Macromolecules 1987, *20*, 1627–1630 1627

Temperature Dependence of Poly(phenylsiloxane) Fluorescence. 1. Comparison of Poly(methylphenylsiloxane) with Its Dimeric and Monomeric Model Compounds

C. Salom,[†] M. R. Gomez-Antón,[‡] A. Horta,[§] I. Hernández-Fuentes,[†] and I. F. Piérola*[†]

Departamento de Química-Física, Facultad de Ciencias Químicas, Universidad Complutense, Madrid 28040, Spain, and Departamento de Tecnología Aplicada, ETSII, and Departamento de Química General y Macromoléculas, Facultad de Ciencias, UNED, Madrid 28040, Spain. *Received September 30, 1986*

ABSTRACT: The dependence on temperature of the poly(methylphenylsiloxane) (PMPS) fluorescence has been studied in the interval 5–60 °C and compared with other similar systems. The excimer to monomer intensity ratio (I_E/I_M) of PMPS dilute solutions shows linear Arrhenius plots with positive slope, but I_E and I_M separately give double linear plots with break points ascribed to a transition temperature. Such behavior has not been found for polystyrene solutions which give single lines for the three magnitudes. In order to interpret the origin of the transition behavior of PMPS, the fluorescence of low molecular weight compounds serving as models for the dimeric and monomeric units of the PMPS chain has also been studied. The dimeric analogue, 1,3-diphenyltetramethyldisiloxane (DS), reproduces the habit of the PMPS Arrhenius plots with a more abrupt discontinuity for I_M. The monomeric analogue, methoxydimethylphenylsilane (MS), gives I_M Arrhenius plots formed by single lines, without any discontinuity. Both PMPS and DS show an isosbestic point below the transition temperature that disappears above it. To explain those results, a polymer effect has been ruled out. It seems more likely that at the transition temperature, T_t, a new mechanism for excimer dissociation with higher activation energy begins to be operative.

Introduction

The excimer to monomer intensity ratio (I_E/I_M) of aromatic synthetic polymers is temperature dependent. Arrhenius plots of I_E/I_M in a broad temperature range show usually[1–7] a maximum with two limits of linear behavior: those of low and high temperatures. At low temperature, it is generally assumed that excimer dissociation is negligible and the slope of the I_E/I_M Arrhenius plot provides then the activation energy for excimer formation.

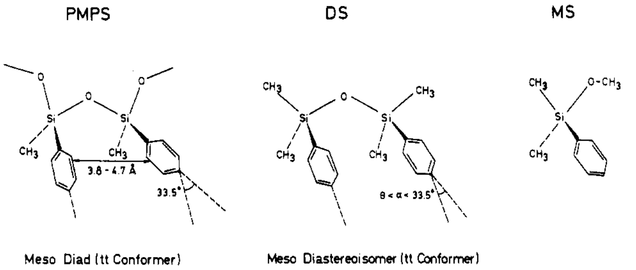
In the high-temperature limit, it is supposed that there is an apparent excited state equilibrium between monomers and excimers and therefore the excimer binding enthalpy is calculated from the I_E/I_M Arrhenius plot. This hypothesis has been severely criticized.[7b] It has been accepted for small molecules that exhibit an isoemissive point,[1] but in polymer solutions radiationless decay of monomer and excimer plays an important role and the isoemissive point is usually not observed at high temperature because the excited state apparent equilibrium is disturbed.

Poly(methylphenylsiloxane) (PMPS) fluorescence spectra show monomer and excimer emissions in dilute solution.[8] In this work we have found that it gives linear I_E/I_M plots typical of the high-temperature limit, in the interval 5–60 °C. But I_M and I_E separately give, in contrast, abrupt discontinuities that have not been found, for example, for polystyrene (PS), the organic-backbone polymeric analogue of PMPS. In order to determine whether it is a polymer effect or not, in this work we compare the temperature dependence of the PMPS fluorescence spectrum with those of its dimeric and monomeric model compounds.

Experimental Section

PMPS was kindly provided by Dow Corning Co. (M_w = 1.15 × 10^5, M_w/M_n = 1.71 after fractionation).[8] The monodisperse PS sample was from Pressure Chemical Co. (M_n = 1.11 × 10^5, M_w/M_n = 1.05). Both were purified by precipitation to eliminate monomer impurities.

Scheme I



Solvents used, cyclohexane (Ch) and dioxane (Dx) of special quality for fluorescence, were purchased from Carlo Erba.

1,3-Diphenyltetramethyldisiloxane (DS) and methoxydimethylphenylsilane (MS) (Scheme I) have been synthesized with chlorodimethylphenylsilane (CS) from Fluka A. G. To prepare the dimeric analogue DS, the reagent CS is mixed with ethanol–potassium hydroxide. The reaction is fast and occurs with phase separation. The most viscous phase is separated and dissolved in cyclohexane (Ch). The DS solution is then washed several times with water, dried with $MgSO_4$, and concentrated by solvent evaporation. The final product has been characterized by IR, ^1H NMR, and mass spectrometry. The monomeric model compound MS has been obtained by dripping CS into a large volume of dioxane–methanol with 10% v/v alcohol. Once isolated by solvent evaporation, MS has been characterized by IR spectroscopy. Fluorescence and absorption spectra confirm that MS is free of DS contamination.

UV absorption spectra were recorded with a Shimadzu UV-240 spectrophotometer. Fluorescence spectra were taken on a Perkin-Elmer LS-3 emission spectrophotometer. Two experiments with aerated and oxygen-free solutions were run. Nitrogen bubbling increases the emission intensity by about 20% but does not modify the temperature dependence more than the experimental error. Solutions with optical density of about 0.5 have always been employed. Monomer and excimer emission intensities were measured as the height of the corresponding peaks at the wavelength of the maximum (285 and 325 nm, respectively). Attempts to correct the emission intensities for spectral overlap have also been made. The mutual influence of monomer and

---

[†] Universidad Complutense.

[‡] Departamento de Tecnología Aplicada, ETSII, UNED.

[§] Departamento de Química General y Macromoléculas, Facultad de Ciencias, UNED.

0024-9297/87/2220-1627$01.50/0

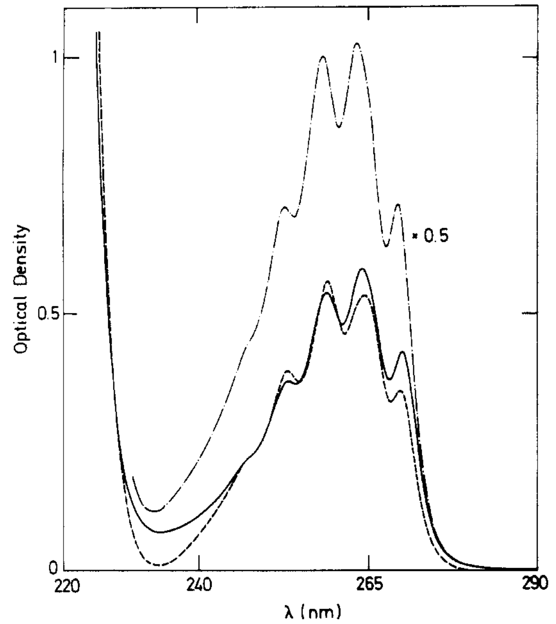


Figure 1. Absorption spectra of PMPS (-·-) and DS (---) in Ch solution and MS (—) in Dx.

excimer bands at their respective maxima has been calculated using as references the spectra of MS and of a PMPS unswollen network which gives only excimer emission.[8] The following relations result for corrected excimer (I_E) and monomer (I_M) fluorescence intensities:

$$I_E = I_{325} - 0.30 I_{285}$$

$$I_M = I_{285} - 0.10 I_{325}$$

Uncorrected I_E and I_M values (I_{325} and I_{285}, respectively) give the same temperature dependence. The slopes of the Arrhenius plots and the transition temperatures calculated with corrected and uncorrected intensities differ in no more than the experimental error.

Results

Absorption spectra of PMPS dilute solution overlap with those of DS and MS with only slight differences in the vibrational resolution (Figure 1). Fluorescence spectra of PMPS and DS dilute solutions show excimer and monomer emissions. The electronic spectra of siloxanes are analyzed in ref 8.

The ratio I_E/I_M is, as expected, larger for the homopolymer than for DS: at 25 °C, in Ch oxygen-free solutions, with optical density of 0.51 in both cases, I_E/I_M is 5.1 for PMPS and 1.55 for DS. Dilute solutions of MS give only monomer emission peaking at 285 nm.

Figures 2–4 show the temperature dependence of the PMPS fluorescence intensity compared with that of polystyrene (PS), DS, and MS dilute solutions. Arrhenius plots of the I_E/I_M ratio are linear for the three cases considered (Figure 2), but the slopes are of different signs, which means that excimer dissociation plays a different role for PS and for siloxanes.

Arrhenius plots of monomer and excimer emissions (Figures 3 and 4) for PMPS and DS show a bending point that is not found for PS and the monomeric model compound MS. The parallelism of the observed behavior for PMPS and DS means that no polymer effect is responsible for those discontinuities. Likewise, it is not a transition intrinsic to the chromophore, since MS displays a normal behavior. Two possible explanations remain: at the temperature of the discontinuity, that we will call transition

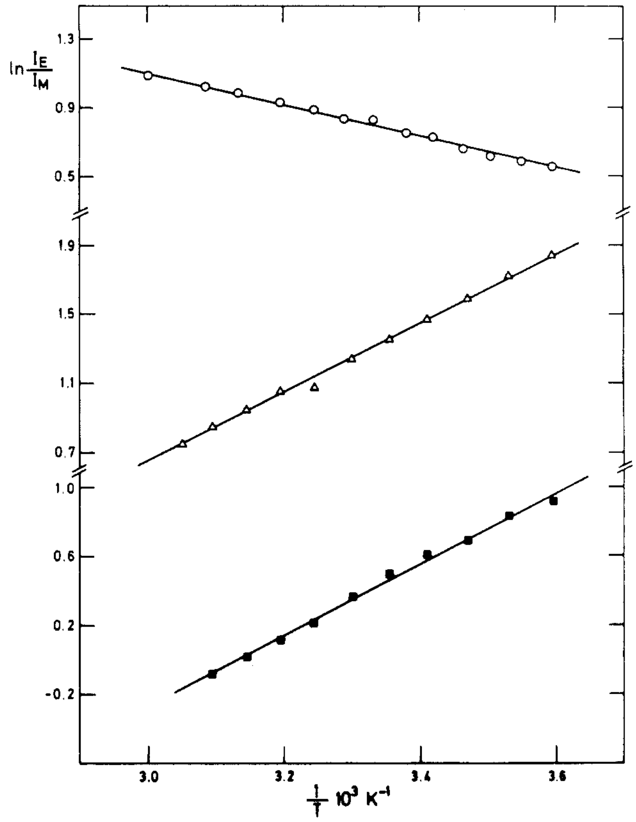


Figure 2. Arrhenius plot of the excimer to monomer intensities ratio for (○) PS in Dx, (△) PMPS in Ch, and (■) DS in Ch.

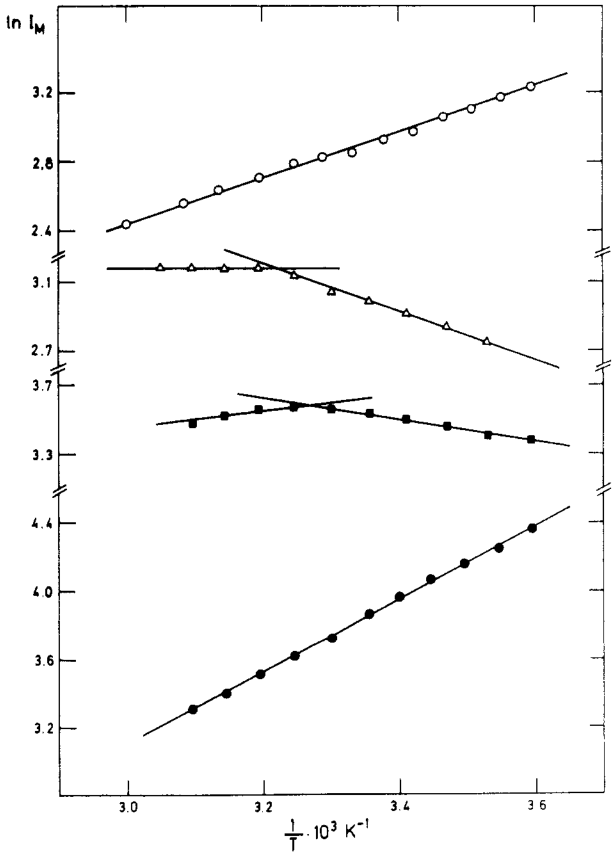


Figure 3. Arrhenius plot of the monomer emission intensity for (○) PS in Dx, (△) PMPS in Ch, (■) DS in Ch, and (●) MS in Dx.

temperature (T_t), a new interaction between couples of neighbor phenyl rings is activated (a) in the ground or (b) in the excited state.

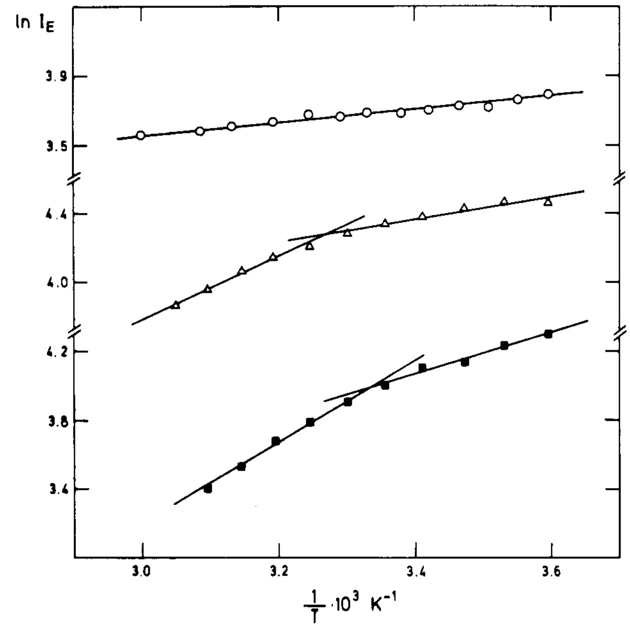


Figure 4. Arrhenius plot of the excimer emission intensity for (○) PS in Dx, (△) PMPS in Ch, and (■) DS in Ch.

Discussion

Temperature dependences of photophysical magnitudes with abrupt changes of slope, similar to those of Figures 3 and 4, have been previously reported for other systems. It can be observed, for example, in ref 4 and 1b for poly(vinylcarbazole). It has also been found for naphthyldisilanes[9] in dilute solutions, for the dimeric model compounds of polystyrene,[10] and for a number of probe molecules in polymer substrates.[11-14] Poly(1-vinylnaphthalene) and poly(acenaphthalene) show also marked discontinuities in nonlinear Arrhenius plots of I_E and I_M.[1a]

A general conclusion can be drawn from the previous cases: above the transition temperature, a new mechanism of higher activation energy is activated. Such a new mechanism is a fast intersystem crossing process in the case of disilanes.[9] It corresponds to the onset of polymer lateral groups rotation for phosphorescent probes in solid polymer matrices,[11] and it is related to the second excimer in poly(vinylcarbazole).[1b]

Some specific features must be considered to explain the nature of the siloxanes transition. PMPS and DS show an isosbestic point at temperatures below T_t that disappears above it (Figure 5). Isosbestic points are frequent in the low-temperature regime,[1,3,15] but they are rarely observed for polymers in the high-temperature limit. They indicate the existence of an excited state equilibrium between excimers and monomers in the first singlet excited state.[16] In terms of rate constants and according to the Birks scheme,[7] in the temperature range in which the isosbestic point is observed ($T < T_t$), excimers formation and dissociation are thermally activated processes,[15] while the rate constants for nonradiative decay are independent of temperature.[1,3]

We must therefore conclude that below T_t, DS and PMPS monomer emission intensity increases with increasing temperature because excimers dissociate to excited state monomer. Above T_t, the excited state equilibrium is broken because thermal energy is then sufficient to activate excimer nonradiative decay by dissociation to ground state monomer. As a consequence, monomer emission no longer increases by increasing the temperature and the isosbestic point disappears (Figure 5). Some more studies on the nature of this high-temperature radiationless deactivation mechanism would be necessary. Dielectric and viscosity measurements on poly(phenylsiloxanes) show abrupt changes of dipole moment and intrinsic viscosity at temperatures close to T_t,[17] and therefore, cooperative motions in backbone chain bonds[18] will be considered as a possible explanation of the observed phenomenon in siloxane solutions.

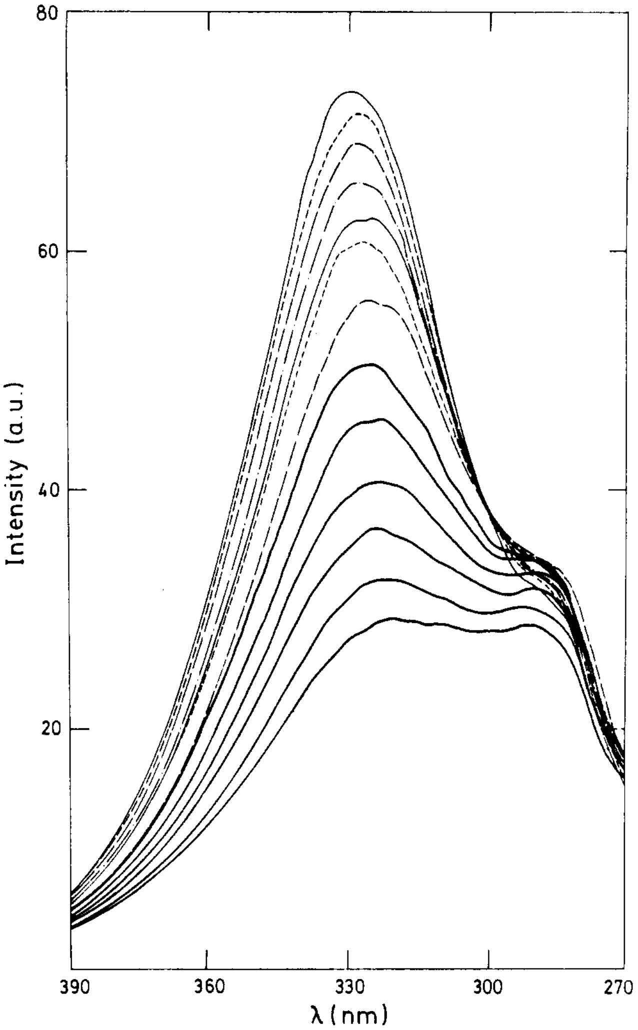


Figure 5. Temperature dependence of the emission spectrum for DS in dilute oxygen-free Ch solution. When the temperature is increased from 5 to 60 °C, I_t decreases. Excitation wavelength, 260 nm.

Acknowledgment. Financial support from CAICYT, Spain, under Grants 0933/81 and 1726/82 is gratefully acknowledged.

Registry No. DS, 56-33-7; MS, 17881-88-8.

References and Notes

(1) David, C.; Piens, M.; Geuskens, G. *Eur. Polym. J.* **1972**, *8*, (a) 1019, (b) 1291.
(2) Harrah, L. A. *J. Chem. Phys.* **1972**, *56*, 385.
(3) Tazuke, S.; Ooky, H.; Sato, K. *Macromolecules* **1982**, *15*, 400.
(4) Skilton, P. F.; Ghiggino, K. P. *Polym. Photochem.* **1984**, *5*, 179.
(5) Ishii, T.; Handa, T.; Matsunaga, S. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 811.
(6) Bokobza, L.; Monnerie, L. *Polymer* **1981**, *22*, 235.
(7) (a) Phillips, D. *Polymer Photophysics*; Chapman and Hall: London, 1985. (b) Guillet, J. E. *Polymer Photophysics and Photochemistry*; Cambridge University: New York, 1985. (c) Semerak, S. N.; Frank, C. W. *Adv. Polym. Sci.* **1983**, *54*, 31.
(8) Salom, C.; Horta, A.; Hernândez-Fuentes, I.; Piérola, I. F. *Macromolecules* **1987**, *20*, 696.
(9) Shizuka, H.; Obuchi, H.; Ishikawa, M.; Kumada, M. *J. Chem. Soc., Faraday Trans. 1* **1984**, *80*, 383.
(10) De Schryver, F. C.; Moens, L.; Van der Auweraer, M.; Boens,

N.; Monnerie, L.; Bokobza, L. *Macromolecules* **1982**, *15*, 64.
(11) Smit, K. J.; Sakurovs, R.; Ghiggino, K. P. *Eur. Polym. J.* **1983**, *19*, 49.
(12) Beavan, S. W.; Hargreaves, J. S.; Phillips, D. *Adv. Photochem.* **1979**, *11*, 207.
(13) Rutherford, H.; Soutar, I. *J. Polym. Sci., Polym. Phys. Ed.* **1977**, *15*, 2213.
(14) Somersall, A. C.; Dan, E.; Guillet, J. E. *Macromolecules* **1974**, *7*, 233.
(15) Goldenberg, M.; Emert, J.; Morawetz, H. *J. Am. Chem. Soc.* **1978**, *100*, 7171.
(16) Aspler, J. S.; Guillet, J. E. *Macromolecules* **1979**, *12*, 1082.
(17) Salom, C.; Hernândez-Fuentes, I., unpublished results.
(18) Tanabe, Y. *J. Polym. Sci., Polym. Phys. Ed.* **1985**, *23*, 601.

Glass Transition and Melting Behavior of Poly(oxy-2,6-dimethyl-1,4-phenylene)

Stephen Z. D. Cheng* and Bernhard Wunderlich

Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York 12181-3590.
Received September 26, 1986

ABSTRACT: Thermal analysis of amorphous and semicrystalline poly(oxy-2,6-dimethyl-1,4-phenylene) (PPO) has been carried out from 220 to 580 K. In the solid state, glassy and semicrystalline PPO were shown to have the same heat capacity up to 420 K (±1.6%, 25 samples, 30 measurements). Liquid PPO follows a linear heat capacity dependence (400–580 K, ±1.5%, 25 samples, 30 runs). Both sets of new data agree with the "Athas recommended data (1985) and (1980)", respectively so that no new recommendation is made (deviation from the recommended solid and liquid data: −0.3% ± 0.5% and +0.25% ± 0.003%, respectively). Based on the confirmed heat capacities, a detailed glass and melting transition study has been performed. Crystals of PPO are, as is well-known, rather imperfect, and it is shown here that they are coupled to a large fraction of "rigid-amorphous" polymer, which, in turn, governs the crystal annealing. Hysteresis at the glass transition, low heat capacity below the glass transition of as-polymerized samples, and decrease in crystallinity with increase in crystal perfection on annealing below the melting temperature are described and discussed.

Introduction

Poly(oxy-2,6-dimethyl-1,4-phenylene) (PPO) has been a commercially important polymer since its discovery over 20 years ago.[1,2] Thermal properties of the homopolymer have first been measured by Karasz et al.,[3] using adiabatic calorimetry.

From 80 to 420 K, it was shown that semicrystalline and amorphous solid PPO had within experimental error identical heat capacities, C_p. Since then the measurements have been repeated and fitted to the vibrational spectrum of solid PPO.[4-6] The group vibrations were approximated by single frequencies and box distributions, while the five skeletal vibrations were described by the $\theta_1 = 564$ K and $\theta_3 = 40$ K temperatures in a Tarasov equation.[4]

Above the glass transition temperature, T_g, at 482 K, the liquid amorphous PPO has a higher heat capacity. The increase in ΔC_p at T_g for amorphous PPO was first reported[3,6] to be 28.8 J/(K mol), close to the present Athas recommended value of 31.9 J/(K mol).[4,5] A suggested absence of the glass transition for a 25% crystalline sample[3] (by X-ray) was surprising and will be shown below to be caused by the existence of "rigid-amorphous" PPO. A large number of additional C_p measurements for solid and liquid PPO which are in agreement with the prior work will be presented in this research report.

The semicrystalline PPO analyzed by Karasz et al.[3] showed a somewhat smaller heat capacity in the temperature range from 420 to 482 K than the expected one for solids. It will be shown here that this is a repeatable phenomenon, although short-time annealing will increase the heat capacity to the expected value. An alternative explanation to the original suggestion of some crystallization below T_g will be offered.

A melting transition endotherm at 510 K was seen for the semicrystalline PPO.[3] From the end of melting, a first estimate of the equilibrium melting temperature was made to be 535 K. Such low melting temperature, T_m, leads to the unusually high T_g/T_m ratio of 0.9 (attributed originally to a low entropy of fusion). More recent extrapolations[7-9] led to estimates ranging from 563 to 583 K for the equilibrium melting temperature, $T_m{}^\circ$. Heats of fusion, $\Delta h_f{}^\circ$, were difficult to assess since PPO crystallizes frequently with incorporation of solvent molecules into the crystal.[9,10] Values of 3–10 kJ/mol have been reported (extrapolated to 100% crystallinity).[3,7,11,12] For the present work it was decided that the most recent values of van den Berg and co-workers[9] are perhaps most reliable ($T_m{}^\circ = \sim 580$ K, $\Delta h_f{}^\circ = 5.95$ kJ/mol).

A wide application of PPO involves compatible blends, in particular with polystyrene.[2] The thermal properties of isotactic polystyrene blended with PPO have been reported as a eutectic system.[13-16] By use of mainly mechanical analysis, blends with nylon 66 have been studied.[17] Effects of bromine[18,19] and phosphonyl[19] substitution on the phenylene group on the glass transition have also been investigated by thermal analysis.

Solution crystallization of PPO was studied,[9,20] and the morphology of the resulting crystals has been reported.[10] It is generally accepted that solvent molecules are incorporated into the PPO crystal.[7] Removal of the solvent on drying leaves severely distorted and defect crystals.[7,10] Melt crystallization, in contrast, has received less attention.[8] It was not possible to crystalline PPO melt in the narrow temperature range between T_g and T_m in isothermal experiments of 8-h duration. It is reported, however,[8] that nucleating agents such as anthraquinone or 2-mercaptobenzimidazole can cause crystallization with Avrami exponents of 1.6. Exposure to solvent vapors, such as 2-butanone, also leads to crystallization.[10]

Compared to other phenylene-containing macromolecules such as poly(ethylene terephthalate),[21] poly(oxy-1,4-phenyleneoxy-1,4-phenylenecarbonyl-1,4-phenylene) (PEEK),[22] and poly(thio-1,4-phenylene) (PPS),[23] the thermal properties of PPO were less well understood. The

0024-9297/87/2220-1630$01.50/0