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ORIGINAL PAPER

Synthesis, characterization and side chains crystallization of comb-like poly(*p*-*n*-alkylstyrene)s

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Abstract A series of comb like poly(*p*-*n*-alkylstyrene)s with linear alkyl groups, containing even numbers of carbon atoms from 12 up to 22 were synthesized by radical polymerization and characterized by FTIR, ^{1}H NMR, TGA, TVA DSC, and WAXS. All polymers were obtained in good yields and were soluble in organic solvents as chloroform, dichloromethane or tetrahydrofuran and insoluble in methanol; they are stable up to temperatures near 300 °C. On the other hand, the alkylic side chains of all series are able to crystallize in a paraffinic phase in which the melting temperature and enthalpy increase with the methylene number of the *n*-alkyl chain.

Keywords Poly(*p*-*n*-alkylstyrene)s · Side chains crystallization · Comb-like polymer · Polystyrene · Radical polymerization

Introduction

The first syntheses of *p*-*n*-alkylstyrenes were reported by Sulzsbacher in 1948 and were tried with the aim to obtain polystyrenes soluble in mineral oil [1]. These alkyl derivatives of styrene had no more than seven carbon atoms in the side chain. Later Overberger described the synthesis and polymerization of a series of *p*-*n*-alkylstyrenes derivatives with side chains up to 18 carbon atoms [2]. Since then, only a few works had been reported in this field, possibly because the process of

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synthesis of these monomers is long and laborious [2–4]. The synthesis of α-*n*-alkylstyrenes had also been reported and the short side chain derivatives are able to oligomerize [5, 6], whereas the long chain derivatives yield dimers with indanic structures when they are treated with $SnCl_4$ [4, 6]. On the other hand, *β*-*n*-alkylstyrenes derivatives are obtained as intermediaries in the syntheses of *p*-*n*-alkylstyrenes but not reports about its polymerization had been found [4].

Afterward of the works reported by Overberger [2], the more relevant studies in the polymerization of *p*-*n*-alkylstyrenes have been focused in the stereospecific synthesis of *p*-substituted polystyrenes using of metallocenic systems [3, 7–9].

In this work we reported on the synthesis and characterization of a series of poly(*p*-*n*-alkylstyrene)s with $n = 12, 14, 16, 18$, and 22. The characterization of the polymers has been performed by Infrared Spectroscopy (FTIR), Nuclear Magnetic Resonance (^{1}H-NMR and ^{13}C-NMR), thermo-gravimetric analysis (TGA), differential scanning calorimetry (DSC), thermal volatilization analysis (TVA) and wide angle X-ray scattering (WAXS). In this way, the ability of the side chain to crystallize was studied. These monomers and polymers will be referred henceforth as *n*AS and P*n*AS, respectively, where *n* is the number of carbon in the *n*-alkyl side chain.

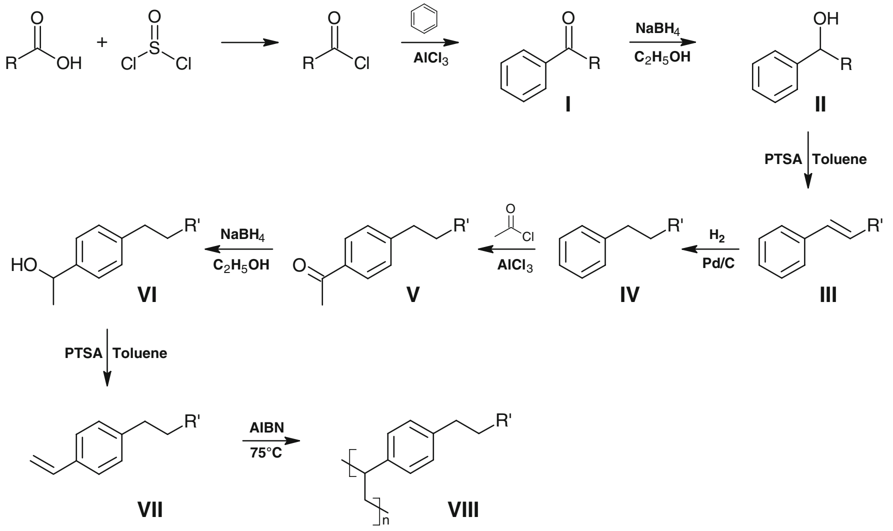
Experimental

Monomer synthesis

The synthesis of *p*-*n*-alkylstyrenes was carried on according to the Scheme 1, which is a modification of the methods previously reported by Overberger [2] and Quirk [3] and was discussed by us in a previous paper [4]. There *p*-subtituted styrenes with *n*-dodecyl, *n*-tetradecyl, *n*-hexadecyl, *n*-octadecyl and *n*-dococyl groups were obtained. The purity of compounds was confirmed by thin-layer chromatography (TLC). All monomers showed the same ^{1}H-NMR pattern, except by the difference in intensity of the signal that appears at 1.28 ppm due to the interior methylenes of the *n*-alkyl chain. A typical ^{1}H-NMR spectrum in $CDCl_3$ exhibit the following signals at δ (ppm): 7.28 (d, 2H, Ar–H (orto)), 7.17 (d, 2H, Ar–H (meta)), 6.71, (dd, 1H, $CH{=}CH_2$), 5.73 (d, 1H, $CH{=}CH_2$), 5.20 (d, 1H, $CH{=}CH_2$), 2.61 (t, 2H, $Ar{-}CH_2$), 1.58 (q, 2H, $Ar{-}CH_2{-}CH_2$), 1.28 (broad band, 2nH, $Ar{-}CH_2{-}CH_2{-}(CH_2)_n$), 0.88 (t, 3H, $(CH_2)_n{-}CH_3$). Main signals in the FTIR appear at ν (cm^{-1}) 3,030 (C–H stretching Ar), 2,925, 2,860 (C–H stretching), 1,629 (C=C), 1,511 (C=C Ar) 1,463 (C–H bending, CH_2), 723 (CH_2 *r*).

Polymerization

Poly(*p*-*n*-alkylstyrene)s were prepared by bulk polymerization of *n*AS at 75 °C during 48 h under nitrogen atmosphere using AIBN (1% mol/mol). The obtained polymers were purified by dissolution in chloroform and precipitation with methanol. The purification procedure was repeated several times.



Scheme 1 Whole synthesis process of poly(*p*-*n*-alkylstyrene)s. PTSA: *p*-toluensulfonic acid

Characterization

Infrared spectra were registered on a Perkin–Elmer 2000 System from KBr discs samples or films prepared by casting.

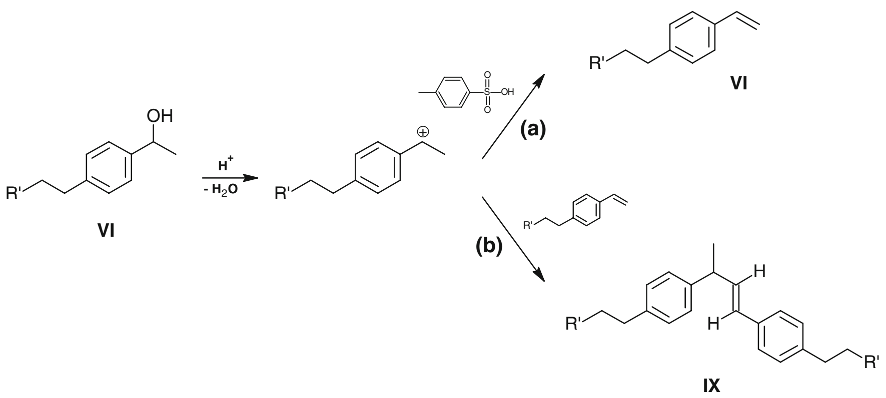
NMR spectra were recorded on a Bruker DRX 400 spectrometer at room temperature from samples dissolved in $CDCl_3$ using tetramethylsilane (TMS) as internal reference.

The GPC measurements were carried out with THF as the eluent using a Waters chromatograph, model 150CV, operated at 40 °C and equipped with three columns connected in series and packed with Ultrastyragel 10^3, 10^4 and 10^5. Calibration was carried out with polystyrene standards with a narrow molecular weight distribution.

Calorimetric measurements were performed with a Perkin–Elmer DSC-7 calibrated with indium. Samples of about 5 mg were heated or cooled at a rate of 10 °C min^{-1} under an ultra pure nitrogen atmosphere for temperatures ranging from –40 to 120 °C. Thermo-gravimetric analysis, TGA, were carried out on a Perkin–Elmer TGA-7 thermobalance with similar conditions as those used in DSC runs but within a temperature range of 25–550 °C.

Thermal volatilization analysis was carried out in a vacuum line heating the samples of about 100 mg from room temperature to 390 °C during 30 min under a moderate primary vacuum. Volatile fractions were condensed at room temperature and analyzed by IR and ^1H NMR.

Wide angle X-ray scattering experiments were performed in a Analytical X'Pert Pro automatic horizontal axis θ–θ diffractometer using Cu Kα–Ni filtered radiation. Spectra were taken at various temperatures in an Anton PAAR Variable Temperature Attachment from 25 to 70 °C with the scattering angle 2θ varying from 3 to 50°.



Scheme 2 Dehydration of *p*-alkylphenylcarbinol. **a** Under diluted condition, *n*AS is obtained. **b** Under concentrated condition, the carbocation formed from the alcohol is attacked by de *p*-*n*-alkylstyrene yielding the dimer

Results and discussion

The synthetic route used in the preparation of the *p*-*n*-alkylstyrenes (*n*AS) is shown in the Scheme 1 and the detail on the procedures may be found in Refs. [5, 10].

All the intermediaries were obtained with yields of 80% or more except for 1-(4-alkylphenyl)ethanones (VI in the scheme) which are obtained with a yield of 50–60%. The dehydration of *p*-alkylphenylcarbinol to yield the *p*-*n*-alkylstyrene must be carried on with a concentration of 1 g of alcohol in 50 ml of toluene. If the concentration is increased a dimer, (E-) 4,4′ (but-1-ene 1,3-diyl) bis (*n*-alkyl benzene) (IX) is obtained instead of the *n*AS, by means of a reaction shown in the Scheme 2.

In Fig. 1 is shown the ^{1}H-NMR spectrum of *p*-*n*-octadecylstyrene, and compared with those obtained for its dimer and polymer. As may be observed in the monomer spectrum (Fig. 1a), even under the experimental conditions described above, very small amounts of dimer were obtained together with the *n*AS.

All the polymers synthesized in this work were obtained in acceptable yields, P*12*AS and P*14*AS are sticky and transparent materials whereas P*16*AS, P*18*AS and P*22*As are yellowish hard pastes. All polymers are soluble in chloroform, dichloromethane and THF and insoluble in methanol. Both, FTIR and ^{1}H-NMR spectra are consistent with the expected structure. Some results obtained for P*n*AS series are summarized in Table 1 and compared with those obtained for polystyrene prepared in the same conditions.

As may be observed in Table 1, the weight average molecular weights was in the order of 2×10^5 Da and the molecular weight distribution is characteristic of a radical polymerization with a main disproportionation termination, which in this case seems logical due to the steric hindrance of the side chain.

As it can be seen in Fig. 1, the disappearance of the signals corresponding to the vinyl protons of the monomers at 5.20, 5.73, and 6.71 ppm in the ^{1}H-NMR spectrum of the polymers, together with the absence of the band at 1,630 cm^{-1} in

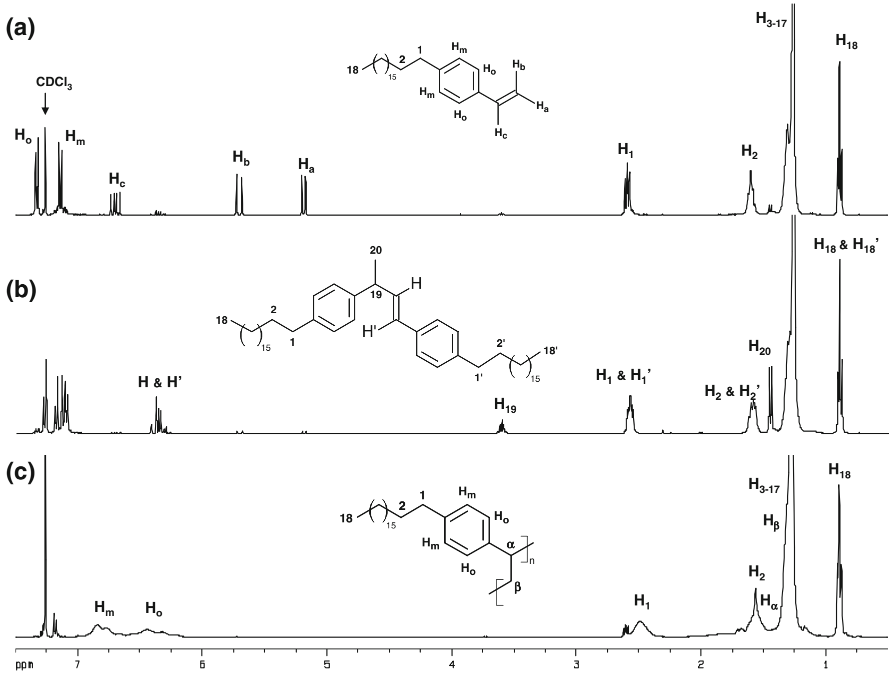


Fig. 1 ^{1}H NMR spectra in deuterated chloroform of **a** *p*-*n*-octadecylstyrene, **b** (E-) 4,4′ (but-1-ene 1,3-diyl) bis (*n*-octadecyl benzene) and **c** poly(*p*-*n*-octadecylstyrene)

Table 1 Results of the polymerization of *p*-*n*-alkylstyrenes[a]

Polymer[b]	Yield (%)	Mw[c] × 10^{-5} (Da)	Mn[c] × 10^{-5} (Da)	Mw/Mn[c]	*Td*[d] (°C)	Loss-weigth[e] (%)
PS	60	2.26	0.80	2.82	435	99.9
P*12*AS	51	2.02	1.04	1.95	465	95.3
P*14*AS	64	1.78	0.93	1.95	459	98.4
P*16*AS	65	ND	ND	ND	457	96.3
P*18*AS	69	2.80	1.06	2.65	464	93.3
P22AS	65	1.38	0.70	1.97	486	95.3

[a] At 75 °C during 48 under nitrogen atmosphere using AIBN (1% mol/mol)

[b] Most of the polymers contain small amounts of dimer with in most cases is <10%

[c] From GPC masured in THF at 40 °C

[d] Decomposition temperature corresponding to the maximum of the DTGA curve

the FTIR spectra (not shown) indicate that a vinyl polymerization process happened, thus confirming the GPC results. NMR spectra also indicate the presence in some samples of small quantities of dimers, which come from the monomers, and are not able to propagate during the polymerization process. These dimers are not easy to separate from the polymers because of their similar solubilities.

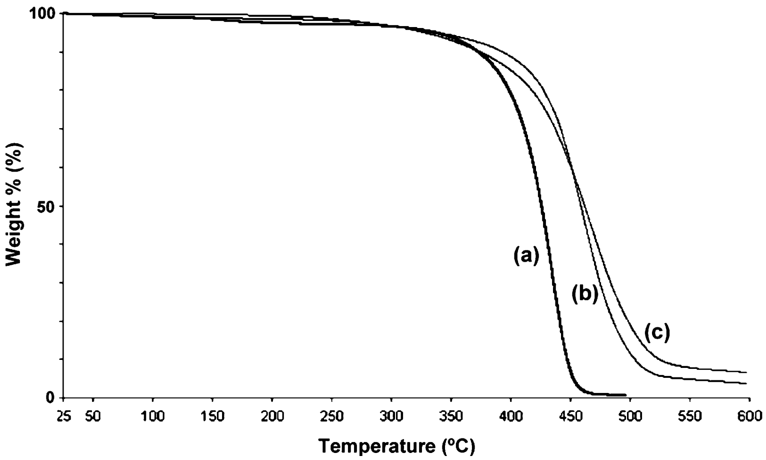


Fig. 2 TGA traces of *a* Polystyrene, *b* P*16*AS and *c* P*18*AS

Thermal properties

The thermal stability of the polymers was evaluated by TGA. In Fig. 2 TGA traces of P*16*AS and P*18*AS which may be considered as representative of the whole series, are shown together with that corresponding to PS synthesized under the same conditions. As it may be appreciated in the same Figure, the degradation process proceeds in one step and P*n*AS begins to lose weight up to 300 °C with a maximum decomposition above 455 °C, higher than in PS which begins to degrade at lower temperature. On the other hand, the analysis by TVA was carried out to examine the volatiles produced during the degradation process. The volatile fraction was examined by ^{1}H-NMR and IR and the spectra show appreciable quantities of *n*AS together with low molecular weight fractions of the polymer. These results indicate that the degradation process of the P*n*AS involved depolymerization as it occurs for PS and others *p*-subtituted polystyrenes [11, 12].

In order to determine if the *n*-alkyl side chains of the P*n*AS are able to crystallize, a DSC study was carried out. As it can be observed in Fig. 3, in the DSC heating scans recorded for all P*n*AS synthesized in this work an endothermic peak at temperatures located between –17 and 59 °C is present and attributed to the fusion of the paraffinic phase made of *n*-alkyl side chains. As illustrated in the insert of Fig. 3, these transitions are reversible on cooling and reheating. Also, the enthalpy involved in the fusion process increased with *n* as observed with the variation of the melting temperature, T_m. These values are summarized in Table 2.

As for others comb like polymer systems [13–15] the enthalpy associated with the melting process may be used to estimate the fraction of methylene units participating in the paraffinic crystalline phase using the following equation [16]:

$$\Delta H_m = \Delta H_{m(e)} + nk$$

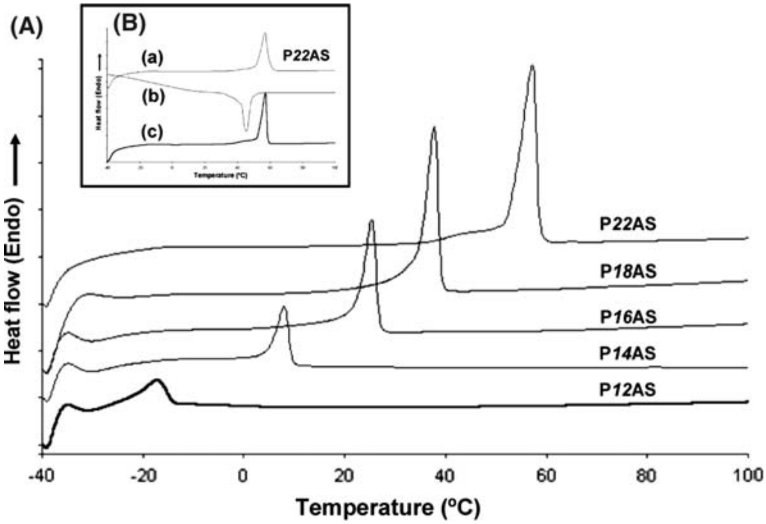


Fig. 3 **A** DSC heating scans at 10 °C/min for series of poly(*p*-*n*-alkylstyrene)s. **B** *Inset* poly(*p*-*n*-docosylstyrene) *a* first heating, *b* cooling, *c* second heating

Table 2 Melting transition calorimetric data for *p*-*n*-alkylstyrenes[a]

Polymer	T_m^b (°C)	ΔH (kJ/mol)	ΔS^c (J/mol K)	n_c^d
P*12*AS	–17	5.1	19.9	1.4/1.9
P*14*AS	6.9	8.7	31.2	2.4/2.9
P*16*AS	25	13.1	44.0	3.6/4.1
P*18*AS	38	20.8	66.9	5.6/6.3
P22AS	59	41.7	125.6	11.3/11.8

[a] Measured by DSC

[b] Peak melting temperature

[c] Entropy changes estimated by the expression $\Delta H/T_m$

[d] Number of crystallized methylenes calculated by using enthalpic and entropic values

where n is the number of methylene units and methyl terminal group in the alkyl chain, $\Delta H_{m(e)}$ is the contribution from the chain ends and k is the fusion enthalpy per mol of CH_2 unit.

When the measured fusion enthalpies (ΔH_m) were plotted versus n a linear correlation was found as can be seen in Fig. 4, and the approximate number of methylene units that are crystallized (n_c) can be estimated by using the equation:

$$n_c = \Delta H_m / k$$

From this plot a value of $n \approx 11$ resulted for $\Delta H = 0$ which roughly represents the minimum length required for the side chain to form a stable crystallization nucleus, above this length each additional methylene is able to crystallize as may be

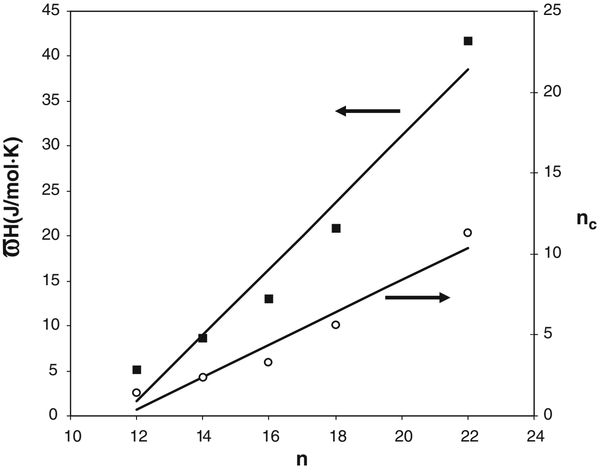


Fig. 4 Variation of enthalpy (*filled square*) and the number of crystallized CH_2 (*open circle*) versus *n* for P*n*AS

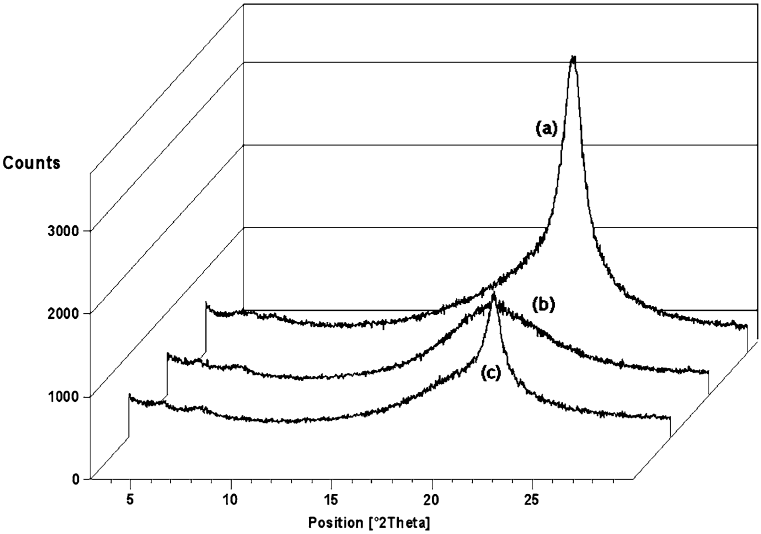


Fig. 5 Diffractograms of P*18*AS at different temperatures. *a* 25 °C, *b* 51 °C, *c* 25 °C after melted

observed in Table 2. Similar values are observed when values of ΔS are plotted instead of ΔH.

The crystallization of the side chain was confirmed by WAXS experiments carried out for P*14*AS, P*18*AS and P22AS. The diffractograms of these samples were recorded at various temperatures and they showed similar features: the sharp reflection, corresponding to an interplanar spacing of at 4.2 Å, characteristic of a crystalline paraffinic phase, exists at temperatures below the melting temperature determined by DSC. At higher temperatures this sharp reflection changes to a broad halo centered at 4.5 Å characteristic of the amorphous material thus indicating the fusion of the paraffinic crystalline structure. The crystalline order is partially recovered after cooling at temperatures below melting. These changes may be appreciated in Fig. 5 for P*18*AS. The intensity difference observed between curves (a) and (c) is attributed to the flattening of the initially powdered sample in the sample holder once the material has melted.

Conclusion

Poly(*p*-*n*-alkylstyrene)s are obtained via radical polymerization with relatively good yields and high molecular weights. These polymers regardless the length of the side chain begin to lose weight at temperatures near 300 °C and the whole degradation process, which involve depolymerization, occurs in one step. DSC and WAXS studies indicate that the side chains in P*n*AS are able to crystallize when they reach a minimum of eleven carbon atoms; from this value the melting temperature and enthalpy increase with the methylene number of the *n*-alkyl chain.

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