BUTTERWORTH
HEINEMANN

Polymer Vol. 36 No. 5, pp. 1003–1007, 1995

0032-3861/95/$10.00+0.00

Polymer blends of polymethylphenylsilane with polystyrene and thermal properties of polymethylphenylsilane

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(Received 19 August 1994; revised 21 September 1994)

In attempting to melt blend polymethylphenylsilane (PMPS) and polystyrene, an unusual morphology was observed which led to a more detailed examination of the thermal and physical properties of PMPS. Thermogravimetric analysis shows that PMPS is stable under the conditions used for the melt mixing. For apparently the first time, the results of differential scanning calorimetry, dynamic mechanical thermal analysis and thermomechanical analysis are reported for PMPS. The curves obtained by these three techniques exhibit two thermal transitions at temperatures which are strongly molecular weight dependent. Optical microscopy and X-ray diffraction results show some evidence of the existence of long range ordered regions in PMPS. From the combination of thermal, microscopic and X-ray diffraction results, we assigned the first thermal transition to a glass transition and the second one, occurring at high temperature, to a phase-disordering transition accompanied by the softening of the polymer.

(Keywords: polymethylphenylsilane; polymer blends; thermal properties)

INTRODUCTION

In recent years polysilane polymers have been intensively studied because of their unusual electronic properties associated with σ-electron delocalization along the silicon backbone. This phenomenon, together with the development of high molecular weight soluble polysilanes, has led to widespread interest in their technological applications as silicon carbide fibre precursors[1–4], initiators for free radical polymerization[5–7], photoresists[8], photoconductors[9–12] and non-linear optical materials[13]. However, until now only two papers on polymer blends containing polysilanes and more conventional polymers have been published[14,15]. A study concerning polymer blends of poly(dimethylsilylene-*co*-phenylmethylsilylene) (PSS) with polystyrene and polypropylene was recently reported by West *et al.*[14]. They obtained good dispersions of up to 5% PSS with polystyrene, but with polypropylene some segregation of PSS was already observed above 1%. They also showed that blending of PSS with polystyrene improved some properties of the polymer. A little earlier, we considered the incorporation of polysilanes into blends and block copolymers with other polymer units[15] in order to improve the mechanical resistance of the polysilanes while reducing their cost and preserving their exceptional electronic properties. Since no study on that topic was reported in the literature at the beginning of our research, we started by doing a morphological analysis of the polymethylphenylsilane (PMPS)/polystyrene (PS) system, selected as a model system in order to get some data on the miscibility between these two polymers. The most common techniques for preparing blends are solution casting and melt mixing. Since the mixing process and the mixing temperature influence strongly the behaviour of the polymer blends, we analysed the morphology of PMPS/PS blends obtained by the two different methods mentioned above.

In this paper, we describe the morphology as observed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) of PMPS/PS blends of different compositions. The unusual morphology of the mixtures prepared by melt mixing led us to examine more carefully the thermal and physical properties of PMPS. Results obtained by thermogravimetric analysis (t.g.a.), differential scanning calorimetry (d.s.c.), dynamic mechanical thermal analysis (d.m.t.a.) and thermomechanical analysis (t.m.a.) are presented herein. In order to assign the two transitions observed by thermal analyses, further investigations on PMPS using polarizing microscopy and X-ray diffraction were carried out.

EXPERIMENTAL

Polymers

Polymethylphenylsilane (PMPS) was synthesized by thermal reductive coupling of the corresponding dichlorosilane with a dispersion of sodium in toluene. The solvent/non-solvent precipitation method was used for the fractionation of the crude polymer[16]. The non-solvent acetonitrile was slowly added with vigorous stirring to a solution of the polymer in toluene. The fractions were recovered by filtration and dried for three days at 60°C under vacuum. The polystyrene (PS) used

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Table 1 S.e.c. characteristics of PMPS and PS samples. Molecular weights are given in PS equivalents

Polymer	M_w	M_n	M_p	Molecular weight distribution
PMPS (1)	28 500	4 250	3 700	Unimodal
PMPS (2)	235 500	10 200	7 300 (LMW)[a] 548 400 (HMW)[b]	Bimodal (40% HMW)
PMPS (3)	653 000	283 000	651 000	Unimodal
PS	240 000	62 000	200 000	Unimodal

[a] Low molecular weight
[b] High molecular weight

in this study was a commercial polymer (Styron E680, lot number E0910403K28) from Dow with a T_g of 104°C by d.s.c.

Physicochemical characterization

Molecular weights of the polymers were determined by size exclusion chromatography (s.e.c.) at 25°C using Waters equipment consisting of five Ultrastyragel columns (10^6, 10^5, 10^4, 10^3 and 500 Å), a Waters 590 pump and a Waters 484 tunable absorbance ultra-violet (u.v.) detector set at 254 nm. Unstabilized tetrahydrofuran (THF) was used as the eluent at a flow rate of $0.8 \text{ cm}^3 \text{ min}^{-1}$. Data analyses were performed on a Digital Microvax 2000 computer with a Millipore Waters handling treatment. Polystyrenes were used for calibration, and therefore all average molecular weights are given in PS equivalents. Dynamic light scattering coupled to s.e.c.[17,18] showed a good correlation between polystyrene equivalents and absolute molecular weight. The characteristics of the initial PMPS and PS samples are summarized in *Table 1*.

Infra-red (i.r.) spectra were recorded on a Perkin–Elmer 1760X Fourier transform i.r. (*FT*i.r.) spectrophotometer from 4000 to 400 cm^{-1}. Samples were thin films of PMPS on an NaCl crystal. Data analyses were performed on an IBM PS/2 computer with Perkin–Elmer software.

Polymer blends

Polymethylphenylsilane was blended with polystyrene for 10 min under a flow of nitrogen and at a rotation speed of 50 rev min^{-1}. A home-made blending set-up equipped with an electrically heated mixing device of 6 cm^3 capacity was used. The blending temperatures were 190 and 250°C.

Electron microscopy

A Hitachi S570 scanning electron microscope was used to examine the fracture surfaces of cast PMPS/PS films. Polymer films were fractured in liquid nitrogen and coated with gold prior to analysis. A Philips EM 301 transmission electron microscope was used to examine PMPS/PS samples cut with an LKB Ultramicrotome III at room temperature and stained with RuO_4 vapour.

Thermal and physical properties

The thermal stability of the samples was investigated with a Perkin–Elmer TGA 7 thermogravimetric analyser. Nitrogen was used as the purge gas. The heating rate was $10°\text{C min}^{-1}$. The d.s.c. study of PMPS was carried out on two different instruments during the course of this work. At first, a Perkin–Elmer DSC-7 was used with a heating rate varying from 2 to $20°\text{C min}^{-1}$. Subsequently, measurements were carried out on a Seiko differential scanning calorimeter at a heating rate of $3°\text{C min}^{-1}$. D.m.t.a. was performed on a Rheometrics RSA II instrument. The special technique used in this work has been recently perfected in our laboratory and is reported elsewhere[19]. This technique shows a high sensitivity to detect thermal transitions in very thin polymer films. PMPS film specimens cast onto copper plates and sandwiched between two other copper layers were analysed over the temperature range 30–300°C at a heating rate of $2°\text{C min}^{-1}$. T.m.a. was performed on a Du Pont 2000 thermomechanical analyser using a penetration probe. T.m.a. was carried out on PMPS films in air at a heating rate of $10°\text{C min}^{-1}$.

Optical microscopy was performed on an Orthoplan Leitz Wetzlar microscope equipped with a Mettler hot stage and a Mettler FP 90 central processor. A small amount of PMPS powder sandwiched between a glass slide and a cover glass was placed on the hot stage of the optical microscope and heated to 260°C in order to form a homogeneous film. The sample was then cooled and heated three times at a scan rate of $10°\text{C min}^{-1}$ and observed through crossed polarizers.

Wide angle X-ray diffraction was performed on a Siemens Diffraktometer D5000. Spectra were recorded in the range 5–50° using a CuKα source.

RESULTS AND DISCUSSION

The analysis by SEM of fractured PMPS/PS films of different compositions (10–50 wt% PMPS (1)), obtained by solution casting from toluene and dichloromethane, reveals that these two polymers form a two-phase system. The dispersion of PMPS in the PS matrix is very coarse. Indeed, the dispersed phase size can reach 5–10 μm in a 50/50 blend[15]. Blends of identical composition and using the same starting homopolymers were prepared by melt mixing. Since Zeigler and coworkers[20,21] reported a value of 122°C for the T_g of PMPS, we first attempted to mix PMPS and PS in a Brabender at 190°C. The morphology observed by TEM for each ultramicrotomed PMPS/PS blend was very surprising and irregular for a mixture of two thermoplastics. In *Figure 1*, we present a TEM

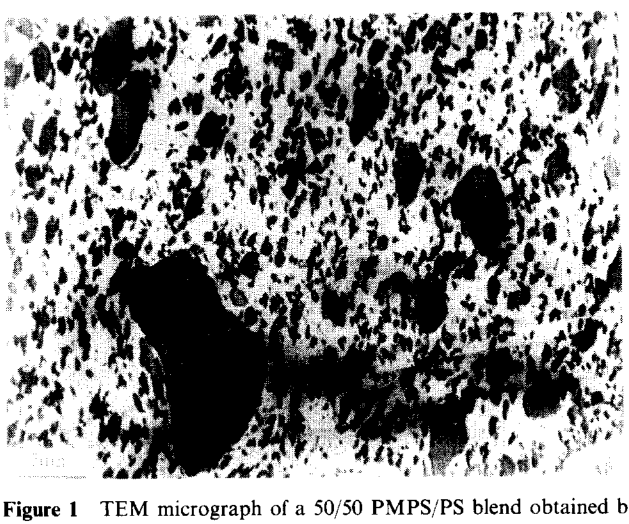

Figure 1 TEM micrograph of a 50/50 PMPS/PS blend obtained by mixing at 190°C

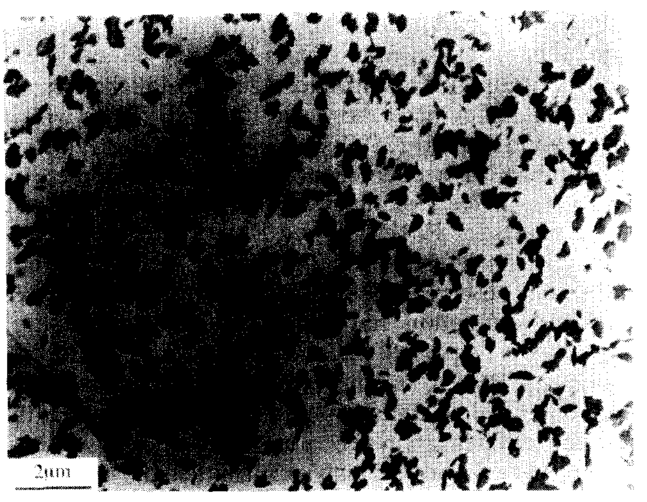

Figure 2 TEM micrograph of a 40/60 PMPS/PS blend obtained by mixing at 250°C

Table 2 Temperatures (°C) at which weight losses occur on heating in a thermogravimetric analyser at 10°C min^{-1} under nitrogen

	Weight loss					
Polymer	2%	5%	10%	25%	50%	Maximum
PMPS (1)	365	390	400	420	485	66% at 700°C
PMPS (2)	350	375	390	405	420	83% at 700°C
PMPS (3)	295	320	345	390	415	85% at 700°C
PS	305	325	340	360	380	100% at 425°C

micrograph of a 50/50 PMPS/PS blend. This picture shows a two-phase system with PMPS particles of non-spherical but elongated shape. A second trial of melt mixing was carried out at a higher temperature. At a mixing temperature of 250°C, as illustrated in *Figure 2* for a 40/60 PMPS/PS blend, PS and PMPS still form a two-phase system, but the PMPS particles are more homogeneously and finely dispersed in the PS matrix. However, the PMPS particle shapes are still unusual and very irregular. The morphology of PMPS/PS blends prepared by melt mixing suggests that PMPS is not soft enough to be processed even at 250°C, which is a temperature much in excess of the temperature reported by Zeigler and coworkers[20,21] as the T_g of PMPS.

In order to elucidate this unusual behaviour of PMPS upon heating, the thermal properties of PMPS were evaluated by means of t.g.a., d.s.c., d.m.t.a. and t.m.a.

First, we investigated by t.g.a. the thermal stability of PMPS under conditions similar to those used during the melt mixing. In a first set of experiments, the thermal degradation of PS and PMPS samples of different molecular weights (PMPS (1), (2) and (3)) was studied by t.g.a. These samples were placed in an aluminium pan and heated from 30 to 700°C at a scan rate of 10°C min^{-1} under a nitrogen atmosphere. Using these experimental conditions, thermogravimetric analyses of PMPS (*Table 2*) show almost no weight loss at temperatures below 300°C, and even at 700°C the weight loss does not reach 100%. PS presents a totally different thermogravimetric behaviour. PS is stable to 300°C, after which a rapid weight loss occurs which reaches 100% at 425°C.

In a second set of experiments, the thermal stability of PMPS at various temperatures was more careflully examined. PMPS (1) and PMPS (3) were heated at 200, 250 and 300°C for 0.5 h in a t.g.a. heater system. After this heat treatment, the samples were analysed by s.e.c. The results presented in *Tables 3* and *4* show that the high molecular weight PMPS is more sensitive to thermal decomposition. Jambe *et al.*[22] have already observed the same phenomenon for polymethyl-n-hexylsilane.

Nevertheless, PMPS samples of low (PMPS (1)) and high (PMPS (3)) molecular weight are not strongly degraded upon heating for a short time at 200 or 250°C. These temperatures correspond to the mixing temperatures used to prepare PMPS/PS blends. The *FT*i.r. spectra of the samples heated at 200, 250 and 300°C for 0.5 h were recorded. They only present minor changes in the 1000–1100 cm^{-1} region, indicating a weak incorporation of oxygen into the polysilane chains and formation of a few Si–O–Si linkages. Recently, Kim and Matyjaszewski[23] reported conditions under which the molecular weight of PMPS is affected by thermal treatment. Oxidation, which is evidence of competing reactions, occurs at a higher rate in their experimental conditions than in ours.

While these experiments demonstrate that the morphology observed for melt-mixed PMPS/PS blends does not come from thermal degradation of the polymers, they yield no information on the phase transitions occurring in PMPS upon heating. Therefore subsequent thermal analyses using d.s.c., d.m.t.a. and t.m.a. were carried out. This seems to be the first time that such measurements have been reported for PMPS.

D.s.c. is often used to determine thermal transitions. Samples of PMPS (1) were sealed in an aluminium pan. At first, we tried to detect phase transitions using a Perkin–Elmer DSC-7. The PMPS was heated between 30 and 280°C at different scan rates ranging from 2 to 20°C min^{-1}. With this instrument, no clear transitions were observed. Further characterization of PMPS was carried out using a Seiko d.s.c. instrument. The sample was heated from 40 to 280°C at a scan rate of 3°C min^{-1}. The resulting d.s.c. curve (*Figure 3*) exhibits two broad thermal transitions. The midpoints of these transitions are situated at 96 and 194°C.

These transitions are also evident in the d.m.t.a. data presented in *Figure 4*. The tan δ curve exhibits two peaks

Table 3 Thermal stability of PMPS (1) at various temperatures

Temperature (°C)	Weight loss (%)	M_w	M_n	M_p
No heating		28 500	4250	3700
200	0	24 750	4100	4000
250	0.2	24 000	3100	3400
300	3.6	28 900	2290	2980

Table 4 Thermal stability of PMPS (3) at various temperatures

Temperature (°C)	Weight loss (%)	M_w	M_n	M_p
No heating		653 000	283 000	651 000
200	0.3	648 000	270 000	593 000
250	4.6	598 000	256 000	513 000
300	17.2	472 000	195 000	314 000

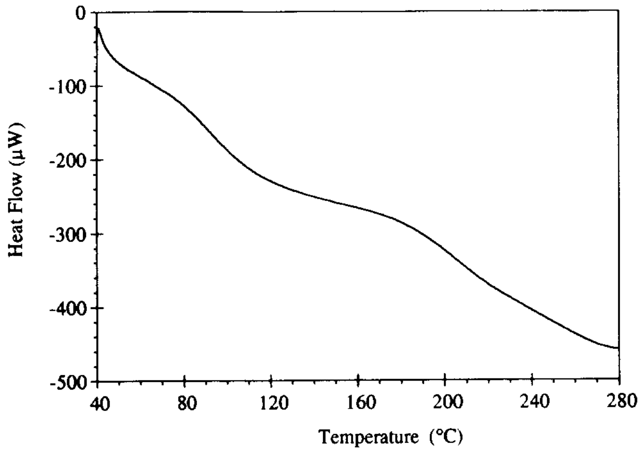

Figure 3 D.s.c. thermogram of PMPS (1) heated at 3°C min^{-1}

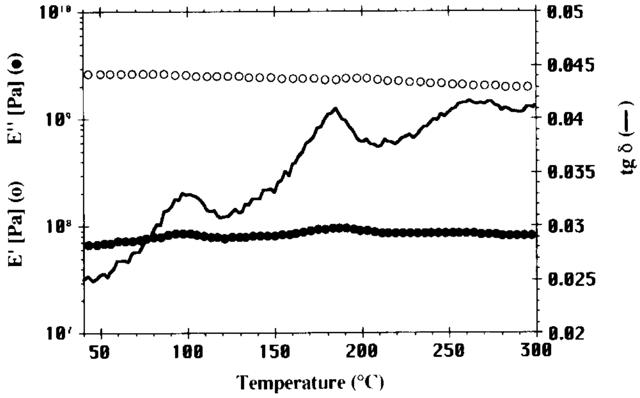

Figure 4 D.m.t.a. plots for PMPS (1) heated at 2°C min^{-1}

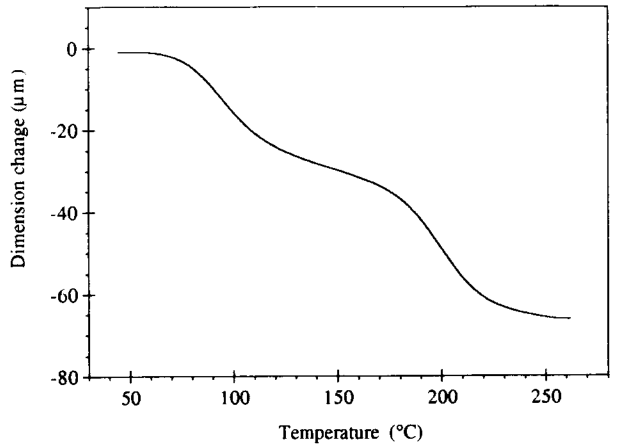

Figure 5 T.m.a. curve of PMPS (1) heated at 10°C min^{-1}

at 97 and 185°C. These d.m.t.a. results were obtained by a particular method perfected in our laboratory[19] and briefly described earlier.

T.m.a. was used to determine the melting behaviour of PMPS as the temperature was raised at a heating rate of 10°C min^{-1}. The t.m.a. curve (*Figure 5*) of PMPS (1) shows a first thermal event between 60 and 125°C with a midpoint situated around 90°C and a second one starting at 150°C and ending at 250°C with a midpoint at around 200°C. The t.m.a. curve (*Figure 6*) of the higher molecular weight sample (PMPS (3)) exhibits two better-separated transitions occurring at higher temperatures. The first transition occurs between 70 and 150°C with a midpoint at around 120°C and the second transition takes place between 200 and 250°C with a midpoint at around 225°C. This increase of the transition temperatures is a phenomenon classically observed for polymers. *Table 5* summarizes the d.s.c., d.m.t.a. and t.m.a. results for PMPS (1) and PMPS (3).

In order to establish the nature of the thermal transitions observed in PMPS, this polymer was analysed by X-ray diffraction and optical microscopy. Maxka[24] has already reported on the existence of crystalline regions in PMPS, but nevertheless PMPS has always been described as an amorphous polymer. However, the powder diffractogram we got indicates that ordered regions do exist in this polymer. Indeed, the PMPS (1) X-ray diffraction pattern[25] recorded at room temperature is dominated by four rather sharp reflections at 9.3, 8.7, 5.3 and 4.3 Å and a broad one peaking at about 3.5 Å.

Optical microscopy analysis of PMPS was also performed. A powder sample of PMPS (1) was placed between two glass slides on the hot stage of the microscope. To form a homogeneous film, the temperature was raised from room temperature to 260°C, the temperature at which the polymer freely flows. The sample was cooled at a rate of 10°C min^{-1} down to room temperature. Then, while the temperature was increased at a heating rate of 10°C min^{-1} from room temperature to 260°C, the PMPS sample was observed through crossed polarizers. At the beginning of this heating run, the PMPS was birefringent. At about 150°C the birefringence started to decrease and progressively went on decreasing upon further heating but did not vanish

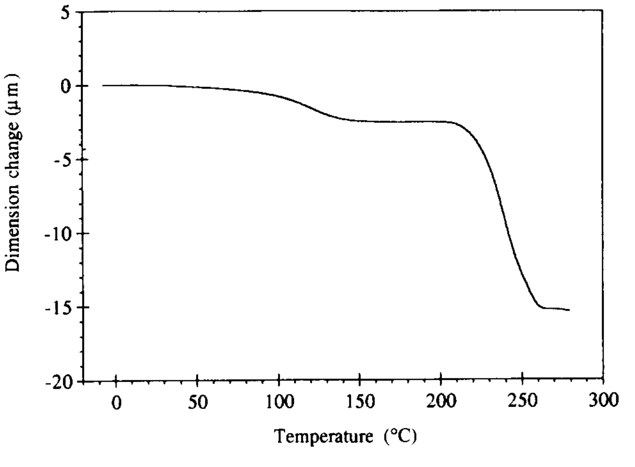

Figure 6 T.m.a. curve of PMPS (3) heated at 10°C min^{-1}

Table 5 Thermal transitions of PMPS (1) and PMPS (3)

	Transition temperature (°C)			
	PMPS (1)			PMPS (3)
	D.s.c.[a]	D.m.t.a.[b]	T.m.a.[c]	T.m.a.[c]
First transition	96	97	90	120
Second transition	194	185	200	225

[a] Determined at a heating rate of 3°C min^{-1}
[b] Determined at a heating rate of 2°C min^{-1}
[c] Determined at a heating rate of 10°C min^{-1}

completely. Above 235°C the polymer melted, becoming freely flowing at 260°C. Upon cooling, the PMPS sample showed a gradual increase in birefringence starting at around 195°C. The phenomenon was quite reversible since reproducible observations were made upon three successive heating and cooling runs. The temperature range in which the decrease in birefringence upon heating or the increase upon cooling occurs is similar to the temperature range in which the second transition was observed by d.s.c., d.m.t.a. and t.m.a. (*Table 5*). On the other hand, in the temperature range corresponding to the first transition previously observed by thermal analysis (*Table 5*), no visible phenomenon took place.

From the thermal, microscopic and X-ray diffraction analyses presented in this paper, we assign the first thermal transition occurring at about 95°C for the low molecular weight (LMW) PMPS and at about 120°C for the high molecular weight (HMW) polymer to a glass transition. The value of the HMW T_g is in quite good agreement with the value reported by Zeigler and coworkers[20,21]. Secondly, the broad transition occurring between 150 and 250°C is tentatively assigned to a phase-disordering transition accompanied by the softening of the polymer. Indeed, in this temperature range a decrease in birefringence upon heating was seen by polarizing microscopy and the beginning of polymer softening was observed at about 235°C. Further research is needed to provide a more detailed understanding of the various phases of PMPS. The structure of PMPS at various temperatures is under investigation by X-ray diffraction. Further characterization by d.s.c. and microscopic techniques will also be carried out.

CONCLUSIONS

Blends of PMPS with PS prepared by melt mixing either at 190 or 250°C present an unusual morphology for a mixture of two thermoplastics. In order to elucidate this phenomenon, the thermal and physical properties of PMPS were carefully examined. From the t.g.a. and s.e.c. analyses, it clearly appears that PMPS and PS are still stable at 250°C and that the irregular morphology observed for melt-mixed PMPS/PS blends does not come from thermal degradation of the polymers. The investigation of PMPS thermal behaviour by d.s.c., d.m.t.a. and t.m.a. shows that two rather broad transitions occur. The first one takes place at around 95°C and the second one at around 195°C for the low molecular weight PMPS (1). These transitions occur at higher temperatures for the high molecular weight fraction PMPS (3). The wide angle X-ray diffractogram of PMPS powder at room temperature exhibits essentially two rather sharp reflections, indicating that some long range ordering does exist in this polymer. A study by optical microscopy showed that PMPS is birefringent. Upon heating the birefringence decreased in the temperature range corresponding to the second thermal transition. Thus, we conclude that this second transition is probably a phase-disordering transition accompanied by the softening of the polymer and that the first transition may be associated with a glass transition. The long range ordered regions which persist well above the T_g and which are probably instrumental in the increase in PMPS softening temperature are surely responsible for the problems encountered during PMPS processing. Since we attempted to mix PS and PMPS at 190 and 250°C, both of which are under the temperature at which PMPS flows freely (260°C), the PMPS was still too rigid and could not be efficiently mixed with PS. However, it seems critical to attempt melt mixing at higher temperatures since thermal degradation becomes rather important above 250°C.

ACKNOWLEDGEMENTS

We are grateful to Professor R. Legras and J. J. Biebuyck for helpful discussions. Thanks go to D. Roedolf from TA Instruments for the t.m.a. measurements. We also thank B. van der Heyden and M. Sclavons for their assistance in acquiring d.s.c. and d.m.t.a. data. S.D.-C. thanks the Belgian National Fund for Scientific Research for her Research Assistant position.

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