polymer

Poly(ether sulphone) copolymers with novel reactive chain-ends

V. Chisari[a], A. Mamo[a], A. Recca[a,*], V. Siracusa[a], J.T. Carter[b], P.T. McGrail[b]

[a]*Istituto Chimico, Facoltà di Ingegneria, Università di Catania, Viale A. Doria 6, 95125 Catania, Italy*
[b]*ICI Technology, PO Box 90, Wilton, Middlesbrough, Cleveland TS90 8JE, UK*

Abstract

This paper describes the synthesis of new model compounds and copolyether sulphones with different reactive chain-ends from the OH and NH_2 ends which are well documented for this type of polymer. These materials were characterised by ^1H NMR, Fourier transformed infrared (FTIR) spectroscopy and elemental analysis. They are seen to have potential applications both in the chain-extension of low molecular weight thermoplastics and in the preparation of well-defined block copolymers. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(ether sulphone); Poly(ether ether sulphone); Block copolymers

1. Introduction

Poly(ether sulphone)s (PESs) are commercially available, thermally stable polymers which are used in high performances applications such as engineering and composite matrices [1]. The key properties of these thermoplastics are their toughness and high temperature performance. For composite applications these amorphous polymers also have the advantage of being solvent soluble, so that they can be readily prepregged from low cost solvents. Unfortunately, this solvent solubility may also result in the composite parts having the propensity to retain solvent, leading to a lowering of T_g and to the formation of voids during moulding, and a lower resistance to aerospace fluids than is desirable [2]. This poor solvent resistance in-use may be improved by crosslinking the polymer through pendant or chain-terminating groups during fabrication of the composite part. The resulting moulding is then, obviously, not truly thermoplastic. Another approach to the environmental resistance problem, which retains the true thermoplastic nature of the polymer, is to prepreg a blend of a reactively terminated amorphous PES-type polymer with a semi-crystalline oligomer of another polyaromatic, which has complementary reactive end-groups, so that a block copolymer is formed in situ during the fabrication process. The semi-crystalline blocks will impart some solvent resistance to the fabricated part.

When used for engineering application the high temperature performance of PES-type polymers is highly desirable but, because of the polymer's high softening point and viscosity, it is necessary to use high temperatures and pressures in order to *injection or compression* mould them. One approach to reducing these temperature and pressure requirements is to use low molecular weight, low viscosity PES with reactive end groups which may be readily processed and then chain-extended to a high molecular weight species after fabrication.

PES-type polymers have been known since 1962 [3] and PES copolymers have developed for some applications [4]. The main features of their synthesis, properties and uses are well documented in the literature. Particularly for engineering applications, in order to ensure maximum thermal stability during processing and use, it has been desirable to manufacture polymers with thermally inert terminals groups such as chlorine. Up to now the possibility to introduce reactive chain ends onto PES-type polymers, which could be useful for the applications described above, as well as, for example, large scale polymer recycling operations [5], has not been fully explored.

The chain extenders reported in literature are bifunctional compounds that react very easily with the end groups of macromolecules (for example –COOH, –OH, $-NH_2$, etc.). These compounds are generally easily prepared, thermally stable, non-volatile at the melting temperature of the polymer, and capable of fast reactions with polymer chain-ends in a nearly irreversibly manner with no formation of volatile products. In fact, to carry out addition or ring-opening type reactions the use of an addition-type chain extender without generation of a by-product is preferable.

The main chain extenders which have been proposed up

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to now are: bis-epoxides, bis-cyclic carboxylic anhydrides, diisocyanates and groups such as vinyl, CN, acrylate, alchyl, carbonylic, bismaleimidic, oxazoline, etc. [6].

The aim of this paper is to present some different reactions which have been used to convert the end groups of PES copolymers into other polymerizable groups (oxazoline, allyl and 1,2,4-benzenetricarboxylic anhydride) in order to obtain polymers which are potential candidates for the preparation of block copolymers. The following model compounds (**4–6**) and PES copolymers (**7–9**) have been synthesised and characterised by ^{1}H NMR, Fourier

transformed infrared (FTIR) spectroscopies and elemental analysis.

2. Experimental

2.1. General

All reagents and solvents used in these experiments were obtained from commercial sources and utilised without any special purification. The PES copolymers were prepared

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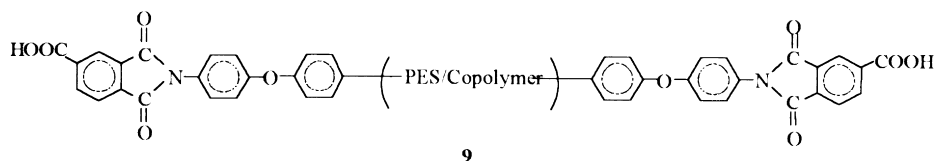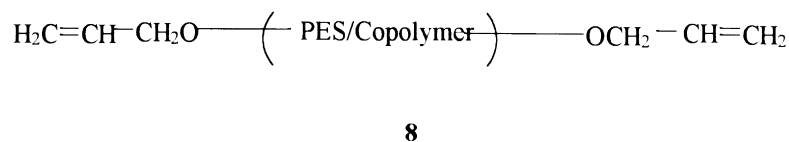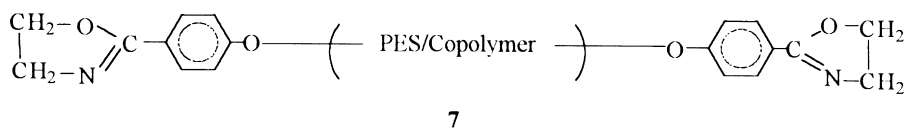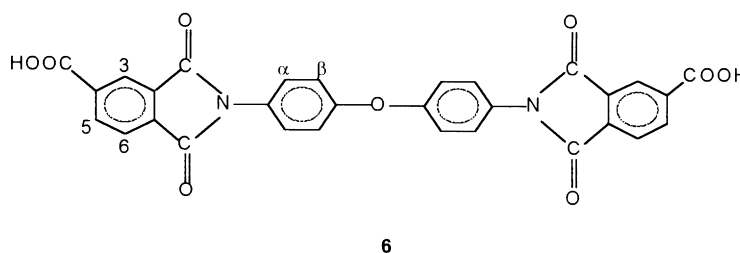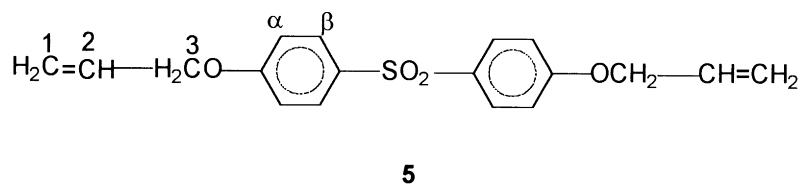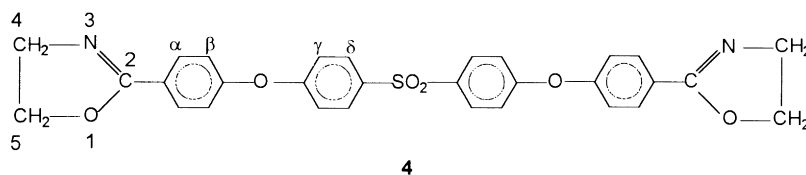
according to a method described in the literature [7]. Melting points were determined on a Kofler apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a Varian VXR 300 MHz spectrometer. All spectra were obtained in deuterated dimethylsulphoxide (DMSO-d$_6$) solution without any internal standard, at room temperature, (the following abbreviation are used: s = singlet, bs = broad singlet, d = doublet, dd = double doublet, m = multiplet, and t = triplet). The Fourier Transform Infrared (FTIR) absorption spectra were recorded on a Perkin–Elmer model 1725X Spectrophotometer as KBr pellets, (the following abbreviations are used: s = strong, m = medium, and w = weak). Elemental analysis was carried out for all samples.

2.1.1. N-(2-hydrooxyethyl)-p-hydroxybenzamide (1)

In a 100 ml three neck round bottom flask equipped with a Marcusson apparatus and a bulbing condenser containing stirred ethanolamine (20.03 g, 0.329 mol) was added by portion methyl 4-hydroxybenzoate (20.0 g, 0.131 mol) and the mixture was allowed to reflux for 20 h. After elimination of the ethanolamine excess (by vacuum distillation) the hot viscous orange oil was poured into hot acetone to get 18.5 g of 1 (77.7%) as white powder. m.p. = 143 − 144°C.

^{1}H NMR: δ 8.14 (s, 1H, phenol –OH), 7.70 (d, 2H, $J = 8.5$ Hz, H$^\beta$ of phenyl), 6.77 (d, 2H, $J = 8.5$ Hz, H$^\alpha$ of phenyl), 4.68 (bs, 1H, –NH–CO), 4.47 (t, 2H, $J = 6.5$ Hz, H^2), 3.l30 (bs, 1H, –OH) 3.28 (t, 2H, $J = 6.5$ Hz, H^1). FTIR (KBr) 3295(s), 3051(s), 1714 (m), 1534 (m), 1057 (s) cm^{-1}. Elemental analysis: Calc. for C$_9$H$_{11}$NO$_3$: C, 59.65; H, 6.12; N, 7.73%. Exp.: C, 60.01; H, 6.34; N, 7.60.

2.1.2. 2-(p-hydroxyphenyl)-2-oxazoline hydrochloride (2)

To a stirred solution of 1 (17.72 g, 0.098 mol) in chloroform (400 ml) was added dropwise thionyl chloride (25.60 g, 0.215 mol) and the mixture was allowed to stir at room temperature for 18 h, to afford, after filtration 17.7 g of 2 (98.3%) as white powder. m.p. = 153–154°C. Elemental analysis: Calc. for C$_9$H$_{10}$ClNO$_2$: C, 54.13; H, 10.08; N, 7.02% Exp.: C, 54.00; H, 10.34; N, 7.50.

2.1.3. 2-(p-Hydroxyphenyl)-2-oxazoline (3)

To a stirred solution of 2 (17.7 g, 0.096 mol) in water (900 ml) was added dropwise a saturated water solution of NaHCO$_3$ in order to reach a pH about 8. After filtration and water washing, followed by two recrystallization from acetone, 5.0 g (32%) of 3 as-white crystals were obtained. m.p. = 194–195°C. (Ref. [8] 195–195°C).

^{1}H NMR: δ 10.41 (s, 1H, phenol –OH), 8.11 (d, 2H, $J = 9.0$ Hz, H$^\beta$ of phenyl), 7.22 (d, 2H, $J = 8.5$ Hz, H$^\alpha$ of phenyl), 4.76 (t, 2H, $J = 9.5$ Hz, H^5 of oxazoline), 4.30 (t, 2H, $J = 9.5$ Hz, H^4 of oxazoline). FTIR (KBr) 2670 (m), 1635 (s), 1127 (w) cm^{-1}. Elemental analysis: Calc. for

C$_9$H$_9$NO$_2$: C, 66.24; H, 5.56; N, 8.58%. Exp.: C, 66.43; H, 5.34; N, 8.60.

2.1.4. 4,4′-[2–(p-phenyl)–2–oxazoline]diphenyl sulphone (4)

To a stirred solution of 4-chlorodiphenylsulfone (1.5 g, 0.0052 mol) in dichloromethane (60 ml) was added 2-(p-hydroxyphenyl)-2-oxazoline (2.13 g, 0.0131 mol), tetra-butylammonium hydrogen sulfate (TBAH) (4.43 g, 0.0131 mol) and a water solution of NaOH 50% (w/w) (60 ml). The reaction mixture was allowed to stir at 40°C for 3 h. After cooling at room temperature and addition of CH$_2$Cl$_2$ (30 ml), the organic phase was washed several times with water, and dried with Na$_2$SO$_4$ anhydrous. After filtration, elimination of the solvent and acetone washing, 2.1 g (75%) of 4 as white powder were obtained. m.p. = 159–161°C.

^{1}H NMR: δ 10.01 (s, 1H, phenol –OH), 8.01 (d, 2, $J = 8.5$ Hz, H$^\delta$), u.83 (dd, 2H, $J = 9.0$, 1.5 Hz, H^4 of oxazoline). FTIR (KBr) 2670 (m), 1635 (s), 1127 (w) cm^{-1}. FTIR (KBr) 3100–2900 (w), 1918 (w), 1651 (s), 1212 (m), 1154 (m), 1074–800 (s) cm^{-1}. Elemental analysis: Calc. for C$_{30}$H$_{24}$N$_2$O$_6$S: C, 66.66; H, 4.48; N, 5.18; S, 5.93%. Exp. C, 66.23; H, 4.69; N, 5.07; S, 5.78.

### 2.1.5. 4,4′-(allyl)diphenylsulphone (5) [9]

To a stirred solution of 4,4′-hydroxydiphenylsulfone (3 g, 0.012 mol) in water (20 ml) NaOH (1.2 g, 0.03 mol) was added and the reaction mixture was stirred at 40–45°C for 1 h. After allyl bromide (3.63 g, 0.03 mol) addition the reaction mixture was allowed to stir at 45°C for 17 h and at 70°C for 1 h to give, after filtration, hot water washing and vacuum drying, 3.55 g. (89.6%) of 5 as white solid. m.p. = 135 − 136°C

^{1}H NMR: δ 7.83 (d, 4h, $J = 8.5$ Hz, H$^\beta$ of phenyl), 7.11 (d, 4H, $J = 8.5$ Hz, H$^\alpha$ of phenyl), 6.01 (m, 2H, H^2), 5.38 (d, 2H, $J = 17.5$ Hz, H^{1a}), 4.65 (d, 2H, $J = 4.5$ Hz, H^3). FTIR (KBr) 3071 (w), 1910 (w), 1592 (s), 1499 (s), 1261 (s), 1147 (s), 993 (s) cm^{-1}. Elemental analysis. Calc. for C$_{18}$H$_{18}$O$_4$S: C, 65.44; H, 5.49; S, 9.70%. Exp.: C, 65.20; H, 5.68; S, 9.25.

2.1.6. 4,4′-(1,2,4-benzenetricarboxylicimide)diphenylether(6) [10]

In a 100 ml round-bottom flask, equipped with a Marcusson apparatus and a bulbing condenser, a mixture of 1,2,4-benzenetricarboxylic anhydride (5.76 g, 0.030 mol), 4,4′-oxydianiline (3 g, 0.015 mol), NMP (30 ml) and toluene (10 ml), was stirred at room temperature for 1 h and at 180°C for 5 h, to afford, after cooling, methanol (50 ml) addition, filtration, and methanol washings, 7.98 g, (95.2%) of 6 as yellow powder. m.p. > 200°C.

^{1}H NMR: δ 13.64 (bs, 2H,– COOH), 8.42 (dd, 2H, $J = 7.5$, 1.5 Hz, H^5 of benzene), 8.32 (d, 2H, $J = 1.5$ Hz,
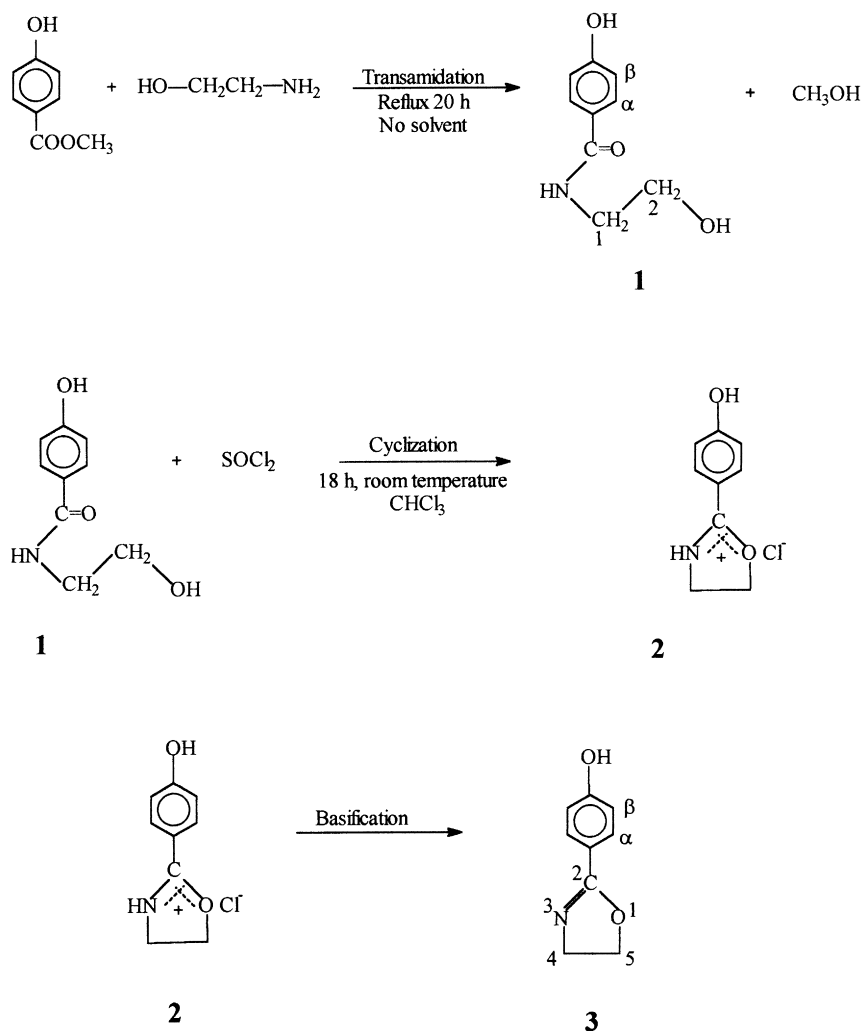
Scheme 1.

H^3 of benzene), 8.09 (d, 2H, $J = 7.5$ Hz, H^6 of benzene), 7.52 (d, 4H, $J = 8.5$ Hz, H^α of phenyl), 7.25 (d, 4H, $J = 8.5$ Hz, H^β of phenyl). FTIR (KBr) 1781 (m), 1720 (m) cm^{-1}. Elemental analysis. Calc. for $C_{30}H_{16}N_2O_9$: 65.70; H, 2.94; N, 5.11%. Exp.: C, 65.06; H, 3.04; N, 5.24.

2.1.7. PES-PEES 2-(p-Phenyl)-2-oxazoline chain-ended PES copolymer (7) [8]

To a stirred solution of −OH ended PES copolymer (1 g, 0.099 mmol) in CH$_2$Cl$_2$ (20 ml) were added 2-(*p*-hydroxy-phenyl)-2-oxazoline (0.0485 g, 0.2970 mmol), TBAH (0.1008 g, 0.2970 mmol) and NaOH 50% (w/w) water solution (20 ml). The reaction mixture was allowed to stir at 40°C for 3 h. After cooling at room temperature, and addition of CH$_2$Cl$_2$ (40 ml), the organic phase was washed with water and poured into methanol, to get, after filtration and several dissolution in chloroform and riprecipitation in methanol, 0.52 g (57%) of 7 as a white powder.

^{1}H NMR: δ 7.95 (m, 40H, H^δ of PES/PEES units + 2H,

H^β of phenyl-oxazoline), 7.60 (m, 1H, −SO$_2$−OH of PES/PEES units), 7.26 (bd, 24H, $J = 8.4$ Hz, $H^\beta + H^\gamma$ of PES unit), 7.20 (bs, 16H, H^β of PEES unit + 2H, H^α of phenyl-oxazoline), 7.13 (bd, 16H, $J = 8.5$ Hz, H^γ of PEES unit), 6.85 (bs, 1H, -phenyl-OH of PES/PEES units), 4.36 (t, 2H, $J = 9.5$ Hz, H^5 of oxazoline), 3.92 (t, 2H, $J = 9.5$ Hz, H^4 of oxazoline). FTIR (KBr) 3543 (w), 3100–2900 (m), 1900 (m), 1650 (m), 1240 (s), 1151 (m), 1070–800 (s), cm^{-1}. Elemental analysis. Calc. for $C_{155}H_{106}NO_{37}S_{10}$: C, 64.31; H, 3.69; N, 0.48; S, 11.05%. Exp. C, 62.94; H, 4.20; N, 0.54; S, 10.01.

2.1.8. PES-PEEs allyl terminated PES copolymer (8) [9,11]

(a) To a stirred solution of −OH ended PES copolymer (2 g, 0.198 mmol) in water (30 ml) were added allyl bromide (0.35 g, 2.9 mmol) and NaOH (0.5 g, 12.5 mmol) and the reaction mixture was allowed to stir at 40–45°C for 18 h. After filtration, hot water washing and vacuum drying, 1.8 g of 8 (90%) as whitish-yellow powder were obtained.

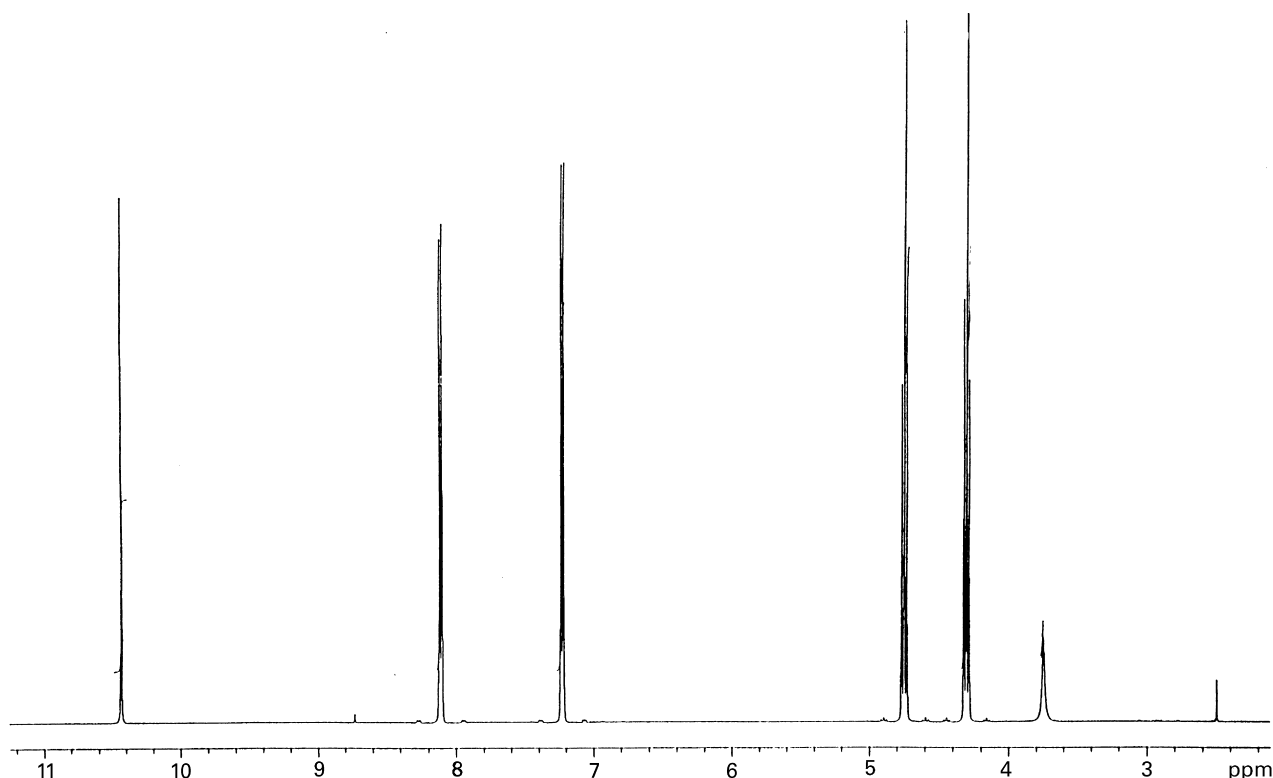Fig. 1. ^{1}H NMR spectrum (DMSO-d$_6$) of 2-(*p*-Hydroxyphenyl)-2-oxazoline (**3**).

Elemental analysis. Calc. for $C_{144}H_{98}O_{36}S_{10}$: C, 63.48; H, 3.63; S, 11.75%. Exp. C, 62.94; H, 3.62; S, 11.44.

(b) To a stirred solution of –OH ended PES copolymer (2 g,0.198 mmol) in acetone (50 ml), Potassium carbonate (0.0274 g, 0.198 mmol) and allyl bromide (0.14 g, 1.2 mmol) was added and the mixture was allowed to reflux for 72 h. After distilling acetone off, the product was stirred with dichloromethane (100 ml) and water (80 ml). The two phases were separated and the organic phase was dried with Na_2SO_4 anhydrous to give after filtration and elimination of the solvent, 1.1 g (5.5%) of 8 as whitish-yellow clear powder.

^{1}H NMR: δ 7.95 (m, 40H, H^δ of PES/PEES units), 7.72 (bs, 0.25H, $-SO_2-OH$ of PES/PEES units), 7.26 (bd, 24H, $J = 8.4$ Hz, $H^\beta + H^\gamma$ of PES unit), 7.24 (bs, 16H, H^β of PEES unit), 7.13 (bd, 16H, $J = 8.5$ Hz, H^γ of PEES unit), 6.89 (bs, 0.25H, -phenyl-OH of PES/PEES units), 6.01 (m, 1.5H, H^2), 5.37 (d, 1.5H, $J = 17.5$ Hz, H^{1a}), 5.25 (d, 1.5H, $J = 10.5$ Hz, H^{1b}), 4.64 (d, 3H, $J = 4.5$ Hz, H^3). FTIR (KBr) 3543 (w), 3068 (m), 1908 (m), 1581 (s), 1484 (s), 1234 (s), 1184 (s), 1009 (s). Elemental analysis. Calc. for $C_{148}H_{104}O_{35}S_{10}$: C, 64:34; H, 3.79; S, 11.58%. Exp.: C, 63.92; H, 3.98; S, 11.14.

2.1.9. PES – PEES 1,2,4-benzenetricarboxylic imide terminated PES copolymer (9) [12]

A mixture of the NH$_2$ ended PES copolymer (3 g, 0.29 mmol) and cyclohexanone (60 ml) was stirred at 70°C for 1 h, after 1,2,4-benezenetricarboxylic anhydride (0.6781 g, 3.5 mmol) addition the heating continued for 2 h more, then acetic anhydride (0.35 ml, 3,7 mmol, $d = 1.082$) and sodium acetate (0.14 g, 1.7 mmol) were added and the heating continued for a further 2.4 h. After cooling the mixture was poured into methanol (200 ml) to get, after filtration water/methanol 1:1 washings, vacuum drying, 2.8 g (94%) of 9 as white powder.

^{1}H NMR: δ 13.60 (bs, 1.4H,– COOH), 8.40 (d, 1.4 H, $J = 7.5$ Hz, H^5 of benzene), 8.30 (bs, 1.4 H, H^3 of benzene), 8.08 (d, 1.4 H, $J = 7.5$ Hz, H^6 of benzene), 7.95 (m, 40 H, H^δ of PES/PEES units), 7.68 (m, 0.75 H, $-SO_2-NH_2$ of PES/PEES units), 7.25 (bd, 24 H, $J = 8.4$ Hz, $H^\beta + H^\gamma$ of PES unit), 7.22 (bs, 16 H, H^β of PEES unit), 7.8 (bd, 16 H, $J = 8.5$ Hz, H^γ of PEES unit), 6.89 (bs, 0.75 H, -phenyl-NH$_2$ of PES/PEES units). FTIR (KBr) 3094–3068 (m), 1783 (m), 1727 (s) 1581 (s), 1488 (s), 1235 (s), cm^{-1}. Elemental analysis. Calc. For $C_{156}H_{103}$ $N_2O_{40}S_{10}$: C, 63.18; H, 3.50; N, 0.94; S, 10.80%. Exp.: C, 63.25; H, 3.56; N, 0.48, S, 11.32.

3. Results and discussion

The synthesis of 2-(*p*-hydroxyphenyl)-2-oxazoline (**3**) was performed in three steps, according to Scheme 1, improving (by a careful choise of experimental parameters) the method reported in the literature [8]. The first step represents, using a 1:2.5 molar ratio, the transamidation of Methyl 4-hydroxybenzoate with monoethanolamine to
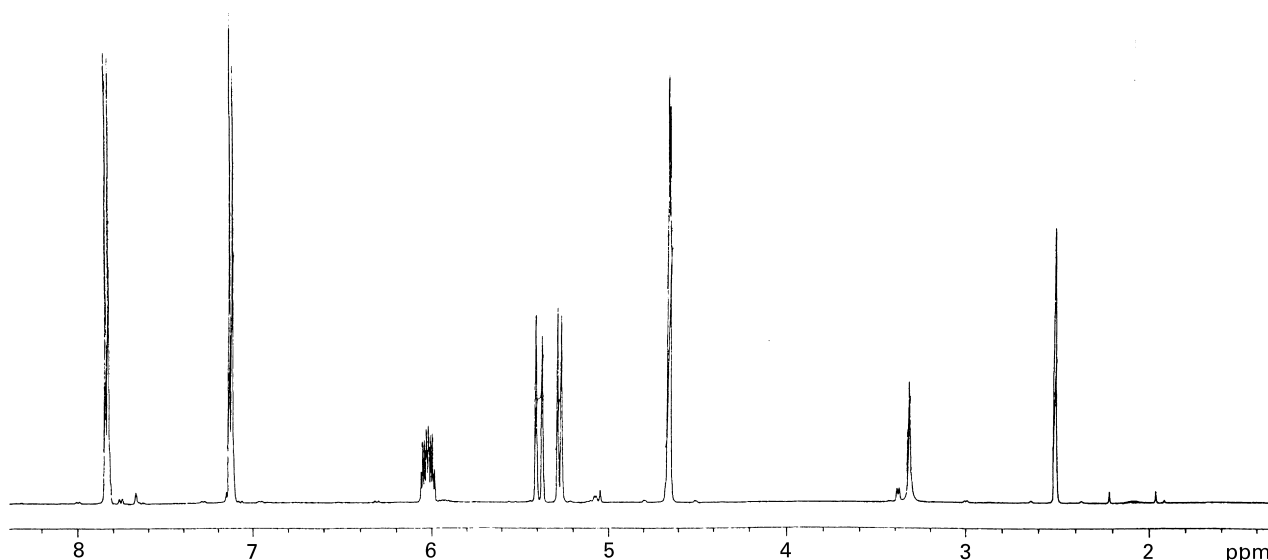
Fig. 2. ^{1}H NMR spectrum (DMSO-d$_6$) of the model compound 4,4$'$ -(allyl)diphenylsulphone (**5**).

afford *N*-(2-hydroxyethyl)-*p*-hydroxybenzamide (**1**). This reaction is an equilibrium reaction so it was necessary to remove completely the methanol by using a Marcusson apparatus and after about 20 h of reaction time the excess of ethanolamine was removed by distillation in vacuum. In this first step it was important not only the stoichiometry but also to control the reaction temperature because in this case the yield is quite high. In order to obtain 2-(*p*-hydroxy-phenyl)-2-oxazoline hydrochloride (**2**), the second step represents the cyclization of the benzamide (**1**) with thionyl chloride in a 1:2.2 molar ratio. The reaction was run at room temperature, under continuos stirring for about 20 h, adding the thionyl chloride very slowly to the mixture. Crude 2-(*p*-hydroxyphenyl)-2-oxazoline (**3**) was obtained by the basifi-cation of a water solution of the oxazoline hydrochloride with a saturated water solution of sodium bicarbonate. Also in this case it was important to basify very slowly and to stir the solution continuously.

The synthesis of the model compound 4,4$'$ -[2–(p–phenyl)–2–oxazoline]diphenyl sulphone (**4**) was accom-plished by a phase-transfer catalysed Williamson ether-ification [13] performed under the reaction conditions described in the Experimental part. By the use of stoi-chiometric amounts of phase transfer catalyst versus the oxazoline phenol group, the oxazoline is transferred to the organic phase, consequently the etherification occurs in solution and the hydrolysis of the oxazoline can be avoided, furthermore the ammonium phenolate interme-dium, being dissolved in a nonpolar aprotic solvent and not solvated, results very reactive. The syntheses of 4,4$'$-(allyl)diphenylsulphone (**5**) and 4,4$'$-(1,2,4-benzenetricar-boxylic imide)diphenylether (**6**) model compounds, were performed by reacting 4,4$'$-hydroxydiphenylsulfone with allyl bromide in H$_2$O in the presence of NaOH as a base, and by mixing together 1,2,4-benzenetrycarboxylic anhy-dride, 4,4$'$-oxydianiline, NMP and Toluene, respectively.

The reactions were run under the conditions described in Section 2.

The PES/PEES-2-(*p*-phenyl)-2-oxazoline chain-end polymer (**7**) was synthesized using the same experimental procedure of the corresponding model compound (**4**), while the PES/PEES allyl terminated copolymer (**8**) was synthe-sised using two different procedures. The procedure *a* is the same used for the model compound (**5**), while the procedure *b* was performed following the literature data, by mixing and heating together all reagents for 3 days in reflux condi-tions. The synthesis of the copolymer (**9**) was performed following the literature procedure [10], adding to stirred cyclohexanone the PES/PEES-NH$_2$ copolymer. To the resulting solution was then added 1,2,4-benzenetrycar-boxylic anhydride, heated and then added acetic anhydride and sodium acetate. The polymer was obtained by precipi-tation in methanol solution.

The purification of the synthesised polymers was achieved by several washings with appropriate solvents in order to avoid the presence of unreacted starting materials. ^{1}H NMR, FTIR and Elemental Analysis support the formu-lation of the synthesised compounds.

The ^{1}H NMR spectrum of (**3**) (Fig. 1) shows the expected pattern of the oxazoline (two triplets at 4.3 and 4.7 ppm assigned to methylene protons) and phenyl (two doublets at 7.2 and 8.1 ppm assigned to aromatic protons) moieties, respectively.

The ^{1}H NMR spectroscopy technique proved to be a useful tool to check the composition of the synthetized poly-mers. By taking advantage of ^{1}H NMR work on model compounds (**4–6**), we were able to make by comparison the overall proton assignments for our polymers. On check-ing the aromatic and/or methylenic regions of the ^{1}H NMR spectra for the synthesized copolymers (**7–9**), it is worth to note that, as expected, are present signals diagnostic for the presence of the oxazoline, of the allyl, and of the
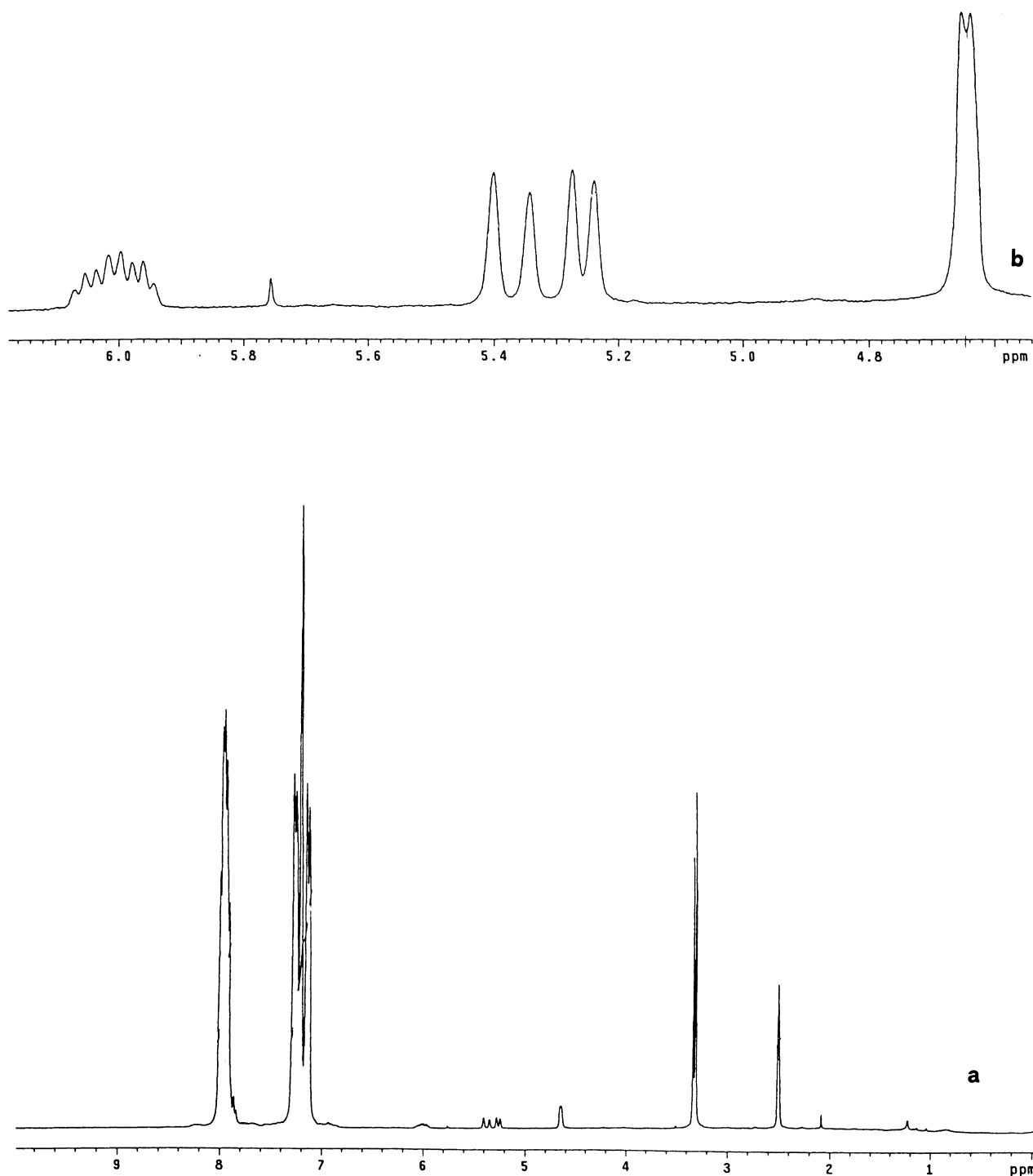
Fig. 3. ^{1}H NMR spectra (DMSO-d$_6$) of PES-PEES allyl terminated PES copolymer (**8**) (a), and its expanded methylenic region (b).

benzenetricarboxylic imide groups, respectively. Fig. 2 shows, as a example, the ^{1}H NMR spectrum of the model compound (**5**) where the aromatic region shows a *AA'XX'* system (two doublets at 7.83 and 7.11 ppm) diagnostic of a *p*-distributed benzene ring that is readily recognized because of its symmetry and apparent simplicity while the methylenic region presents the characteristic pattern of a allylic group with a ABX system that shows two doublets

at 5.38, and 5.26 ppm, along with a quartet at 6.01 ppm, respectively, and a doublet at 4.65 ppm. Fig. 3(a) shows the ^{1}H NMR spectrum of the related copolymer (**8**) where are present both the resonances of the chain-ended allyl group and the resonances of the unsubstituted –OH terminated groups at 7.72 and 6.85 ppm, while Fig. 3(b) shows an expansion of the methylenic region where it is easy to recognize the allylic pattern. The intensity of the signals

reflect the copolymer composition, so by their integration ratio we desumed a 05% substitution degree that rises at 70% when the copolymer (**8**) is synthesized by b procedure (see Section 2), and a 60 and 70% substitution degree for the copolymers (**7**) and (**9**), respectively.

The FTIR spectra of the synthesised compounds are characterised, as a common feature, shown by (i) prominent aromatic C–H and C–C ring stretching bands at 3100–2900 and at 1592–1449 cm^{-1}, respectively; (ii) a band at 1918–1900 cm^{-1} associated at the SO_2 group; (iii) bands ranging between 1261 and 1147 cm^{-1} associated to the ether C–O–C moiety; (iv) well-resolved absorption bands at lower frequencies, which can be ascribed to the in-plane and out-of-plane ring deformation. *Viceversa* are present bands that are diagnostic for the presence of the chain-ended groups, in particular (**3**), (**4**), and (**7**) show bands at 1650–1635 (C = N stretching) cm^{-1} referring to the 1,2,4-benzenetricarboxylic imide group. It is worth to note that in (**7**) and (**8**) there is also a weak band at 3543 cm^{-1} associated to the polymeric phenol group not reacted.

In conclusion, new methods to modify by substitution the chain-end chemical groups of the PES copolymers are successfully reported. The total substitution of the starting –OH and $-NH_2$ ended PES copolymer was not fully achived till now, but by a probably careful purification of the starting material and/or by stressing the experimental condition this target will be reached, while it is worth to note that such materials are relatively easy to prepare without any side reactions. Studies on the possibility of preparing new well-defined block copolymers are in progress.

References

[1] Kobayashi S, Kaku M, Mizutani T, Saegusa T. Polymer 1991;32:140.
[2] Kennedy PE. Thermally stable polymers, syntheses and properties. New York: Marcel Dekker, 1980.
[3] Jones MEB, Br Patent 1016245, 1962; Vogel HA, Br Patent 1060546, 1963; Farnham AG, Johnson RN, Br Patent 1078234, 1963; Gabler R, Studinka J, Br Patent 1234008, 1969, to Inventa AG.
[4] Cinderey MB, Rose JB. Ger Offen 1978;2803873.
[5] Kobayashi S, Kaku M, Mizutani T, Saegusa T. Polym Bull 1983;9:169.
[6] Bikiaris DN, Karayannidis GP. J Polym Sci: Part A. Polym Chem 1995;33:1705.
[7] US Patent 5231150.
[8] Percec V, Nava H, Rodriguez-Parada JM. J Polym Sci: Polym Lett Edn 1984;22:523.
[9] Chemical Abstracts, 115 (1991) 1 828 322w.
[10] Matsuo, Mitsuhashi. J Polym Sci: Part A. Polym Chem 1994;32:1581.
[11] Itoh M, Mita I. J Polym Sci: Part A. Polym Chem 1994;32:1581.
[12] Naik HA, et al. Polymer 1991;32:140.
[13] Dehmlow EV, Dehmlow SS. Phase transfer catalysis, 3rd edn. Stuttgart: VCH, 1999.