that of pure PST. As shown in Table 3, the *Tg* of P4 was higher than that of other synthesized polymers. This effect might be attributable to bulky substituent groups; a polymer bearing bulky side groups generally has a high glass transition temperature, because for such a chain the moving segment is necessarily large [13]. On the other hand, a polymer that has high attraction forces between the chains will expand less readily than a noninteracting polymers, therefore such an interacting polymer must be heated to a higher temperature before the free volume becomes as large as required at the glass transition temperature. The glass-transition temperature of P4 is considerably higher than that of the others, because the bulky naphthyl side group apparently decreases the flexibility of the chain and the free volume more than the other side group.

Thermal stability of the polymers

The thermal stabilities of the polymers were investigated by TG in a nitrogen stream at a heating rate of 20 °C min^{-1}. In Fig. 4, TG curves of the polymers are shown. While P1 and P4 have nearly the same initial decomposition temperature (ca. 315 °C), P2 decomposes relatively lower (ca. 305 °C). P3 is more stable than that of other polymers and decompose at ca. 320 °C. The reason why the new polymers are less stable than PST (325 °C) is due to in the presence of benzyl ether group in PST structure. The residues of synthesized polymers obtained at 500 °C are very interestingly much higher than PST. It is 28 % for P2, 25 % for P3, and 40 % for P1 and P4, but it is only % 2 for PST.

The degradation of all synthesized polymers occurred at two stages. The first stage was observed at about a temperature range of 309–380 °C, while the second stage decomposition commenced at that of 408-484 °C. Pure

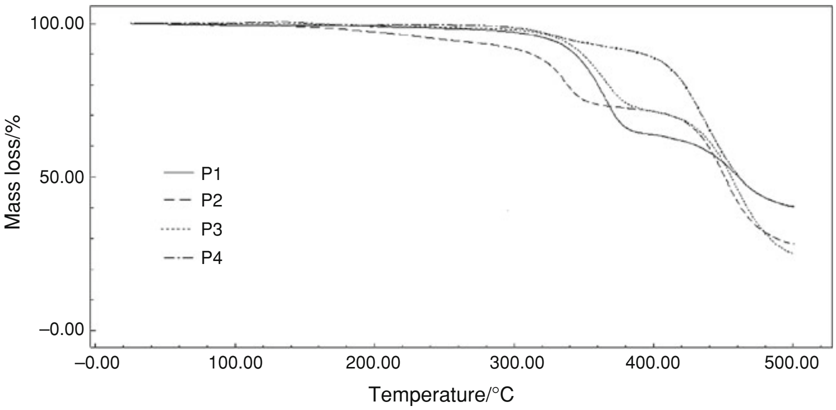


Fig. 4 TG curves of the polymers heated in nitrogen atmosphere at a heating rate of 20 °C min^{-1}

Table 4 Some TG results of the polymers

Polymer	IDT	Temperature for a mass loss/°C			Residue at 500 °C/%
		20 %	50 %	70 %	
P1	314	360	460	–	40
P2	315	338	451	490	28
P3	319	367	455	483	25
P4	305	422	460	–	40
PST	325	380	400	450	2

IDT initial decomposition temperature/°C

PST is more stable than new polymers, since new polymers have flexible side group as benzylic ether in the structure. This group is can be transformed at lower temperatures into stable benzylic intermediate products. This accelerates degradation of new PST derivatives.

Some of the degradation characteristics are summarized in Table 4. The results show that main-chain scission is an important reaction in the degradation of polymers, at least in the beginning. PST is a polymer which undergoes depolymerization to afford the monomer by pyrolysis. Numerous studies of the thermal degradation of PST have been reported and the predominant mechanism is accepted to be that of random chain scission followed by intermolecular transfer, with smaller amounts of unzipping and intramolecular transfer. Complete volatilization is usual and, depending upon precise conditions, monomer yield may be up to 40 %, with the balance made up mostly of dimer and trimer. McNeill et al. [14], McNeill [15] and Shapi and Hesso [16], give useful details of degradation products for various sets of conditions.

Thermal decomposition kinetics

The activation energies on the thermal decomposition of polymers were determined by thermogravimetric analysis. In the case of thermal degradation of polymers, in which depolymerization is competing with cyclization or crosslinking due to side groups, the TG at various heating rates is much more convenient than ITG for the investigation of thermal degradation kinetics. In this section, the degradation parameters of polymers are estimated by two methods. TG was used to investigate the activation energies. The thermal degradation expression results differ based on the different assumptions and derivatives, for example, bulk or powder, carrier gas, flow rate, would directly affect the results of parameters [17, 18]. The different analysis methods are described. These methods require several TG curves at different heating rates. Hence, the dynamic thermogravimetric analysis in nitrogen of the polymers has been performed at various heating rates 5, 10, 15 and 20 °C min^{-1}. Figure 5 shows the TG curves at the different heating rates of P2.

Using Kissinger's method and the experimental data recorded in the Fig. 5, the activation energy of the decomposition of polymers was calculated from a straight line fit of a plot of $\ln(\beta/T_{\mathrm{p}}^{2})$ versus $1{,}000/T_{\mathrm{p}}$. The value obtained from Fig. 6 for the activation energy of P3 was 186 kJ mol^{-1}. The Ea value of P1, P2 and P4 from Kissinger plots were obtained as 148, 139 and 152 kJ mol^{-1}. The Ea value of PST is 190 kJ mol^{-1} [19]. DTG curve of the P3 are shown in Fig. 7. From this information we can conclude that PST has higher activation energy than the new polymers. Thus, the new styrene polymer has low thermal resistance.

According to Hay and Kemmish [20], degradation in polymer with ether group is initiated by random homolytic scission of the ether bonds in the polymer chains, however there is conflicting evidence about which bond is more stable. The radicals produced abstract hydrogen from adjacent phenylene units, or terminate by combination to produce crosslinks. The products of the scission, if sufficiently mobile will volatilize. Cyclization to benzofuran derivatives can also occur.

The results of the Ozawa analysis are given in Fig. 8, which shows that the best fitting straight lines are nearly parallel, indicating a constant activation energy range of conversions analysed and confirming the validity of the approach used. Activation energies corresponding to the different conversions are listed in Table 5. *E*a calculated

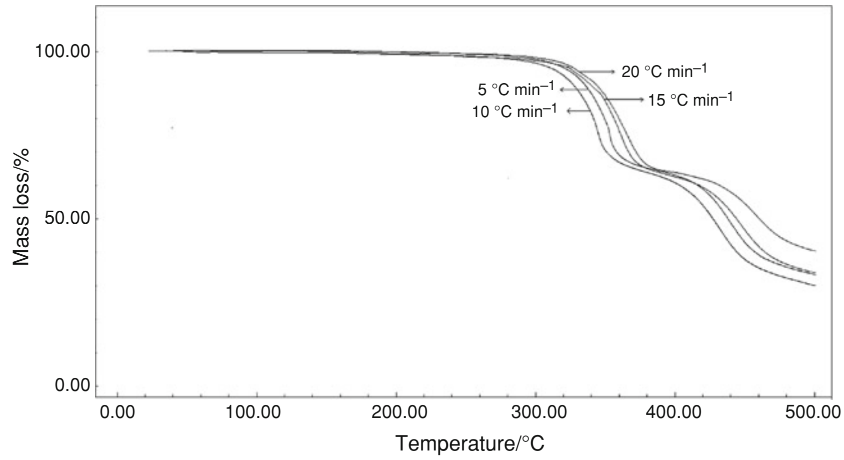


Fig. 5 Thermal degradation curves of P2 at different heating rates

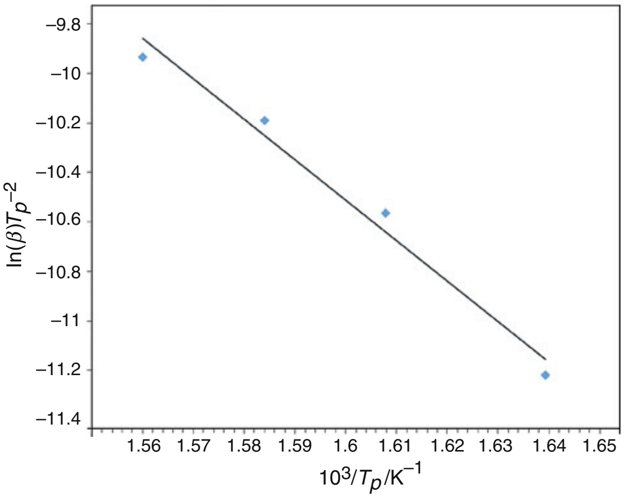


Fig. 6 Kissinger plot of P3 in nitrogen atmosphere

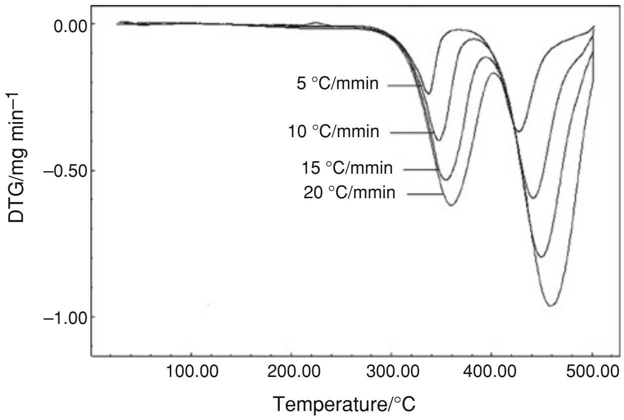


Fig. 7 DTG curves of P3 in nitrogen atmosphere

from the Ozawa method is superior to other methods for complex degradation, since it does not use the reaction order in the calculation of the decomposition activation energy. Therefore, *E*a calculated from the Ozawa method was superior to the former methods for complex degradation.

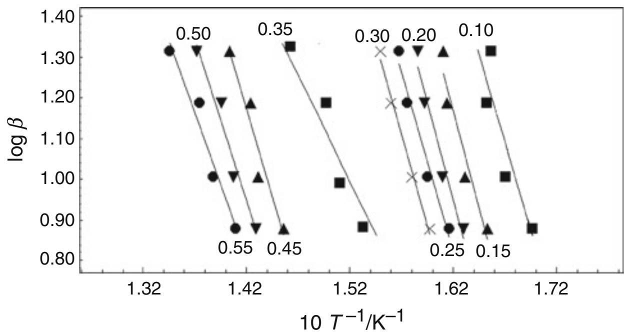


Fig. 8 Ozawa plots of the logarithm of the heating rate (log β) versus the reciprocal of the temperature ($1/T$) at different conversions for P4

Ultraviolet stability of the polymers

According to the UV–Vis spectra results of the polymers in DMF, the maximum wavelength of the peaks are 274, 282 and 289 nm for P1, 292 nm for P2, 278 and 285 nm for P3, and 283, 294 and 321 nm for P4.

After using 10 h near-UV irradiation, no significant decomposition (less than 1 %) of P1, P2 and P3 in DMF was observed. However, the results showed that P4 is not stable in the same experimental conditions and ca. 13 % photo-decomposition of P4 was observed by following λ_{max} values at 294 nm (see Fig. 9 a). Figure 9b gives photo-decomposition of P4 in DMF during irradiation time. The values were determined by using decreasing values of absorbance at 294 nm. This result could be explain by two different ways; (i) the probable decomposition product of P4 is naphthalene which is most stable intermediate (due to delocalisation) with respect to other probable main intermediates of the other polymers which are chlorobenzene, methoxybenzene and ethylbenzene, therefore it could be removed very easily, (ii) only P4 has an significant absorbance value at 365 nm, ca. 0.238. Due to the experiments have been performed in homogenous media and without using any catalyst, photodecomposition could be occur only if the substrate could absorb the irradiate

Table 5 The apparent activation energies of polymers for different mass loss percentage values under thermal degradation in N_2

Activation energy E_a/kJ mol^{-1}

Sample	10 %	15 %	20 %	25 %	30 %	40 %	45 %	50 %	55 %	Average
P1	164	170	168	150	160	138	133	128	148	151
P2	41	118	128	80	175	188	185	180	181	142
P3	157	161	157	149	276	230	207	195	184	191
P4	61	122	167	176	175	165	176	166	177	154

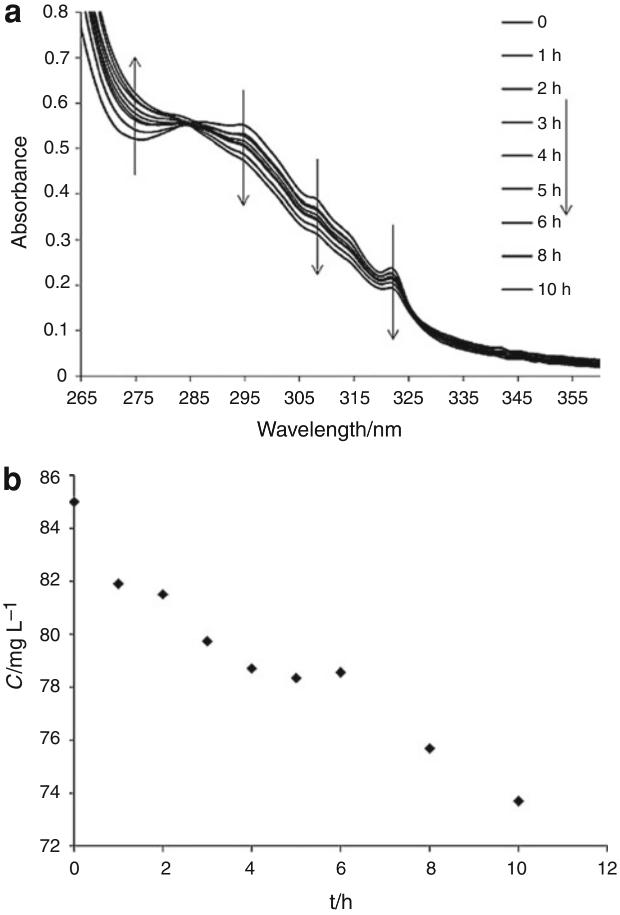


Fig. 9 a UV–Vis absorption spectra of P4 in DMF during the photolysis (λ = 365 nm) and **b** photo-decomposition of P4 in DMF during irradiation time. The values were determined by using decreasing values of absorbance at 294 nm

radiation, in the present case it was at 365 nm [21]. Isobestic point of P4 is at 284 nm. During the irradiation, the absorbance peaks at 283, 294 and 321 nm decreased, while the absorbance coming before isobestic point increased. This increase could be due to increasing amount of naphthalene which probable main intermediate product of P4. Indeed, the maximum peak absorbance of naphthalene is at 275 nm and at this wavelength the increasing was observed from photodegradation of P4.

Conclusions

The synthesis of new styrene monomers with pendant benzylic ethers groups has been reported for the first time. The structures of the monomer and polymer were characterized with spectroscopic methods. It was obtained that the thermal stability of new polymers was lower than that of PST. Glass transition temperatures of the polymers were much more less than PST. The activation energies of decomposition were calculated with the Ozawa and Kissinger method. Finally, it was observed that most the synthesized polymers are quite stable under near-UV irradiation.

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