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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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To cite this Article Schulzet, T. , Saini, A. K. , Labreque, D. and Patterson, H. H.(1997) 'Curing Studies of New Polyimide Model Compounds with Molecular Weights of About 1000 g/MOL', *Journal of Macromolecular Science, Part A*, 34: 9, 1535 – 1552

To link to this Article: DOI: 10.1080/10601329708010025

URL: <http://dx.doi.org/10.1080/10601329708010025>

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CURING STUDIES OF NEW POLYIMIDE MODEL COMPOUNDS WITH MOLECULAR WEIGHTS OF ABOUT 1000 G/MOL

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Key Words: Polyimides; Oligomer model compounds; Raman spectroscopy, FT-IR spectroscopy; Imine links

ABSTRACT

Two new polyimide model compounds with molecular weights of ~ 1000 g/mol have been synthesized. While the amino terminated compound, 4,4'-bis-N-[N'-(4-aminophenoxy-4'-phenyl)-pyromellitimido]diphenylether, O(PO)₂, undergoes a branching or crosslinking side reaction, the corresponding anhydride terminated oligomer N,N'-bis[4(N-(3',4'-bishydroxycarbonyl)phthal-imido)phenoxy-4'-phenyl]pyromellitimide dianhydride, P(OP)₂, loses its anhydride functionality completely upon thermal treatment. In the case of O(PO)₂, the formed C=N species can be detected with Raman spectroscopy rather than FT-IR spectroscopy because of its low molecular absorptivity in the infrared region. The formation of imine bonds caused by the attack of terminal amino groups on the imide carbonyl group is evident by the appearance of peaks at about 1665 cm⁻¹ in the Raman spectra. The same behavior can be observed in bulky polyimides blended with an increasing amount of O(PO)₂ upon curing.

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INTRODUCTION

Polyimides are a class of thermally stable polymers which are usually produced by a two-step synthesis involving the polyaddition of dianhydrides and diamines followed by a subsequent thermal treatment of the intermediate poly(amic acid)s to achieve the ring closure to polyimides [1]. Although the extent of the imide ring formation is known to be almost quantitative, a number of side reactions are likely, since the mechanism of conversion consists of a variety of reversible reaction steps [2]. These undesired reactions can occur either during the imide ring closure e.g., as intermolecular amide links [3], or after the completion of the imide formation as crosslinking reactions leading to imide or hydrazide links as well as benzophenone-type bonds between imide chains after bond homolysis [4]. Knowledge of all the processes taking place during polyimide curing is of major interest because of industrial applications. Branching or crosslinking reactions will change the material properties significantly and irreversibly.

In 1988, Walker published the first successful chromatographic separation of oligo(amic acid)s ($O(PO)_n$ with $n = 0, 1, 2, 3$, etc.) obtained from non-stoichiometric mixtures of 4,4'-oxydianiline (O) and pyromellitic dianhydride (P) [5]. His statement that slight imbalances in the starting material weights can produce short chain oligomers, and our results [6,7] obtained from vapor deposited poly[N,N'-bis-(phenoxyphenyl)pyromellitimide], led us to the investigation of short chain amino- (OPO) and anhydrido- (POP) terminated oligomers [8, 9]. Based on a proposed side reaction [10] of the attack of terminal amino groups to imide carbonyl groups and further imine formation, we found that amino-terminated rather than anhydride-terminated model compounds undergo such imide-imine conversions. The peaks that appear at 1665 cm^{-1} and 1740 cm^{-1} in the Raman spectra as the curing temperature increases have been assigned to C=N and C=O bonds in the same ring, respectively. The C=N bonds cannot be seen in the IR spectra as long as their concentration remains low because of their low molecular absorptivity.

In addition, we were able to show that all imide carbonyl bonds in a model compound can be converted into imine linkages. Using N,N'-bis(phenoxyphenyl)-pyromellitimide as a substrate and treated with an excess of phenoxyaniline, 4 different species having 1, 2, 3, and 4 C=N instead of C=O carbonyl bonds could be distinguished by FAB-MS [9]. Because of their low molecular absorptivity the formed C=N species can be detected only at high concentrations in the IR spectra at 1665 cm^{-1} . However, in the Raman spectra these C=N signals appear even at low concentrations and reach high intensities replacing the carbonyl functionality at 1790 cm^{-1} completely with high conversions.

The present paper presents curing studies of two new model compounds obtained from OPO and POP. The NH_2 -terminated model compound $\text{O}(\text{PO})_2$ consists of three ODA and two PMDA moieties, while the second model compound $\text{P}(\text{OP})_2$ has three PMDA and two ODA units with two active anhydride end groups. The structure of both compounds has been confirmed by $^1\text{H-NMR}$ and FT-IR spectroscopy. The combination of FT-IR and Raman spectroscopy show, that $\text{C}=\text{N}$ bonds are formed at low temperatures in just detectable amounts. Additionally, we can show that short chain oligomers like $\text{O}(\text{PO})_2$ added to bulky polyimides in small amounts can crosslink in the same way as mentioned before leading to $\text{C}=\text{N}$ bonds.

This work was done in order to study the influence of oligomers on polymer side reactions. Another objective was to show how oligomers of the NH_2 -type can react, either in the case of curing in bulk, or as a potential component in polyimides. The NH_2 -terminated oligomers $\text{O}(\text{PO})_n$ with $n = 1, 2$ were found to react to different extents in bulk. If one compares the results obtained from different $\text{O}(\text{PO})_n$ model compounds ($n = 1, 2$), it can be easily established that chain mobility must have a significant influence on the amount of side reactions which take place.

EXPERIMENTAL

Chemicals and Materials

Pyromellitic dianhydride (Polyscience Inc.) was recrystallized from acetic anhydride and sublimed in vacuum at 190°C and 0.03 torr. 4,4'-Oxydianiline (4,4'-diaminodiphenylether, Aldrich, >97%) was first recrystallized from methanol and sublimed at 0.03 torr and 20 K below the melting point ($\sim 170^\circ\text{C}$) likewise. Dimethylacetamide (DMAc, Aldrich, 99+%) and acetone (Fisher) were stored over molecular sieves and used without further purification.

The model compounds OPO, N,N'-bis[4-(4-aminophenoxy)-4'-phenyl]-pyromellitimide and POP, 4,4'-bis[N-(3,4-bis(hydroxycarbonyl)phthalimido)]diphenylether dianhydride, used as starting materials were prepared as described previously [8].

Synthesis of $\text{O}(\text{PO})_2$

A solution of 0.4 g (2 mMol) 4,4'-oxydianiline in 6 ml DMAc was kept under a dry nitrogen atmosphere while adding a solution of 0.120 g (0.2 mMol) POP in 15 ml DMAc dropwise within 90 minutes. The resulting mixture was stirred for 2 hours at room temperature to complete the reaction. The solvent was

distilled off under reduced pressure at 100-120°C until approximately 1/4 of the original volume was reached and the remaining viscous deep orange solution was poured into stirred acetone. After the ochre-yellow precipitate had been separated, it was washed with acetone several times and extracted with hot acetone for 6-8 hours. After drying in vacuum for several hours, a pale yellow solid was obtained.

Yield: 0.100 g (50% of theoretical). MW(VPO) = 861 g/mol.

IR(KBr): 1777 (C=O, in plane); 1724 (C=O, out of plane); 1601 (C=C, stretch); 1380 (C-N, imide); 1243 (C-O-C, as); 1165 and 1118 (imide III); 724 cm⁻¹ (imide IV, def.).

¹H-NMR (300 MHz, d₆-DMSO): δ = 6.61 (d, 2H, H_a); 6.78 (d, 2H, H_b); 6.90 (d, 2H, H_c); 7.38 (d, 2H, H_f); 7.55 and 7.63 (d, 2H, H_d + H_e); 8.13 and 8.23 (s, 2H, H_g + H_h); 8.38 (s, 1H, NH); 10.61 ppm (s, 1H, COOH).

Synthesis of P(OP)₂

0.436 g (2 mMol) Pyromellitic dianhydride was dissolved in a small amount of DMAc, which allowed a complete dissolution at room temperature. Under vigorous stirring, a solution of 0.124 g (0.2 mMol) OPO in 5 ml DMAc was added slowly within 60 minutes while flushing the apparatus with dry nitrogen. The mixture was stirred for 2 hours at room temperature. Then the solvent was removed completely in vacuum and the yellow residue was cured at 200°C and 0.07 torr for 90 minutes. During this procedure, the main amount of unreacted PMDA was sublimed and the remaining PMDA removed by extraction with hot acetone for 6-8 hours. After drying in vacuum at 120°C, a yellow product was obtained.

Yield: 0.137 g (65% of theoretical).

IR(KBr): 1859 (C=O, anhydride); 1776 (C=O, in plane); 1716 (C=O, out of plane); 1386 (C-N, imide); 1256 (C-O-C, as); 1167 and 1120 (imide III); 722 cm⁻¹ (imide IV, def.).

¹H-NMR (300 MHz, d₆-DMSO): δ = 7.28 (2 dd, 8H, H_{b,b'}); 7.56 (2 dd, 8H, H_{a,a'}); 8.16 (s, 2H, H_c); 8.57 ppm (s, 4H, H_d).

Measurements

The ¹H-NMR spectra of P(OP)₂ and the soluble precursor of O(PO)₂ were recorded with a 300 MHz-NMR spectrometer Varian-XL-300 in d₆-DMSO. The FT-IR measurements were performed using a Bio-Rad Digilab FTS-60 spectrometer and the compounds were prepared as thin pellets (~ 1% in KBr). All Raman spectra were taken with a holographic double monochromator (Ramanor 2000 M) equipped with a Pelletier cooled quantum photometer (Model 1140,

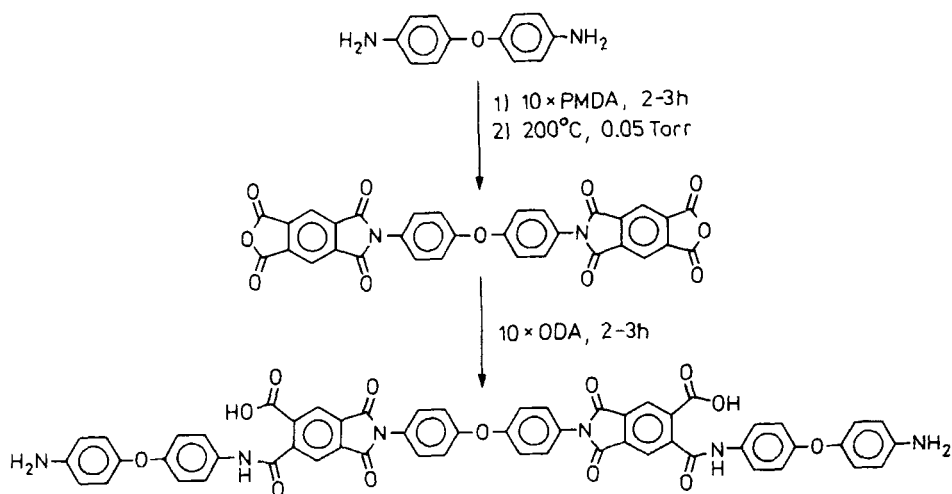
Princeton Appl. Res.). A 20W argon ion laser (Coherent, Innova 90-2) operating at 457.9 nm and adjusted to 50 mW was used as the light source. Raman measurements were taken for pellet samples under vacuum. The angle of the incident light was adjusted between 60-120° until the signal of the scattered light was maximized. All samples showed a strong luminescence background with very weak Raman scattering. Raman spectra in this report are displayed after averaging 20-25 scans in the range 1100-1900 cm^{-1} followed by subtracting the background which was assumed to follow the quadratic equation $y = ax^2 + bx + c$. The Raman spectra reported here are typically recorded with 20-30 minutes per scan.

The curing of the model compounds was carried out in a tube furnace under a dry nitrogen atmosphere in 50 K increment steps. The molecular mass was confirmed by vapor pressure osmometry (Corona Wescan model 232A) calibrated with sucrose octaacetate, operating at 80°C. DMF was used as the solvent. The deviation of the MW data from the theoretical values is due to the fact that amic acids are very polar compounds in monomeric form as well as in polymers or oligomers. Also, the VPO measurements were carried out in DMF. The polarity of both the solvent and the substance resulted in a non-linear behavior for concentrations lower than 5 g/L if one plots the (instrument response/concentration) versus the concentration. That is why only a few points which show a linear-type plot (5-12 g/L concentration range) were used to calculate the linear dependence. The measured MW lies within the error of the method for such polar structures. This was also confirmed by measuring other amic acids, such as the *m*-/*p*-bisphenylpyromellitic amic acid ($M = 404 \text{ g/mol}$) synthesized from aniline and pyromellitic dianhydride, which gave a $M(\text{VPO}) = 456 \text{ g/mol}$. MS data are not available, since the volatility is much too low to get a sufficient spectrum.

RESULTS AND DISCUSSION

Synthesis of the Model Compounds

As reported previously [8], the reaction of 4,4'-oxydianiline (ODA) with a tenfold excess of pyromellitic dianhydride (PMDA) in DMAc gives a yellow compound after removing the solvent and curing the residue for 90 minutes at 200°C (Scheme 1). This compound (POP) can be used as an anhydride terminated starting material for a further reaction step to extend the chain length. The reaction of POP with a tenfold excess of oxydianiline leads to a light yellow amorphous powder. The structure of $\text{O}(\text{PO})_2$ was confirmed by FT-IR and ^1H NMR



Scheme 1 Reaction pathway for the synthesis of POP and O(PO)₂.

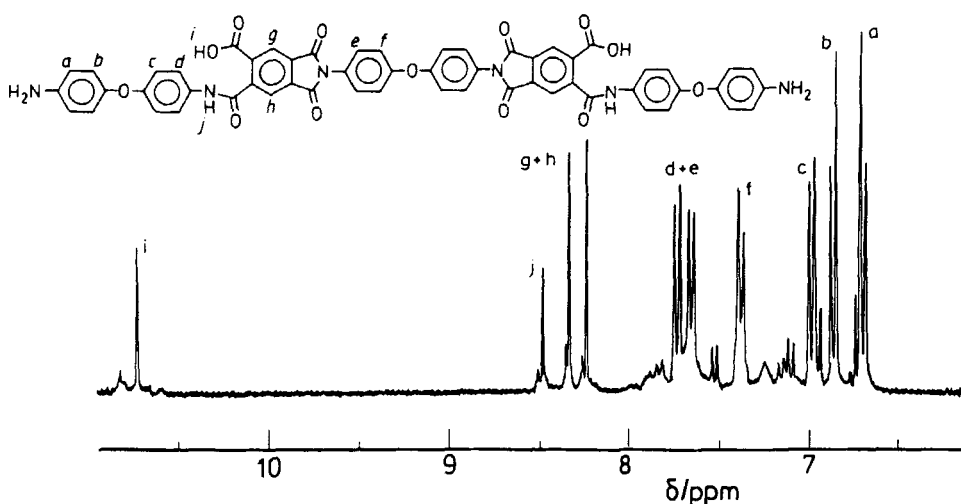


Figure 1. ¹H NMR spectrum of O(PO)₂, uncured (300 MHz, d₆-DMSO).

spectroscopy. The NMR spectrum was taken for uncured O(PO)₂ (Figure 1) because the cured material is insoluble in common solvents. Using the data for OPO [8], all peaks can be assigned to the corresponding protons. H_A, H_B, H_C, H_D, H_E and H_F are doublets having a similar coupling constant. The H_{A-F} : H_{G-J} integrated ratio was 2:1. Small side signals and multiplets between the main signals are due to higher molecular weight byproducts. They can also be found in the NMR

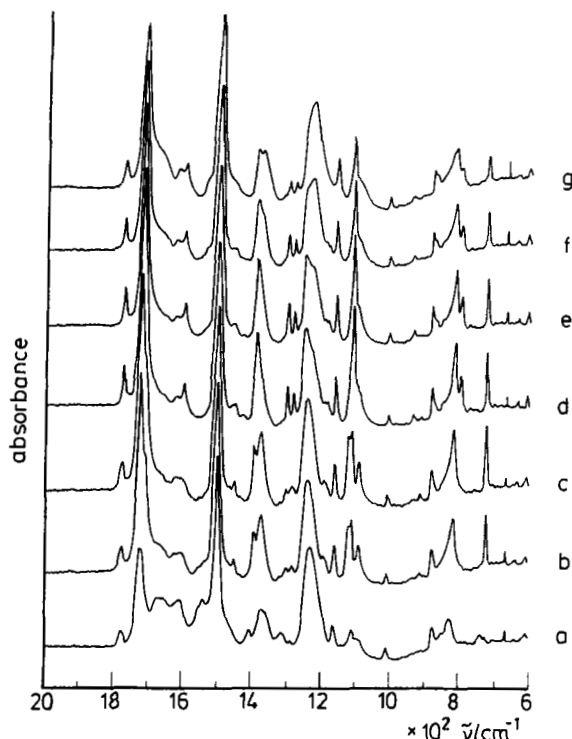
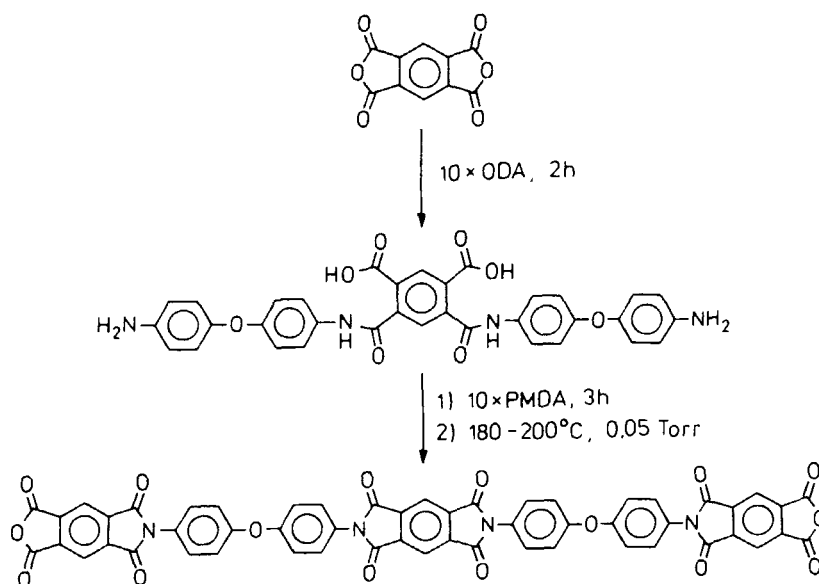


Figure 2. FT-IR spectra of O(PO)₂ versus curing temperature (in absorbance) a) O(PO)₂ uncured; b) O(PO)₂ cured for 1 hour at 150°C; c) O(PO)₂ cured for 1 hour at 200°C; d) O(PO)₂ cured for 1 hour at 250°C; e) O(PO)₂ cured for 1 hour at 300°C; f) O(PO)₂ cured for 1 hour at 350°C; g) O(PO)₂ cured for 1 hour at 400°C.

spectra of OPO at approximately the same positions (~ 7.0 and 7.7 ppm as multiplet) and belong to assigned protons HC and HD in longer chain oligomers. This higher oligomer formation follows the extended Carother's equation, $P_n = (1+r)/(1+r-2rp)$, where p is the extent of the reaction and $r = N_{AA}/N_{BB}$. Assuming that $p \geq 95\%$, a tenfold excess of one starting component over the other leads to $P_n = 1.2$. In the case that a twenty-fold excess would be applied, the average degree of polymerization would only rise to 1.1.

The FT-IR spectrum (Figure 2, spectrum b) shows the typical structural elements of the completely ring closed model compound O(PO)₂. The C=O in-plane vibration at 1777 cm⁻¹, the C=O out-of-plane vibration at 1724 cm⁻¹, the C-N vibration (imide II) at 1380 cm⁻¹, the double peaks (imide I) at 1165 and 1118 cm⁻¹ and the imide-VI-vibration at 724 cm⁻¹ are suitable to prove the completion of the amic acid-imide conversion.



Scheme 2 Reaction pathway for the synthesis of OPO and P(OP)₂.

The opposite case, the reaction of PMDA with a tenfold excess of ODA in DMAc gives a pale white powder, which was identified as OPO in Saini *et. al* [8]. Based on the reaction given above, the treatment of OPO with a tenfold excess of PMDA, removal of the solvent and curing for 90 minutes at 200°C, gave a yellow compound (Scheme 2), that was found to be the anhydride terminated extension of OPO with a complete ring closed structure. The proton NMR spectrum (Figure 3) shows the protons a and a', as well as b and b' as a set of double doublets, whereas both the proton c and d are singlets. The less intense signal at 8.4 ppm can also be found in the spectra of POP at 8.57 ppm and is assignable to the aromatic protons of the terminal units caused by small amounts of longer chain oligomers. Remaining higher oligomers from the starting material OPO can be removed easily in this case. These oligomers are completely insoluble, whereas P(OP)₂ is slightly soluble in polar aprotic solvents (DMF, DMAc, NMP). In this way, the insoluble fraction can be separated by filtration, whereas its low concentration in solution (< 2 g/L) is not sufficient for precise VPO measurements.

Typical peaks in the FT-IR spectrum of P(OP)₂ are the C=O anhydride vibration at 1859 cm⁻¹, the C=O in-plane vibration at 1776 cm⁻¹, the C=O out-of-plane vibration at 1716 cm⁻¹, the C-N (imide II) vibration at 1386 cm⁻¹, the imide (III) double peaks at 1167 and 1120 cm⁻¹, and the imide (IV) deformation at 722 cm⁻¹.

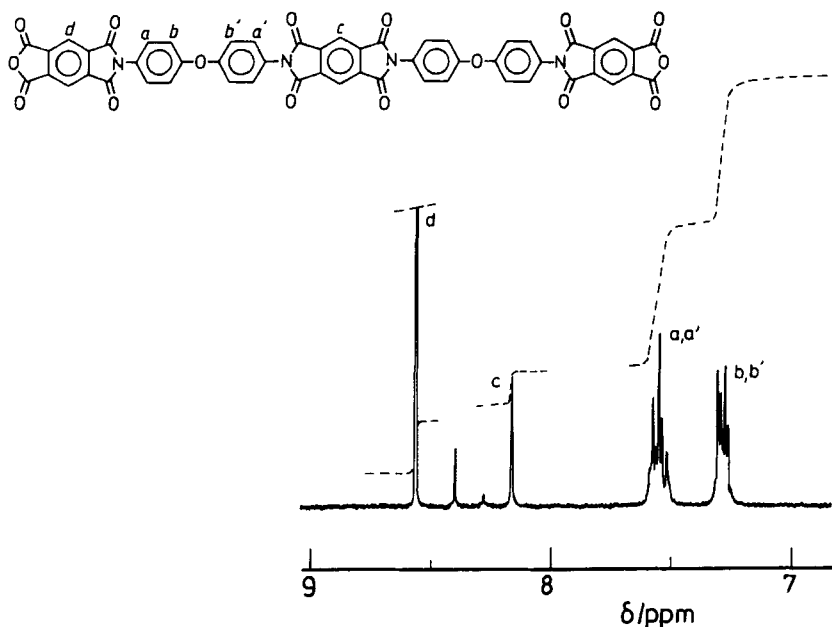


Figure 3. ^1H NMR spectrum of P(OP)_2 , (300 MHz, d_6 -DMSO).

The polycondensation of O(PO)_2 and P(OP)_2 was carried out in DMAc using the same experimental conditions as usually used for PMDA/ODA polyimides. The resulting polymer starts to precipitate during the reaction due to the ring closed units in the chain (60%). Insignificant polycondensation occurs if the starting materials are PMDA and ODA or O(PO)_2 and P(OP)_2 as well as mixtures of these. Oligomer formation can not be prevented in this case. Both oligomers seem to be of equal reactivity.

Curing Studies of O(PO)_2 and P(OP)_2

The curing of O(PO)_2 and P(OP)_2 were carried out in a dry nitrogen atmosphere in 50°C increments until 400°C . The FT-IR spectra taken from the same sample pellet are plotted versus the wavenumber for different curing temperatures in Figure 2 for O(PO)_2 . It is obvious that there are no significant changes in peak positions and shapes after the completion of the imide ring formation. All peaks which support the observed structure (as discussed above) remain unchanged over the whole range of curing temperatures. The assignments are shown in Table 1.

TABLE 1. FT-IR Results for OPO, POP, O(PO)₂, P(OP)₂ and Bulky PI

P(OP) ₂	POP*	OPO*	O(PO) ₂	PI	assignment [†]
1859	1863				v(C=O), anhydride
1776	1779	1776	1777	1777	v(C=O), in phase imide
1716	1721	1716	1724	1720	v(C=O), out of phase, imide
		1601	1601	1595	aromatic C=C stretch
			1559		
1508	1507	1503	1504	1501	aromatic breathing mode
			1454		
1386	1385	1391	1380	1379	v(C-N), imide II
1309		1307	1303	1307	
1289		1286	1286	1289	
1256	1245	1252	1243	1241	v(C-O-C)
1167/ 1120	1119	1166/ 1118	1165/ 1118	1168/ 1116	v(C=O) ₂ NC imide III
		1093		1092	
		1014	1012	1013	v ₆ 1,2,4,5-C ₆ H ₂
906	903				
		881	881	881	
819		822	821		γ _w 1,2,4,5-C ₆ H ₂
803	806				
722	719	726	724	725	deformation, imide IV

*Ref. [8]

†Ref. [3]

The uncured starting material consists of 2 imide and 2 amic acid units. Thus, the spectroscopic features of both can be seen. As the curing progresses, the C=O stretch of the amide group at 1656 cm⁻¹ (amide I) and the amide N-H deformation at 1545 cm⁻¹ disappear and the imide features start to appear. In addition, the amide aromatic C-N vibration at 1410 cm⁻¹ starts to merge with the adjacent C-N (imide II) peak and becomes invisible at 250°C.

Despite the overlap of the spectra of the cured and uncured molecules some changes in the spectroscopic features can be observed. First, both peaks at 1093 and 1118 cm⁻¹ merge as the curing proceeds and the 1093 cm⁻¹ feature appears as a shoulder starting at 250°C. Second, the weak N-H-deformation peak at 1620 cm⁻¹ decreases intensity relative to the adjacent ν₁₃ 1,4-C₆H₄ peak. Third, the most interesting change is the shift of two peaks, namely the C-O-C antisymmetric

vibration and the C-N imide (II) vibration. The C-N peak shifts from its initial position at 1374 cm^{-1} (Figure 2a) to 1395 cm^{-1} at 400°C , while the C-O-C vibration shifts from 1237 cm^{-1} to 1257 cm^{-1} for the same temperature change. While the C-N peak is continuously shifted to higher wavenumbers, the C-O-C peak becomes structured after passing a maximum at 300°C and a change in peak width and fine structure results. Additionally, the very weak ν_{13} 1,2,4,5- C_6H_2 peak at 1460 cm^{-1} starts to be hidden by the broadening of the strong adjacent aromatic breathing mode (ν_{13} 1,4- C_6H_4) peak at 1504 cm^{-1} . All the observed changes cannot be positively assigned to distinctive structural changes, but they are an indication for side reactions happening while the curing is in progress.

From the literature [8,11,12] it is known that the ring closure of OPO as well as the PMDA/ODA polyimide is essentially complete after heating to 250°C for 1 hour. The conversion was monitored by FT-IR spectroscopy in the present study using the C=O in-plane vibration of the imide units at $\sim 1775\text{ cm}^{-1}$ and the C-N imide II vibration at 1370 cm^{-1} . Some references [3,11] recommend the use of the ν_{13} 1,4- C_6H_4 vibration (aromatic breathing mode) as an internal standard. The main requirement for an internal standard, a constant absorbance at all steps of curing, could not be provided for this peak at 1500 cm^{-1} . Additionally, almost all peaks in the spectra were affected or showed some interference with their adjacent peaks. The only exception was the weak ν_6 1,2,4,5- C_6H_2 vibration at 1015 cm^{-1} which was not affected. Figure 4 shows the intensity ratios of the $1775\text{ cm}^{-1}/1015\text{ cm}^{-1}$ as well as the $1375\text{ cm}^{-1}/1015\text{ cm}^{-1}$ peaks plotted versus the curing temperature. Despite the fact that both graphs have different slopes, the conversion reaches about 100% between 250 and 300°C .

The observed changes can be related to conformation changes [14] and/or side reactions if the extent of imide formation is $>90\%$ since the temperatures are higher than 250°C [13]. The main spectral features did not disappear after 1 hour of curing at 400°C despite the fact that the PMDA/ODA polyimides start to degrade at $\sim 500^\circ\text{C}$ [15] (measured by thermogravimetry with heating rates of 5-10 K/min).

The anhydride terminated model compound P(OP)_2 shows a different behavior. A complete ring closure can be accomplished at $\sim 200^\circ\text{C}$ and is a part of the pathway. Therefore the curing series was started at 250°C (Figure 5) and interrupted at 400°C . Unlike the POP, OPO, and O(PO)_2 model compounds, P(OP)_2 undergoes significant structural changes upon curing. A decrease in signal intensity was observed between the 300 and 350°C steps and the anhydride C=O peak at 1859 cm^{-1} disappeared completely below 400°C . Other intense peaks at 906 , 1205 , and 1601 cm^{-1} were also affected. These peaks were tentatively assigned [3] as ν_{11} ,

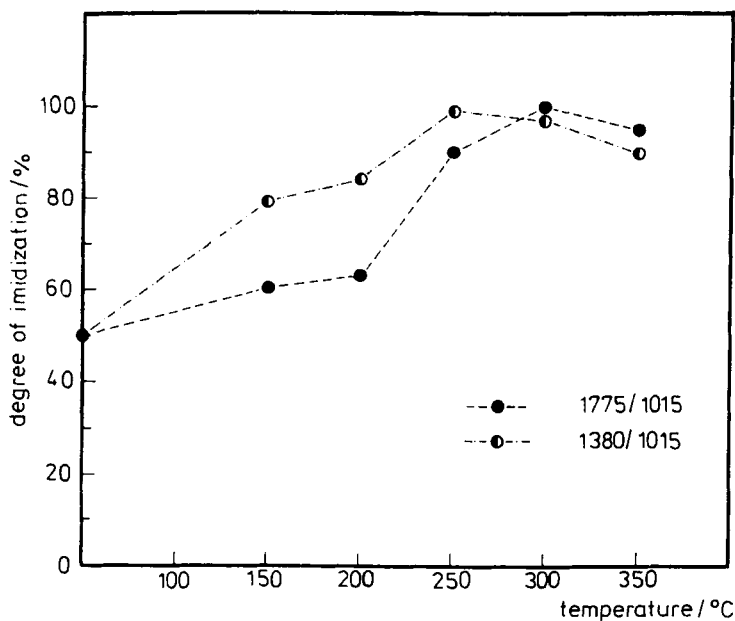


Figure 4. Degree of imidization in $O(PO)_2$ as a function of the cure temperature.

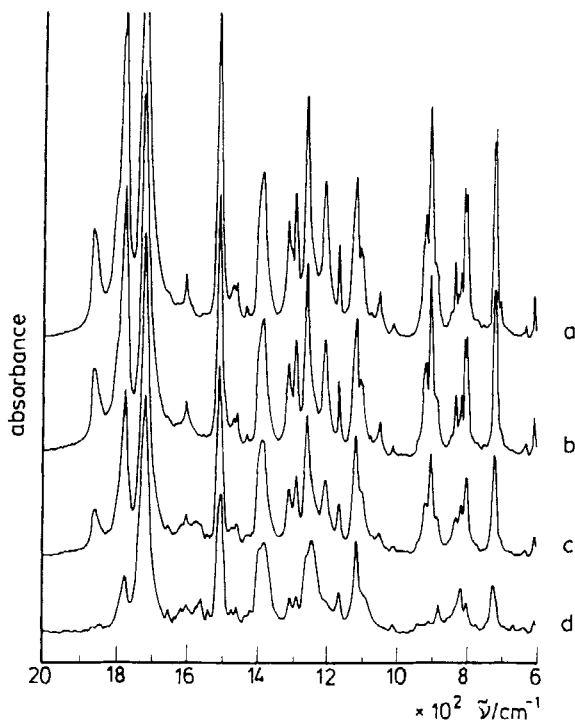


Figure 5. FT-IR spectra of $P(OP)_2$ versus curing temperature (in absorbance)
 a) $P(OP)_2$ cured for 1 hour at 250°C; b) $P(OP)_2$ cured for 1 hour at 300°C; c) $P(OP)_2$ cured for 1 hour at 350°C; d) $P(OP)_2$ cured for 1 hour at 400°C.

TABLE 2. Raman results for OPO, POP, O(PO)₂, P(OP)₂ and Bulky Polyimide

POP*	P(OP) ₂	OPO*	O(PO) ₂	PI	assignment†
1857	1854				C=O, anhydride
1783	1784	1792	1789	1787	C=O, anhydride
1613	1620/ 1608	1612/ 1598	1610	1608	aromatic C=C stretch
1512	1518	1516	1520	1514	PMDA mode
1389	1382	1390	1389	1385	C-N stretch, imide
1304	1308				
		1278			
		1244			C-O-C stretch
1172	1168	1168	1168	1175	(C=O) ₂ NC, imide III
1131	1126	1128	1123	1120	(C=O) ₂ NC, imide III

*Ref. [8]

†Ref. [3]

1,2,4,5-C₆H₂, ν_{17} 1,2,4,5-C₆H₂, and ν_{16} 1,4-C₆H₄, respectively. In fact, only signals of the terminal aromatic systems were affected while the signals of the internal pyromellitimide unit remained intact. On the other hand, the C=O in-plane vibration at 1776 cm⁻¹, the C=O out-of-plane vibration at 1716 cm⁻¹, the ν_{13} 1,4-C₆H₄ vibration at 1508 cm⁻¹, the C-N vibration at 1380 cm⁻¹, the anti-symmetrical C-O-C vibration at 1256 cm⁻¹, and the imide deformation vibration at 722 cm⁻¹ remained present in the spectra even after treatment at 400°C for 1 hour.

It can be concluded from these results that the terminal anhydride system undergoes a complete degradation, e.g. the loss of CO₂ or CO. Therefore, such terminal groups formed statistically by the polyaddition of dianhydrides and diamines should not be responsible for side reactions between polyimide chains at a later state of curing or higher temperatures. However, terminal anhydride functions can be of importance at lower temperatures since they can be generated during the thermal ring closure reaction [4] (Table 2).

The Raman spectra of O(PO)₂ and the cured P(OP)₂ are shown in Figure 6. Unlike OPO [8], the O(PO)₂ precursor amic acid contains two imide moieties. Three main changes occur with the temperature increase upon curing. The side peak

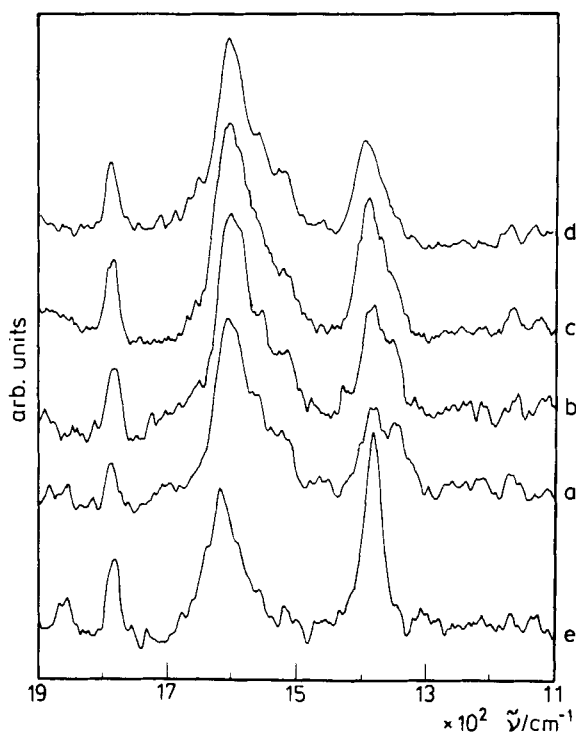
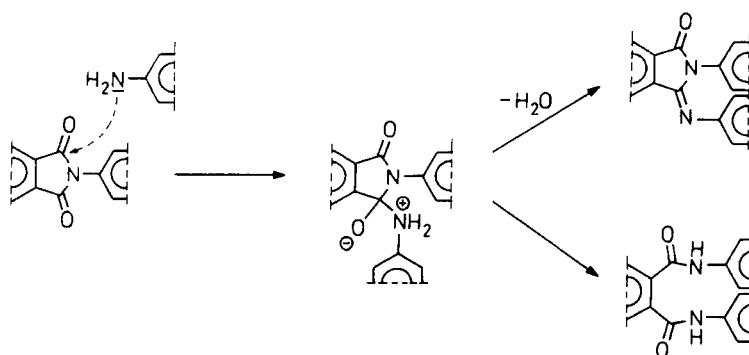


Figure 6. Raman spectra of (a) $O(PO)_2$ uncured; (b) $O(PO)_2$ cured for 1 hour at 200°C ; (c) $O(PO)_2$ cured for 1 hour at 250°C ; (d) $O(PO)_2$ cured for 1 hour at 300°C ; (e) $P(PO)_2$ cured for 1 hour at 250°C .

at 1350 cm^{-1} belonging to the amide C-N stretch disappears as the temperature increases. The C=O vibration at 1790 cm^{-1} increases in intensity and remains constant after the ring closure has ended. At the low energy side of the broad peak centered at 1610 cm^{-1} (combined aromatic stretches) a small side peak is formed at a 200°C curing temperature. An increase in the intensity or shift in the position of the peak does not occur as the temperature increases. This feature is assigned to the C=N bonds formed according to the mechanism given in Scheme 3. The rearrangement of the intermediate leading to *o*-bis(amides) can be excluded since the C-N amide peak at 1330 cm^{-1} is missing. These assignments are in support of previous results. For example, the FT-IR spectrum of N,N',N'',N'''-tetraphenylpyromellitimide [8] shows no indication for neither the amide C=O functionality at 1650 cm^{-1} nor the N-H mode at 1550 cm^{-1} . On the other hand, the concentration of the formed C=N species must be low since the intensity of the 1665 cm^{-1} Raman peak is moderate and the corresponding C=O peak at 1740 cm^{-1} cannot be located.



Scheme 3 Proposed mechanism of the side reaction.

In the case of OPO, this feature appears as a very weak peak and we were able to show that it can increase in intensity as the imine bonds form in *N,N'*bis(phenoxyphenyl)pyromellitimide. But even at very high concentrations of between 2 and 3 imine bonds per pyromellitimide unit, this peak remains weak and broad.

From the above mentioned results we can conclude that the imine formation is slightly hindered in $O(PO)_2$ compared to OPO and does not change in intensity depending on the temperature. For OPO the imine formation starts to occur during the imide ring closure at comparatively low temperatures so that imide and imine formation can happen simultaneously.

Imine Crosslinks in Bulky Polyimide

Based on our previously reported results [9] in which the $C=N$ formation was initiated by adding small amounts of OPO to bulky polyimides, we used the amino-terminated model compound $O(PO)_2$ in the same way as an additive (10 and 20%) in solid poly(amic acid) derived from PMDA and ODA. The mixtures were cured as pellets for 90 minutes at 250°C in nitrogen gas. The Raman results are plotted in comparison to the pure polyimide in Figure 7. Both spectra, shown after curing at 250°C for 90 minutes, are influenced by the content of the oligomer. If heated without the addition of the low molecular weight NH_2 -terminated model compounds, no significant change could be observed. Broadening of the $C=C$ peak at 1610 cm^{-1} and the $C-N$ vibration peak at 1390 cm^{-1} are typical indications for the presence of $O(PO)_2$, since the same effect can be observed in pure $O(PO)_2$. Spectrum b in Figure 7 (10% $O(PO)_2$) exhibits a shoulder on the low energy side of

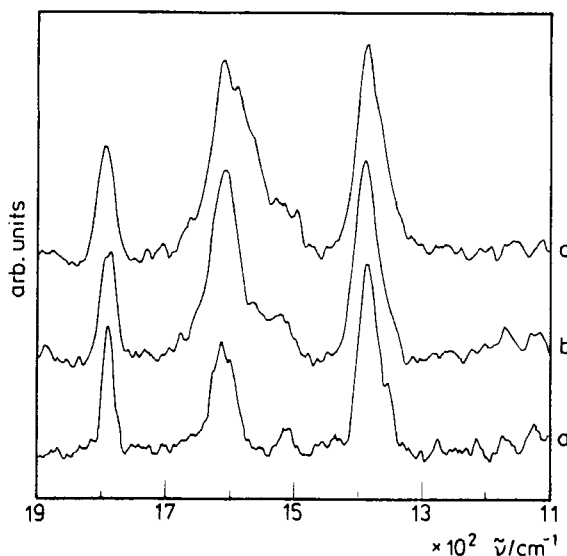


Figure 7. Raman spectra of: (a) poly[N,N'-bis(phenoxyphenyl)pyromellitimide]; (b) PI containing 10% O(PO)₂ and cured at 250°C for 90 minutes; (c) PI containing 20% O(PO)₂ and cured at 250°C for 90 minutes.

the C=C peak. The intensity of the C=C peak increases to approximately that of the strongest peak in the spectrum, the C-N peak at 1390 cm⁻¹. The addition of 20% O(PO)₂ produces a distinctive peak at 1665 cm⁻¹. This is in good agreement with the results we have reported previously [9]. Upon mixing with a high molecular weight poly(amic acid), O(PO)₂ acts like a low molecular oligomer and undergoes a branching side reaction. The concentration of the C=N species must be low because of the low intensity of the corresponding signal in the Raman spectra.

CONCLUSIONS

The curing behavior of amino- and anhydride terminated model compounds are different. Further, it has been shown that the tendency to undergo side reactions decreases with the increase of the chain length. Thus, the observed side reaction yielding C=N links is more likely in the short chain model compound OPO than in O(PO)₂. Such imine formation reactions can start at comparatively low temperatures simultaneously with the imide ring formation reaction. Before the imide

formation is complete at 250-300°C, the imine species are formed and no further increase can be detected at higher curing temperatures.

A comparison of OPO, O(PO)₂ and O(PO)_n (bulky polyimide) clearly shows that the probability of imine bond formation decreases with the chain length unless short chain oligomers are present. While bulky polyimides do not show any indication for these imine bonds, the addition of 10% and 20% O(PO)₂ generates moderate amounts of C=N bonds as shown by the C=N stretch vibrational mode at 1665 cm⁻¹ in their Raman spectra. On the other hand, the corresponding weak C=O vibration of the carbonyl functionality in the same ring system is hidden in the baseline noise caused by the comparatively low abundance of the above mentioned side reactions.

In summary, the research of O(PO)_n oligomers has been extended herein from n=1 to n=2 for both kinds of oligomers (anhydride- and amino- terminated compounds). These n=2 compounds exhibit more polymer-like properties. In this case, it was possible by the use of Raman spectroscopy to detect very small amounts of imine species in the presence of a high fluorescence background. Finally, mixing of O(PO)₂ with poly (amic acid) and then curing allowed us to study how the lower oligomers (n=2 case) react with polyimides.

ACKNOWLEDGMENT

We are very grateful to the German Academic Exchange Service Bonn (Germany) for the financial support of this research.

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Received February 21, 1997

Revision received March 31, 1997