In situ preparation of blends of polystyrene and poly(2,6-dimethyl-1,4-phenylene ether)

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A new approach to prepare blends of polystyrene (PS) and poly(2,6-dimethyl-1,4-phenylene ether) (PPE) directly in the reactor is presented. The key step in this new route is the *in situ* 'cold' end-capping of PPE, dissolved in styrene, but the acetylation of the reactive phenolic end group of PPE. Without isolation of the PPE-acetyl (Ac), the reaction mixture is subjected to a classical styrene suspension polymerization procedure, yielding homogeneous beads of PS/PPE-Ac. The presence of PPE-Ac does not interfere chemically with the styrene polymerization as demonstrated by g.p.c. analysis of the separated constituents of the blend. A series of blends with different compositions was prepared. The maximum content of PPE in these reaction blends is 35 wt%, due to a limitation in viscosity of the PPE-styrene solution. Homogeneous transparent amorphous beads of PS/PPE-Ac were obtained, possessing a single glass transition temperature between 105°C and 140°C, depending on the composition.

(**Keywords: poly(2,6-dimethyl-1,4-phenylene ether); polystyrene; suspension polymerization; blending; *in situ* end-capping**)

INTRODUCTION

Blends of poly(2,6-dimethyl-1,4-phenylene ether) (PPE) and (high-impact) polystyrene [(HI)PS] are the paradigm of a miscible polymer pair over the entire composition range[1], at least at atmospheric pressure[2]. In practice, PPE and (HI)PS are mixed via extrusion-(melt)blending and the properties can be tailored according to the ratio of constituents. The thermal instability of PPE requires the use of large amounts of stabilizers during the blending process. The same thermal instability of PPE, giving rise to an increase of melt viscosity in time[3,4], hampers its use as an engineering plastic as such, despite its excellent mechanical properties[5]. Therefore, PPE is used as a blend component only, notably in blends with HIPS [Noryl®, (General Electric Company), Vestoran® (Hüls) and Luranyl® (BASF)]. The aforementioned thermal instability of PPE is due to the specific reactive end groups of the polymer. The amine–Cu(II) salt complex catalysed the oxidative polymerization of 2,6-dimethylphenol and is terminated with the use of dialkylamines, furnishing 2-(*N*,*N*-dialkylaminomethyl)-6-methylphenol end groups. Elimination of dialkylamines by a retro-Michael reaction at elevated temperatures is easily achieved furnishing methide quinone functionalities. The latter is well-known as a reactive species, yielding chain grafting, crosslinking or other radical reactions. Several modifications of the end group have been presented[6–9]. However, the reaction temperature used in these modifications often leads to significant side reactions, and further optimization of the process of blending PPE and (HI)PS is useful.

In this paper we report on a new approach of blending the polymers PPE and PS[10]. Since PPE is soluble in styrene, a process of polymerizing styrene in the presence of PPE can be envisaged. In order to minimize the expected inhibition/retardation of the radical polymerization of styrene by the (latent) PPE end groups, a low-temperature, *in situ*, end-group modification of PPE is presented.

EXPERIMENTAL

Materials

Styrene was used without distillation from the inhibitor tert-butylcatechol (11–17 ppm; Shell Nederland Chemie BV, Rotterdam, The Netherlands). The water was distilled from extraneous minerals. Suspension polymerization chemicals were used as received; dibenzoyl peroxide (DBPO) contains 25 wt% water (Janssen Chimica, Tilburg, The Netherlands).

Poly(2,6-dimethyl-1,4-phenylene ether) (PPE-800) was used as received and the terminal xylenol group was incorporated with a Mannich base (General Electric Co., Bergen op Zoom, The Netherlands). D.s.c.: glass transition temperature (T_g) = 218°C; intrinsic viscosity: 0.489 dl g^{-1} [chloroform, $CHCl_3$, 25°C]; g.p.c. ($CHCl_3$): $M_n = 19.2 \pm 1.0$ kg mol^{-1} and $M_w = 54.0 \pm 2.3$ kg mol^{-1}; *FT*i.r.: $\nu = 3450$ (aromatic OH), 3050 (aromatic C–H), 2971/2930/2874 (aliphatic C–H), 1603 (aromatic ring), 1478 (aromatic C=C), 1306/1181 (aromatic ether), 1018 (aromatic C–H), 865 (C=C–H) cm^{-1}; ^1H *FT*n.m.r.: $\delta = 2.02$ (6H, s, CH_3), 6.65 (2H, s, C_6H_2) ppm; ^{13}C *FT*n.m.r.: $\delta = 16.2$ (CH_3), 114.8 (*m*-C), 132.3 (*o*-C), 145.1 (*p*-C), 154.8 (C–O) ppm.

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PPE end-capping agents, acetic anhydride (Ac_2O) and 4-(N,N-dimethylamino)pyridine (DMAP), were used as received from Janssen Chimica.

Characterization techniques

D.s.c. measurements. Melting endotherms and T_gs were recorded using a Perkin-Elmer DSC-7 differential scanning calorimeter. The samples were first heated to 250°C, quenched from the melt to ambient temperature and recorded with a standard heating rate of 10 K min^{-1}. Indium was used for temperature- and heat of fusion calibration ($T_{m,onset} = 156.6°C$ and $\Delta H_f = 28.45 J g^{-1}$). The T_gs were determined using the intercept of the tangent at the point of maximum slope and the extrapolated baseline at the low temperature side of the transition.

Electron microscopy. Transmission electron microscopy was performed using a Jeol JEM 2000 FX transmission microscope, operating at 80 kV. The samples were embedded in epoxy and thin sections were obtained by ultra microtomy at liquid nitrogen temperature using a Reichert Ultracut E. The cut sections were stained with osmium tetroxide at room temperature for 24 h.

I.r. measurements. I.r. spectra were recorded with a Mattson Polaris *FT*i.r. spectrometer equipped with a standard DTGS detector and He/Ne laser. The frequency spectrum can be obtained by a dedicated fast Fourier transform routine. The spectra were obtained after accumulating 32 scans at a resolution of 4 cm^{-1} between 4000 cm^{-1} and 400 cm^{-1}. The sample compartment was held at room temperature under nitrogen atmosphere. The sample powder was mixed with KBr.

N.m.r. measurements. ^1H n.m.r. spectra were recorded at room temperature with a 200 MHz (Bruker AM 200) spectrometer, by using C_6D_6 as solvent and tetramethylsilane as an internal standard. The spectra were obtained after accumulating 64 scans and at a sample concentration of 3 wt%. ^{13}C n.m.r. (decoupled) spectra were recorded at room temperature with a 50.3 MHz (Bruker AM 200) spectrometer operated in the Fourier transform mode. The sample concentration was 10 wt% in C_6D_6 and spectra were obtained after accumulating 2000 scans.

Molar mass measurements. G.p.c. was used to determine the relative number-average molar mass (M_n), the mass-average molar mass (M_w) and the molar mass distribution ($M_w M_n^{-1}$) of PS and PPE. G.p.c. was performed using Waters apparatus composed of pump model 510, injector WISP 711; u.v. detector 254 nm model 440, equipped with 10^5, 10^4, 10^3 μ-Styragel (40°C) columns, calibrated with monodispersive PS standards, and using tetrahydrofuran (THF, PS) and $CHCl_3$ (PPE) at 0.6 ml min^{-1} as the eluent. The polymer sample was dissolved in the solvent, filtered and injected on columns.

Solid content measurements. Solid content analysis was used for determination of the polymerization conversion. During or at the end of the polymerization process, 25 ml of reaction mixture (containing water, sytrene, PS and PPE) were collected from the polymerization vessel. Benzoquinone (25 ppm) was added to the viscous solution and heated for 6 h on a steam bath. The rest mass of the solid content, at the end of this procedure, was measured and from the value the polymerization conversion was calculated.

Synthesis of PPE-Ac

PPE (37.5 g) was dissolved in styrene (212.5 g) at room temperature. A homogeneous solution was obtained after stirring for 1 h. Subsequently, Ac_2O (75 mg) and DMAP (19 mg) were added. After stirring for 1–2 h at room temperature, the PPE-acetyl(Ac)/styrene solution was poured into the non-solvent methanol at room temperature. PPE-Ac was filtered, washed twice with methanol and dried under vacuum (1 mm Hg) at 150°C for 15 h.

By using the same procedure as above, PPE solutions in styrene were prepared containing, 5, 10, 15, 18, 23, 30 and 35 wt% PPE, and end-capped with an acetyl group.

D.s.c.: $T_g = 218°C$; g.p.c.: $M_n = 20 kg mol^{-1}$, $M_w = 57 kg mol^{-1}$; *FT*i.r.: $v = 3450$ (Ar-OH), 3050 (Ar-H), 2971/2930/2874 (Ar-H), 1765 ($ArO(O)CCH_3$), 1306/1181 (Ar-O-Ar) cm^{-1}; ^1H *FT*n.m.r.: $\delta = 2.02$ (6H, s, CH_3), 6.65 (2H, s, C_6H_6) ppm; ^{13}C *FT*n.m.r.: $\delta = 16.2$ (CH_3), 114.8 (*m*-C), 132.3 (*o*-C), 145.1 (*p*-C), 154.8 (C-O) ppm.

Preparation of PS/PPE-Ac blends

PPE (45 g) was dissolved in styrene (205 g) at room temperature. A homogeneous solution was obtained after stirring for 1 h. Subsequently, Ac_2O (90 mg) and DMAP (22.5 mg) were added. After stirring for 1–2 h at room temperature, the temperature was increased to 70°C, and DBPO (0.615 g) and tert-butyl peroxybenzoate (0.41 g) were added.

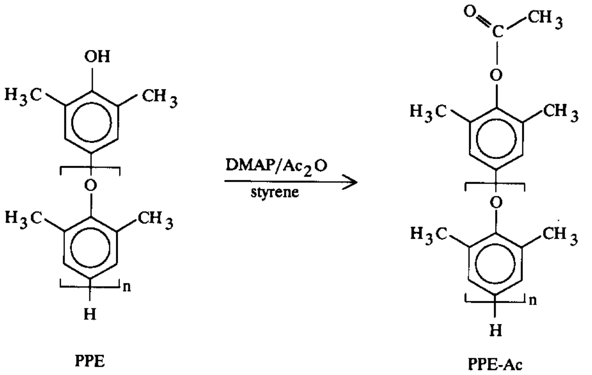
Hereafter the PPE-Ac/styrene solution was added to water (225 ml) at 70°C, containing hydroxyethyl cellulose (0.45 g). The suspension reaction mixture thus obtained was heated to 90°C. After polymerization for 6 h at 90°C with a stirring rate of 300 rev min^{-1}, the mixture was heated to 120°C and stirred for 4 h. Finally, the reaction mixture was quenched to room temperature and filtered. Regular spherical beads of PS/PPE-Ac (18 wt%) were obtained. Solid content analysis: ~99% PS.

By using the above recipe, seven different PS/PPE-Ac blends were prepared containing 5, 10, 15, 18, 23, 30 and 35 wt% PPE and possessing T_gs of 105, 108, 114, 118, 121, 127 and 133°C, respectively (measured by d.s.c.).

For characterization of the blend constituents, the PS/PPE-Ac blend was dissolved in CH_2Cl_2, and the organic layer was separated and concentrated. G.p.c.: PS, $M_n = 75 kg mol^{-1}$, $M_w = 210 kg mol^{-1}$; PPE-Ac, $M_n = 20 kg mol^{-1}$, $M_w = 58 kg mol^{-1}$.

RESULTS AND DISCUSSION

PS was synthesized via suspension polymerization using DBPO and tert-butyl peroxybenzoate as a radical initiator and hydroxyethyl cellulose as a suspension agent. Typically a 1:1 water/styrene ratio was used. In a reference experiment PPE was added to styrene in a ratio of PPE:styrene of 1:10 w/w. The polymerization temperature was raised stepwise and slowly from 70°C via 90°C to 120°C, with a total reaction time of 10 h. The radical polymerization of styrene was inhibited/retarded significantly and PS could be isolated only as soft viscous beads in a yield of ~60%. The anticipated retardation of the polymerization of styrene in the



Scheme 1 Acetylation of virgin PPE in styrene in the presence of Ac$_2$O and the catalyst DMAP

presence of compounds exhibiting functionalities similar to the PPE end groups is well documented[11]. Hence, end-group modification seems to be a prerequisite for a successful *in situ* blending process of PPE and PS.

The excellent solubility of PPE in styrene prompted us to explore the possibilities of an *in situ* end capping of PPE in styrene. For this purpose PPE was acetylated in styrene using a modified Höfle method at room temperature yielding PPE-Ac (*Scheme 1*)[12]. Upon transferring the reaction mixture of PPE-Ac in styrene to the suspension medium, the polymerization of styrene could be performed successfully. In this case PS/PPE-Ac blends are obtained as regular spherical beads in a yield of >98%.

In the following we will describe the results of the reaction steps of this reactive blending process.

End-capping of PPE

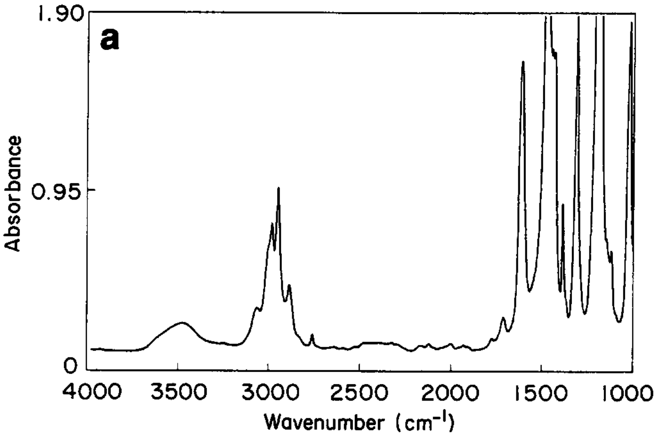
In the modified Höfle method, we used Ac$_2$O as the acetylating agent and DMAP as the catalyst. In the blending process, the modification of PPE is carried out *in situ*, without the isolation of PPE-Ac. In order to study the efficiency of this first step, we isolated the PPE-Ac from styrene and the other reaction ingredients by precipitating PPE-Ac in the non-solvent methanol. A detailed characterization of the product is hampered by the low concentration of end groups (the M_w of the PPE used is 54 kg mol^{-1}, on the basis of g.p.c. with PS standards as reference).

Of all the methods used, *FT*i.r. spectroscopy has proved to be the most successful in the identification of the acetate group. At 1765 cm^{-1} a small C=O stretch vibration is found, while the small O-H stretch vibration in PPE at 3450 cm^{-1} has vanished completely (*Figure 1*).

G.p.c. analysis shows no change in molar mass (distribution) during the acetylation and there are no differences found in the T_g at 215°C for PPE and PPE-Ac, as measured by d.s.c. (*Figure 2*).

In our hands, n.m.r. spectroscopy is not successful in the determination of the end groups. This is in contrast to the method recently published by Reuben and Biswas[13]. However, their analysis of PPE by ^{13}C *FT*n.m.r. is demonstrated on low molar mass non-commercial PPE only.

In order to verify the extent of conversion of PPE in the acetylation, we conducted the same procedure on a number of model phenols (**1**–**4**, *Scheme 2*). In all cases, the acetylated products were formed in quantitative yield, without the formation of by-products. Apparently, the



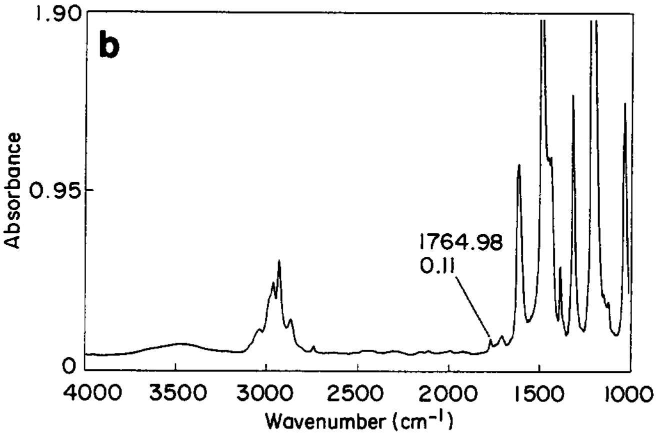


Figure 1 Comparison of *FT*i.r. absorption spectra of (a) PPE and (b) PPE-Ac

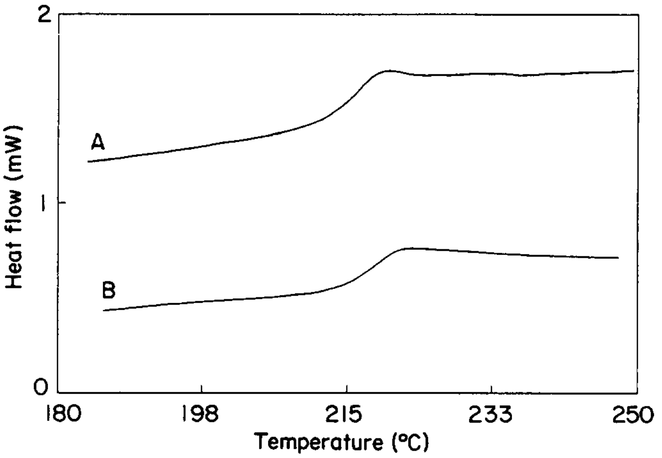
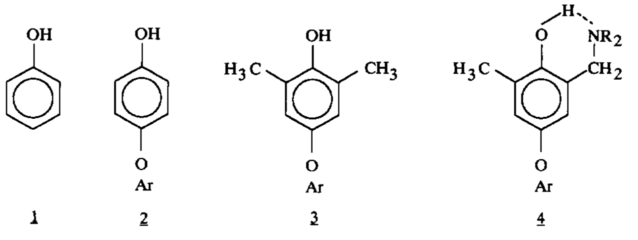


Figure 2 Comparison of the T_gs of (A) PPE and (B) PPE-Ac by d.s.c.



Scheme 2 PPE model compounds

steric hindrance present in the end group does not influence the reactivity of the phenol.

Preparation and properties of the PS/PPE-Ac blend

The polymerization of styrene is studied in comparison with a reference experiment in which no PPE-Ac has been added to the suspension polymerization. In both cases, classical (standard) conditions are used as outlined above (see Experimental section). The yield of PS in all these cases is >98%. A series of blends with different concentrations of PPE-Ac has been synthesized. The maximum PPE-Ac content in the blends is 35 wt%. This limitation is due to the limiting viscosity of the PPE-Ac styrene solutions. All the prepared blends possess the characteristic C=O vibration at 1765 cm^{-1} in the *FT*i.r. spectra. Hence, no hydrolysis of the acetate is observed. Despite the fact that the PPE-Ac in styrene solution is not isolated and purified before applying it to the suspension polymerization, we found no evidence for the presence of chemical impurities in the blends.

The catalyst of the Höfle acetylation and the acetic acid formed are soluble in water, hence, they are eliminated from the polymer beads during the suspension polymerization.

In order to characterize the polymer constituents of the PS/PPE blend, the blend was separated into its constituents using methylene chloride (CH_2Cl_2). At room temperature, PPE (and PPE-Ac) forms a complex with CH_2Cl_2, while PS is completely soluble[14].

The molar mass (distribution) of the polymers in the blend is determined by g.p.c. and compared with the homopolymers, made individually. The results are given in *Table 1*.

Within the experimental error of the g.p.c. analyses, the molar mass (distribution) of the PS samples is similar in both cases. Hence, no chemical interference of PPE-Ac is present in the suspension polymerization. Moreover, the data indicate no side reaction of PPE-Ac during the polymerization. The results presented in *Table 1* show that an ideal reactive blending procedure has been found.

Figure 3 shows the T_gs of the six different PS/PPE blends prepared. The blends possess a single T_g between 100°C and 140°C. Within the accuracy of the d.s.c. apparatus no melting endotherm has been recorded. These data emphasize that this preparative route results in a homogeneous PS/PPE-Ac blend. In *Figure 3* the theoretical curve is also presented according to the Fox equation. The experimental data are in excellent agreement with the calculated predictions.

Transmission electron microscopy experiments were performed to demonstrate the homogeneity of the PS/PPE blends. No impurities or concentrated phases were detected in these blends, again affirming the homogeneity of the materials.

Table 1 Molar masses (distribution) obtained by g.p.c. (THF, $CHCl_3$, with PS standards) of the homopolymers PS and PPE-Ac, and polymer constituents separated from the PS/PPE-Ac blend

	Homopolymer		Blend	
	M_w (kg mol^{-1})	$M_wM_n^{-1}$	M_w (kg mol^{-1})	$M_wM_n^{-1}$
PS	220	2.5	210	2.5
PPE-Ac	57	2.8	58	2.85

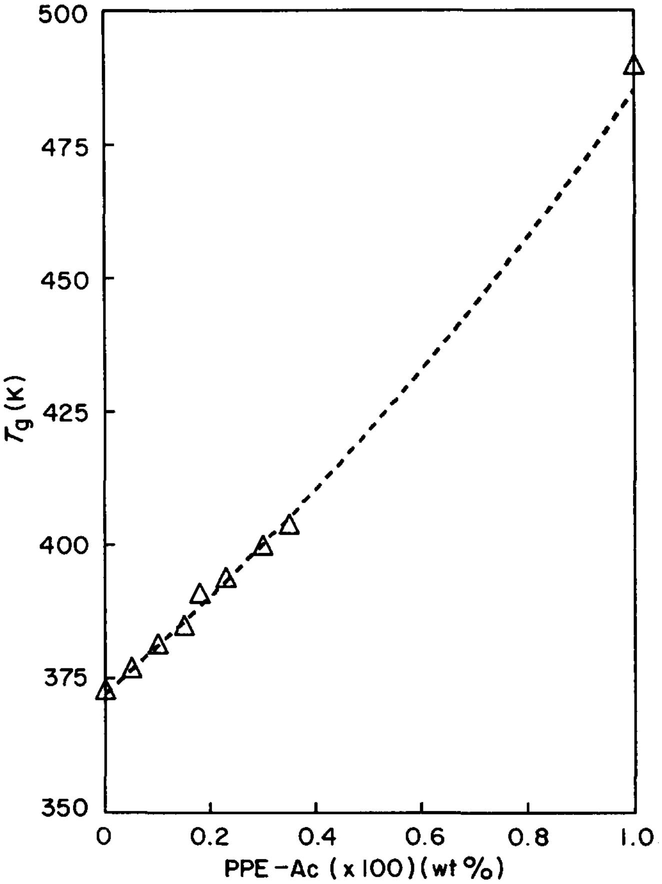


Figure 3 T_gs of PS/PPE blends: (△) experimental data and (– – –) according to the Fox equation

CONCLUSIONS

In contrast with the extrusion-(melt) blending process to obtain blends of PPE and (HI)PS, we have explored an alternative reaction blending route. The polymerization of styrene is significantly inhibited/retarded in the presence of PPE. However, for a successful preparation of these PPE/PS blends in the reactor, PPE is end-capped to avoid extensive chain transfer. Acetylation of PPE proves to be sufficient and an *in situ* preparation of PPE-Ac is presented, in which styrene is used as solvent in this reaction, leading to an end capping of the phenolic end group at room temperatures. This *in situ* modification to PPE-Ac is followed by a classical suspension polymerization of styrene. Full conversion is achieved resulting in transparent PPE/PS beads and the characteristics of the suspension polymerization of styrene are not influenced by the presence of PPE-Ac. Several advantages for this catalytic *in situ* end-group modification followed by reactive blending are envisaged:

1. The modification of PPE is carried out in styrene under mild reaction conditions at room temperature, leading to minimum side reaction.
2. It is an *in situ* acetylation, in which no purification or isolation of the PPE-Ac is needed, since the reaction ingredients are eliminated from the polymer beads in the suspension polymerization.
3. The suspension polymerization of styrene is not effected at all, leading to high yields of PS.
4. The blends prepared are completely homogeneous.

This novel approach using reactive blending offers great flexibility with respect to possible applications, for instance in high T_g PS foams[10,15].

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