



Infrared spectral assignments for a semicrystalline thermoplastic polyimide

H. ISHIDA and M. T. HUANG

NSF Center for Molecular and Microstructure of Composites (CMMC), Department of Macromolecular Science, Case Western Reserve University, Cleveland, OH 44106, U.S.A.

(Received 17 February 1994; accepted 11 May 1994)

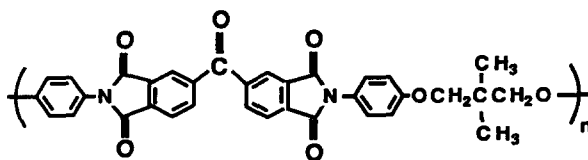
Abstract—Infrared spectral assignments are made for the semicrystalline thermoplastic polyimide derived from 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) and 2,2-dimethyl-1,3-(4-aminophenoxy)propane (DMDA). Model imide compounds have been synthesized to assist in the interpretation of the polyimide's infrared spectrum. The infrared and Raman spectra of BTDA and DMDA have also been analyzed to aid in the identification of the peak assignments for the polyimide.

INTRODUCTION

The widespread use of aromatic polyimides in high performance applications results from its outstanding mechanical, electrical, and thermal properties. The structural origin of the material properties must ultimately be determined to better understand and control these attractive properties. To obtain structural information at the molecular level, infrared spectroscopy has been widely utilized.

In the study of aromatic polyimides, infrared spectroscopy has been applied to determine and monitor the degree of imidization [1–3] as well as to study the imidization process itself [3–5]. The origin of infrared spectral features has also been examined [6–8] in addition to interactions of polyimide films on metal substrates [9, 10]. Infrared spectroscopy has also been used to investigate molecular structural changes of polyimides upon deformation [11–14] and crystallization [8, 15].

The application of infrared spectroscopy to the study of polyimides relies upon an understanding of the vibrational assignments. Despite the existence and continued development of a great variety of polyimides, only few detailed vibrational assignments of polyimides have been made [8, 10, 16]. This paper focuses on the infrared vibrational assignments for a recently developed semicrystalline thermoplastic polyimide derived from 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) and 2,2-dimethyl-1,3-(4-nitrophenoxy) propane (DMDA) [17]. Vibrational assignments are also made for the polyamic acid and model imide compounds.

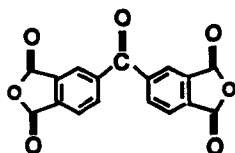


BTDA-DMDA Polyimide

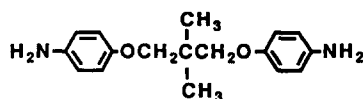
EXPERIMENTAL

Materials

The starting materials used to synthesize the polyimide were 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA)



and 2,2-dimethyl-1,3-(4-nitrophenoxy) propane (DMDA)



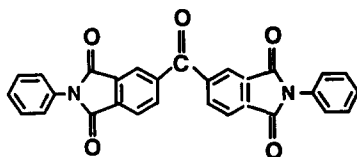
Ultra pure (99.15%) BTDA (Allco Chemical Corporation) was dried prior to usage in a vacuum oven at 165°C for 8 h and then allowed to cool overnight under vacuum. DMDA was synthesized [17] and obtained from the research group of Professor Harris. Anhydrous grade N,N-dimethylacetamide (DMAc) was purchased from Aldrich Chemical and used as the solvent in the synthesis of the polyimide and the model imide compounds.

For the synthesis of the model imide compound, N,N'-diphenyl-3,3',4,4'-benzophenonetetracarboxylic diphthalimide, aniline (Aniline Chemical) was used as the diamine. For the synthesis of the model imide compound, N,N'-di(4-methoxyphenyl)-3,3',4,4'-benzophenonetetracarboxylic diphthalimide, 4-methoxyaniline (Aldrich Chemical) was obtained and vacuum sublimed prior to usage.

Polyamic acid synthesis

The polyamic acid synthesis was performed at room temperature under a nitrogen gas atmosphere. The diamine DMDA (2.005 g, 0.007 mol) was first dissolved in 25 ml of DMAc. BTDA (2.256 g, 0.007 mol) was then added into the reaction mixture with an additional 25 ml of DMAc and stirred for 2 h. The resulting 8.3 wt% solution of polyamic acid was then stored in dry, sealed bottles at -15°C until usage.

Synthesis of N,N'-diphenyl-3,3',4,4'-benzophenonetetracarboxylic diphthalimide

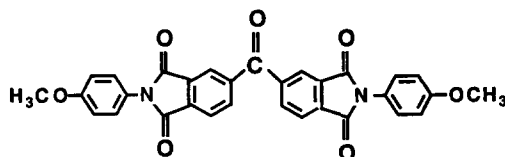


Compound A

The amic acid of N,N'-diphenyl-3,3',4,4'-benzophenonetetracarboxylic diphthalimide was synthesized by mixing aniline (0.559 g, 0.006 mol) in 10 ml of DMAc. BTDA (0.967 g, 0.003 mol) was then added into the reaction mixture with an additional 1 ml of DMAc and stirred at room temperature under a nitrogen gas atmosphere for 3 h.

To obtain the imidized material for infrared analysis, a diluted amic acid solution was cast onto a KBr plate, dried in an air circulating oven at 55°C for 30 min, and transferred to a high temperature furnace for thermal imidization at 280°C for 30 min.

Synthesis of N,N'-di(4-methoxyphenyl)-3,3',4,4'-benzophenonetetracarboxylic diphthalimide



Compound B

The amic acid of N,N'-di(4-methoxyphenyl)-3,3',4,4'-benzophenonetetracarboxylic diphthalimide was synthesized by dissolving 4-methoxyaniline (0.739 g, 0.006 mol) in 5 ml of DMAc. BTDA (0.967 g, 0.003 mol) was then added into the reaction mixture along with an additional 5 ml of DMAc and stirred at room temperature under a nitrogen gas atmosphere for 3 h.

The thermal imidization procedure for model compound B followed the procedure discussed for model compound A.

Thermal imidization/annealing treatments

A polyamic acid solution was cast onto a KBr plate and placed in a high temperature furnace for thermal imidization at 280°C for 30 min. After cooling to room temperature, the sample was placed

in the infrared spectrometer and its infrared spectrum collected. The spectrum of this initially imidized material represented the amorphous polyimide spectrum. To obtain a semicrystalline polyimide spectrum, the sample was annealed at 280°C in a high temperature furnace and once again examined by infrared spectroscopy after cooling to room temperature.

The amorphous and semicrystalline polyimide spectra were then baseline corrected in a consistent manner. Spectral subtraction of the initially imidized sample from the annealed sample was used to remove the amorphous information from the semicrystalline information and produce a crystalline enhanced polyimide difference spectrum.

FTIR transmission spectra

The infrared transmission spectra were obtained by a Michelson 110 MB Fourier transform infrared spectrophotometer equipped with a liquid nitrogen cooled, mercury–cadmium–telluride (MCT) detector with a specific detectivity, D^* , of $1 \times 10^{10} \text{ Hz}^{1/2} \text{ cm W}^{-1}$. The sample chamber was purged with nitrogen gas. For all infrared spectra, 200 coadded scans were collected with a spectral resolution of 2 cm^{-1} .

Raman spectra

The Raman spectra of the dianhydride, BTDA, and the diamine, DMDA, were acquired on a Dilor XY dispersive spectrometer equipped with a triple monochromator and an 18 bit charge coupled device (CCD) detector. A Raman excitation frequency of 750.7 nm was obtained from a tunable Coherent Model 8900 Titanium:Sapphire laser pumped by a Coherent Innova model 305 argon ion laser operating at multiline visible. A spike filter with a 61% transmittance at 750.7 nm was used to remove a small amount of background emitted from the Titanium:Sapphire laser. The samples were placed in a capillary bulb and positioned into the macro sample chamber. The spectra were collected using a power of 40–70 mW measured at the sample along with a detector integration time of 120 s. A 300 μm slit width was used and resulted in a 5.8 cm^{-1} resolution for this excitation frequency.

RESULTS AND DISCUSSION

The infrared spectral assignments for the BTDA–DMDA polyimide were made by comparison with the spectra of the polyimide's precursor materials and model imide compounds in addition to assignments from literature [8, 16, 18–27]. The infrared spectrum of the polyamic acid prior to thermal imidization is shown in Fig. 1. An amorphous polyimide spectrum, a semicrystalline spectrum, and a crystalline enhanced difference spectrum obtained by subtracting the spectrum of an amorphous sample from that of a semicrystalline sample are presented in Figs 2–4. The spectra of the model imide compounds are displayed in Figs 5 and 6. The detailed band assignments for the polyamic acid is presented in Table 1 whereas Table 2 includes the detailed assignments for the amorphous and crystalline components of the polyimide as well as for the model

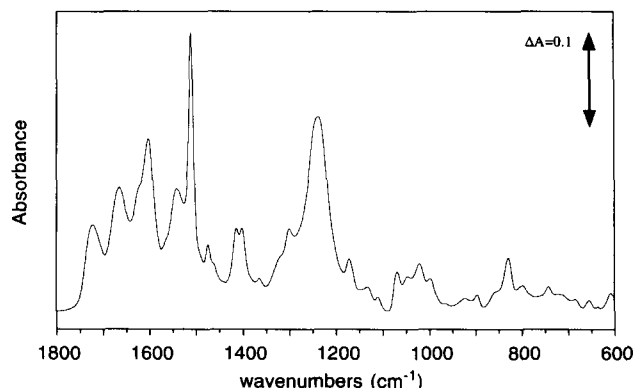


Fig. 1. Infrared spectrum of the BTDA–DMDA polyamic acid.

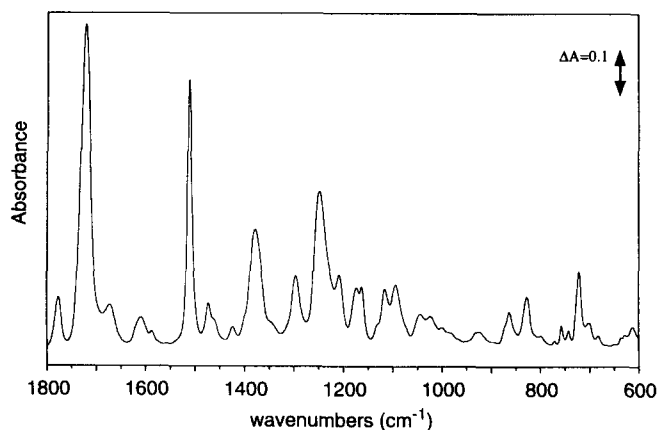


Fig. 2. Infrared spectrum of amorphous BTDA-DMDA polyimide.

imide compounds. Discussion of the band assignments will be grouped into vibrations involving imide rings, aromatic rings, and non-cyclic groups.

Imide ring vibrations

The imide group exhibits five characteristic vibrational bands in infrared spectroscopy—the imide carbonyl in-phase stretching, the imide carbonyl out-of-phase stretching, the CNC axial stretching, the CNC transverse stretching, and the CNC out-of-plane bending [18].

The two imide carbonyl absorptions have been explained in terms of an in-phase and out-of-phase coupling between the two carbonyl groups in the imide ring. This coupling produces a characteristic doublet with the out-of-phase mode absorbing at the lower frequency, but with a much stronger intensity than the in-phase vibration [7]. In the spectrum of the amorphous BTDA-DMDA polyimide the in-phase vibration occurs at 1778 cm^{-1} , while the out-of-phase vibration absorbs at 1722 cm^{-1} . In the crystalline difference spectrum, the 1778 cm^{-1} amorphous band splits into bands at 1785 and 1770 cm^{-1} , while the 1722 cm^{-1} amorphous band splits into bands at 1716 and 1708 cm^{-1} . The in-phase imide carbonyl stretching vibration absorbs at 1786 cm^{-1} for both model compound A and model compound B with a shoulder at 1771 cm^{-1} for model compound B. The out-of-phase vibration occurs at 1720 cm^{-1} for model compound A with a shoulder at 1715 cm^{-1} and at 1718 cm^{-1} for model compound B with a shoulder at 1712 and 1695 cm^{-1} .

The vibrational bands at 1380 , 1117 , and 722 cm^{-1} in the amorphous polyimide represent the imide CNC axial stretching mode, the imide CNC transverse stretching

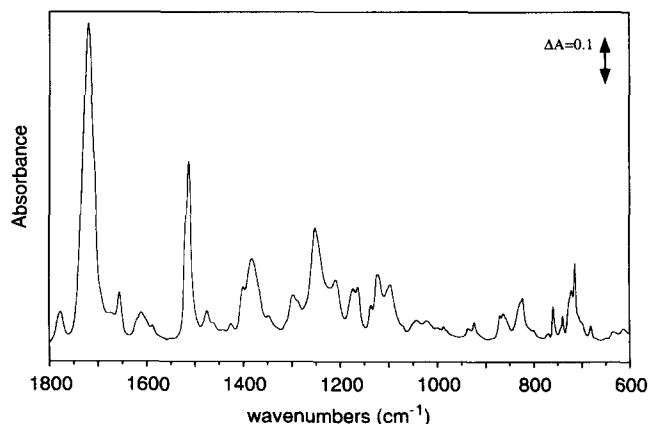


Fig. 3. Infrared spectrum of semicrystalline BTDA-DMDA polyimide.

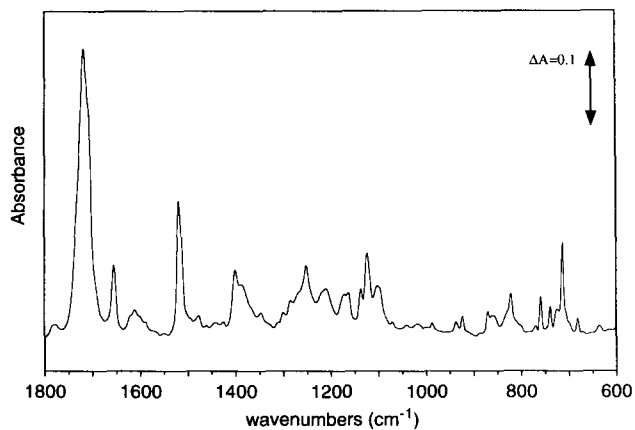


Fig. 4. Infrared crystalline enhanced difference spectrum for the BTDA-DMDA polyimide.

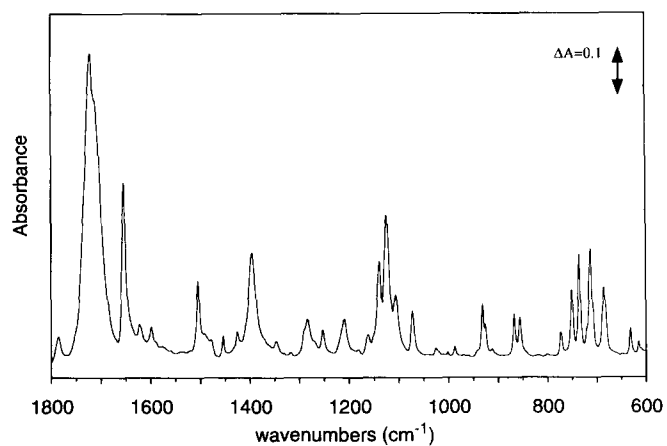


Fig. 5. Infrared spectrum of compound A.

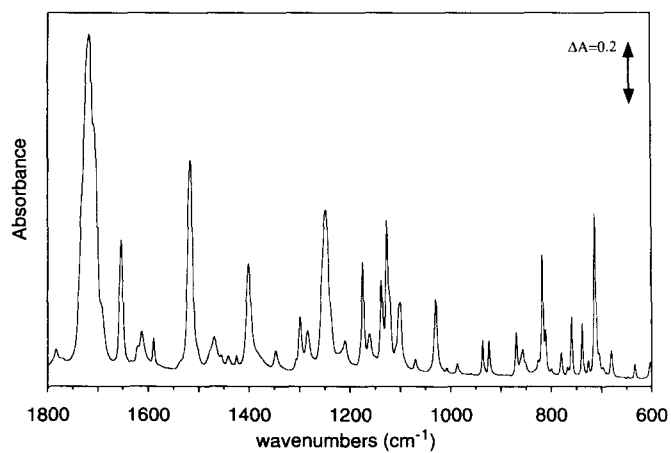


Fig. 6. Infrared spectrum of compound B.

Table 1. Tentative infrared spectral assignments for the BTDA–DMDA polyamic acid

Paacid	Tentative assignments
3050(vw)	
2963(w)	$\nu_{as}CH_3$
2930(w)	$\nu_{as}CH_2$
2875(w)	ν_sCH_3
1723(w)	$\nu(C=O)$, acid
1667(m)	$\nu(C=O)$, amide I
1623(sh)	$\nu(8b)1,2,4-C_6H_3$
1603(m)	$\nu(8a)1,2,4-C_6H_3$
1543(m)	$\delta(CNH)$, amide II
1511(s)	$\nu(19a)1,4-C_6H_4$
1475(w)	$\nu(19b)1,2,4-C_6H_3$
1461(sh)	$\delta_s(CH_2)$
1415(w)	$\nu(19a)1,2,4-C_6H_3$
1402(w)	$\delta(OH)$, acid
1364(vw)	$\delta_s(CH_3)$
1315(sh)	
1301(w)	$\nu(C-OH)$
1238(s)	$\nu_{as}(COC)$
1172(w)	$\nu(9a)1,4-C_6H_4$
1132(vw)	
1111(vw)	$\delta(18b)1,4-C_6H_4$
1069(w)	$\delta(18b)1,2,4-C_6H_3$
1047(vw)	$\nu_s(COC)$
1021(w)	$\delta(18a)1,4-C_6H_4$
999(vw)	
964(vw)	$\gamma(17a)1,4-C_6H_4$
924(vw)	$\gamma(10a)1,2,4-C_6H_3$
898(vw)	
859(sh)	$\nu(1)1,4-C_6H_4$
830(w)	$\gamma(11)1,4-C_6H_4/1,2,4-C_6H_3$
800(vw)	
743(vw)	$\nu(12)1,2,4-C_6H_3$
685(vw)	$\gamma(4)1,2,4-C_6H_3$
655(vw)	
637(vw)	$\nu(6b)1,4-C_6H_4$
609(vw)	
591(sh)	
525(vw)	

mode, and the imide CNC out-of-plane bending mode, respectively. Crystallization of the polyimide produces spectral shifts from 1380 to 1401 cm^{-1} , 1117 to 1124 cm^{-1} , and 722 to 714 cm^{-1} . For model compound A, the axial stretching vibration appears at 1395 cm^{-1} while it appears at 1401 cm^{-1} for model compound B. The transverse stretching mode is situated at 1124 cm^{-1} for model compound A and 1127 cm^{-1} for model compound B. The out-of-plane bending mode appears at 713 and 714 cm^{-1} for model compounds A and B, respectively.

Aromatic ring vibrations

The BTDA–DMDA polyimide and model compound B contain *para*-disubstituted (1,4-substituted) phenyl rings as well as asymmetric trisubstituted (1,2,4-substituted) phenyl rings. Model compound A possesses monosubstituted and asymmetric trisubstituted phenyl groups. Following the classification of phenyl ring vibrations by Varsanyi [19], the aromatic ring modes will be discussed in terms of tangential vibrations, radial skeletal vibrations, and out-of-plane vibrations.

Table 2. Tentative infrared assignments for the amorphous BTDA–DMDA polyimide spectrum (a-PI), the BTDA–DMDA polyimide crystalline difference spectrum (c-Pi), the compound A spectrum (Comp. A), and the compound B spectrum (Comp. B)

a-PI	c-PI	Comp. A	Comp. B	Tentative assignment
3487(vw)	3487(w) 3070(vw)	3490(vw)	3487(w)	} $\nu(2)1,2,4\text{-C}_6\text{H}_3/\nu(2 \text{ or } 20a)1,4\text{-C}_6\text{H}_4$
3064(vw)		3061(w) 3048(vw)	3067(w)	
			3048(vw) 3015(w)	
2966(w)	2963(w)		2963(w)	$\nu_{as}\text{CH}_3$
2930(w)	2927(w)			$\nu_{as}\text{CH}_2$
2872(w)	2872(w)			$\nu_s\text{CH}_3$
			2837(w)	$\nu\text{CH}_3(\text{phenyl-OCH}_3)$
1778(w)	1785(vw)	1786(w)	1786(w)	} $\nu(\text{C=O})$ in-phase[imide I]
	1770(vw)		1771(sh)	
1722(vs)		1720(vs)	1718(vs)	} $\nu(\text{C=O})$ out-of-phase[imide I]
	1716(vs)	1715(sh)		
	1708(vs)		1712(sh)	
1673(w)			1695(sh)	} $\nu(\text{C=O})$ -phenyl
	1655(m)	1654(s)	1655(m)	
	1622(sh)	1624(w)	1622(sh)	$\nu(8b)1,2,4\text{-C}_6\text{H}_3$
1610(w)	1612(vw) 1602(vw)		1614(w)	$\nu(8a)1,4\text{-C}_6\text{H}_4$
		1600(w)		$\nu(8a)1,2,4\text{-C}_6\text{H}_3$
1589(w)	1590(vw)	1590(sh)	1590(w)	$\nu(8a)\text{C}_6\text{H}_5$
1512(s)	1520(s)		1518(s)	$\nu(8b)1,4\text{-C}_6\text{H}_4/\text{C}_6\text{H}_5$
		1503(m) 1493(sh)		} $\nu(19a)1,4\text{-C}_6\text{H}_4$
		1479(w)		
1474(w)	1479(sh)		1477(sh) 1470(w)	$\nu(19b)1,2,4\text{-C}_6\text{H}_3$
1464(sh)	1462(vw)			$\delta_{as}\text{CH}_3$
			1457(sh)	$\delta_s\text{CH}_2$
		1455(w)		$\nu(19b)\text{C}_6\text{H}_5$
	1442(vw)		1443(vw)	$\delta_s\text{OCH}_3$
1424(w)	1426(vw)	1426(w)	1426(vw)	} $\nu(19a)1,2,4\text{-C}_6\text{H}_3$
	1401(m)		1402(m)	
		1395(m)		} $\nu(\text{CNC})$ [axial-imide II]
1380(m)			1350(w)	
1353(sh)	1347(w)	1346(w) 1319(vw)		$\nu(14)\text{C}_6\text{H}_5$
	1312(w)		1309(sh)	$\nu(14)1,4\text{-C}_6\text{H}_4$
1297(w)	1301(w)		1300(w)	
	1285(w)	1291(sh) 1285(w) 1275(sh) 1254(w)	1285(w)	$\delta(3)1,2,4\text{-C}_6\text{H}_3$
1248(m)	1252(m) 1217(w)		1249(s)	$\nu_{as}(\text{COC})$
1209(w)		1210(w) 1183(vw)	1211(w)	$\nu(13)1,2,4\text{-C}_6\text{H}_3$
1174(w)	1172(w)		1175(m)	$\delta(9a)\text{C}_6\text{H}_5$
1163(w)	1164(w)	1163(w)	1162(w)	$\delta(9a)1,4\text{-C}_6\text{H}_4$
			1152(sh)	$\delta(15)1,2,4\text{-C}_6\text{H}_3$
	1137(w)	1139(m)	1138(m)	} $\nu(\text{CNC})$ [transverse-imide III]
1131(sh)			1127(s)	
1117(w)	1124(m)	1124(m)		
		1107(w)		

Table 2. (Continued)

a-PI	c-PI	Comp. A	Comp. B	Tentative assignment
1095(w)	1103(w)		1101(w)	} $\delta(18b)1,4-C_6H_4$
1045(w)	1070(w)	1072(w)	1072(vw)	$\delta(18b)1,2,4-C_6H_3/C_6H_5$
	1041(w)		1031(w)	} $\nu_s(COC)$
		1026(vw)		$\delta(18a)C_6H_5$
1024(w)	1020(w)		1009(vw)	} $\delta(18a)C_6H_4$
		1003(vw)		$\nu(12)C_6H_5$
1001(vw)				
988(vw)	988(vw)	990(w)	988(vw)	
983(vw)				
968(sh)		970(vw)	971(vw)	$\nu(7b)1,2,4-C_6H_3$
	961(vw)	961(vw)	960(vw)	$\gamma(17a)1,4-C_6H_4/C_6H_5$
		941(sh)		} $\gamma(10b)1,4-C_6H_4$
	939(w)		937(w)	
		931(w)		} $\gamma(10a)1,2,4-C_6H_3$
928(w)		927(w)		
	924(w)		925(w)	
897(vw)				
	871(w)	869(w)	870(w)	} $\gamma(10b)1,2,4-C_6H_3$
864(w)				} $\nu(1)1,4-C_6H_4$
	857(w)	857(w)	858(w)	
			852(sh)	
828(w)			826(sh)	
	822(w)	822(vw)		} $\gamma(11)1,4-C_6H_3/1,2,4-C_6H_3$
			818(m)	
			813(w)	
800(vw)	800(sh)	800(vw)	802(vw)	
			782(w)	
772(vw)		774(w)		
	768(w)		768(vw)	
758(w)	760(w)		761(w)	$\nu(12)1,4-C_6H_4$
		752(w)		$\gamma(11)C_6H_5$
745(w)				
	740(w)		740(w)	} $\nu(12)1,2,4-C_6H_3$
		737(m)		
	728(vw)		727(vw)	
722(m)				
	714(m)	713(m)	714(s)	} $\gamma(CNC)[\text{imide IV}]$
			708(sh)	
702(w)				
			698(sh)	
		687(w)		
684(vw)	682(w)		682(w)	} $\gamma(4)1,2,4-C_6H_3$
	661(vw)			
652(vw)			650(vw)	
		649(vw)		
637(vw)	635(vw)		635(vw)	$\nu(6b)1,4-C_6H_4$
		632(w)		
	623(vw)			
			615(w)	$\nu(6b)C_6H_5$
614(w)				
	601(w)		605(vw)	
585(vw)	584(w)	584(w)	584(vw)	$\nu(16a)1,2,4-C_6H_3$
			569(vw)	
		564(w)		
561(w)				
550(w)	551(w)	553(w)	551(w)	$\nu(1)1,2,4-C_6H_3$
		533(vw)		
527(w)	525(w)		527(w)	
		508(w)		

Tangential vibrations

The vibrational modes, referring to the Wilson numbers (8a, 8b, 19a, 19b, 14), involve tangential C–C stretching vibrations. For the disubstituted phenyl group, the vibrational pair 8a and 8b are assigned in the amorphous state of the polyimide to 1610 and 1589 cm^{-1} and in the crystalline state to 1612 and 1590 cm^{-1} . The assignment of these absorption frequencies to the disubstituted phenyl group is supported by examination of the model compound spectra. Compound B, which possesses *para*-disubstituted phenyl groups, displays spectral bands at 1614 and 1590 cm^{-1} . On the other hand, compound A, which does not contain *para*-disubstituted phenyl groups, does not display spectral bands at these positions. Furthermore, the spectrum of the *para*-disubstituted aromatic diamine, DMDA, also exhibits bands at 1612 and 1583 cm^{-1} .

For the trisubstituted phenyl group, the vibrational mode 8b is seen in the crystalline state of the polyimide at 1622 cm^{-1} . In the amorphous state, this band is hidden from view by the overlapping band from mode 8a of the disubstituted phenyl group. Both compounds A and B contain asymmetric trisubstituted phenyl groups and similarly display mode 8b at 1624 and 1622 cm^{-1} , respectively. A very prominent peak at 1621 cm^{-1} in the Raman spectrum of the trisubstituted aromatic dianhydride, BTDA, also supports the assignment to the trisubstituted phenyl group. This assignment also agrees well with vibrational assignments of asymmetric trisubstituted phenyl groups made by Green *et al.* [20] and Sarma [21].

The semicircle stretch mode 19a for *para*-disubstituted phenyl groups appears as a very strong band at 1512 cm^{-1} in the amorphous state and at 1520 cm^{-1} in the crystalline state of the polyimide. The assignment to the *para*-disubstituted phenyl group is supported by the appearance of a similarly strong band in the spectra of the polyamic acid (1511 cm^{-1}), the diamine, DMDA (1510 cm^{-1}), and model compound B (1518 cm^{-1}), all of which contain the *para*-disubstituted phenyl group. Furthermore, this characteristically strong band is not seen in the spectra of model compound A or the dianhydride, BTDA, both of which do not contain the *para*-disubstituted phenyl ring. Varsanyi [19] positions mode 19a for *para*-disubstituted phenyl in the region 1480–1520 cm^{-1} depending upon the electron donating ability of the substituents. The greater the electron donating ability, the greater the absorption frequency in this region. Colthup *et al.* [22] assigns mode 19a to a band at 1510 cm^{-1} with strong intensity for electron donor substituents.

For the trisubstituted phenyl group, mode 19a appears at 1424 cm^{-1} in the amorphous polyimide spectrum and 1426 cm^{-1} in the crystalline difference spectrum of the polyimide. This band is consistently found in the spectra of materials containing the trisubstituted phenyl groups (compound A, 1426 cm^{-1} ; compound B, 1426 cm^{-1} ; BTDA, 1423 cm^{-1}) while it is not apparent in the spectrum of the diamine, DMDA, which does not possess any trisubstituted phenyl groups. This assignment also falls within the range, 1370–1450 cm^{-1} , given by Varsanyi [19] for mode 19a in asymmetric trisubstitution.

Mode 19b for the trisubstituted phenyl group is assigned to the band at 1474 and 1479 cm^{-1} in the amorphous and crystalline spectrum of the polyimide, respectively. A similar band is found in the spectra of trisubstituted phenyl materials (compound A, 1479 cm^{-1} ; compound B, 1477 cm^{-1} ; BTDA, 1484 cm^{-1}), all within the range, 1460–1530 cm^{-1} , given by Varsanyi [19] for mode 19b in asymmetric trisubstitution.

The peak at 1297 and 1301 cm^{-1} in the amorphous and crystalline spectrum of the polyimide respectively probably arises from mode 14 of the *para*-disubstituted phenyl group. The disubstituted aromatic materials, compound B and the diamine, DMDA, possess spectral bands at 1300 and 1297 cm^{-1} , respectively. This band does not appear in the spectrum of compound A, which lacks the disubstituted phenyl groups. Varsanyi [19] gives a range of 1240–1380 cm^{-1} for mode 14 in *para*-disubstitution.

Mode 9a for the *para*-disubstituted phenyl group appears at 1174 cm^{-1} in the amorphous spectrum and 1172 cm^{-1} in the crystalline polyimide spectrum. The disubstituted aromatic materials display a band at this position (BTDA–DMDA polyamic acid, 1172 cm^{-1} ; compound B, 1175 cm^{-1} ; DMDA, 1171 cm^{-1}) while materials that do not possess disubstitution, such as compound A, do not contain a band at this position.

Katritzky [23] also found this vibrational band at 1175 cm^{-1} for *para*-disubstituted benzenes.

Another group of tangential phenyl ring vibrations is the C–H in-plane bending vibrations which includes modes 3, 9a, 15, 18a, 18b. The peak at 1285 cm^{-1} in the crystalline polyimide spectrum is attributed to mode 3 of the trisubstituted phenyl group. This peak at 1285 cm^{-1} is also found in the spectrum of such other trisubstituted aromatic materials as compound A and compound B. This assignment also agrees well with that of Sarma [21] who designates a peak at 1283 cm^{-1} to mode 3 for asymmetric trisubstitution.

The peak at 1163 cm^{-1} in the amorphous polyimide spectrum and 1164 cm^{-1} in the crystalline polyimide spectrum is attributed to mode 15 for asymmetric trisubstitution. The assignment of this band to the trisubstituted phenyl group is supported by the appearance of this band in the other trisubstituted aromatic materials (compound A, 1163 cm^{-1} ; compound B, 1162 cm^{-1} ; BTDA, 1166 cm^{-1}). The frequency values also fall within the range, $1140\text{--}1170\text{ cm}^{-1}$, given by Varsanyi [19] for mode 15 with asymmetric trisubstitution.

For vibrational pair 18 in *para*-disubstitution, vibration 18a is assigned to the bands at 1024 cm^{-1} (amorphous polyimide) and 1020 cm^{-1} (crystalline polyimide), while vibration 18b is associated with 1095 cm^{-1} (amorphous polyimide) and 1103 cm^{-1} (crystalline polyimide). These assignments agree fairly well with that of Young *et al.* [16] (18a C_6H_4 , 1015 cm^{-1}) and (18b C_6H_4 , 1093 cm^{-1}) and Varsanyi [19] (18a C_6H_4 , $1004\text{--}1022\text{ cm}^{-1}$) and (18b C_6H_4 , $1085\text{--}1128\text{ cm}^{-1}$).

The band at 1070 cm^{-1} in the crystalline polyimide spectrum is assigned to mode 18b in asymmetric trisubstitution. The other trisubstituted aromatic materials also exhibit this band (compound A, 1072 cm^{-1} ; compound B, 1072 cm^{-1} ; BTDA, 1074 cm^{-1}). The frequency interval given by Varsanyi [19] for this vibrational mode is $1070\text{--}1120\text{ cm}^{-1}$.

Radial skeletal vibrations

The radial skeletal vibrations of the aromatic ring include vibrational modes 1, 12, 6b, 13, and 7b. Mode 1 for the *para*-disubstituted phenyl group probably contributes to the overlapped band at 864 cm^{-1} in the amorphous polyimide spectrum. This assignment is based upon the strong Raman line typically associated with the ring breathing character of mode 1 found at 864 cm^{-1} in the Raman spectrum of the diamine, DMDA. The infrared spectral region from 850 to 870 cm^{-1} , however, also contains contributions from out-of-plane bending aromatic modes which will be discussed later.

Mode 1 for the asymmetric trisubstitution is identified as the band at 550 and 551 cm^{-1} in the amorphous and crystalline polyimide spectrum, respectively. Compounds A and B also show this trisubstituted phenyl band at 553 and 551 cm^{-1} , respectively. A medium intensity band in the Raman spectra of the trisubstituted aromatic dianhydride, BTDA, is also found at 553 cm^{-1} . A band at 553 cm^{-1} is also observed by Green *et al.* [20] for trimethylbenzene and lies within the range, $500\text{--}600\text{ cm}^{-1}$, given by Varsanyi [19] for mode 1 in asymmetric trisubstitution.

The band at 758 cm^{-1} in the amorphous polyimide spectrum and at 760 cm^{-1} in the crystalline polyimide spectrum is attributed to mode 12 in *para*-disubstitution. The assignment of this band to the *para*-disubstituted phenyl group is supported by the possession of a band at 761 cm^{-1} in the spectrum for *para*-disubstituted compound B and the absence of a band at this location in the spectrum for compound A which lacks the *para*-disubstituted phenyl group.

Vibrational mode 12 in asymmetric trisubstitution appears at 745 cm^{-1} in the amorphous polyimide spectrum and at 740 cm^{-1} for the crystalline polyimide spectrum. The other trisubstituted aromatic materials also contain this band in their spectra (compound A, 737 cm^{-1} ; compound B, 740 cm^{-1} ; BTDA, 742 cm^{-1}). Furthermore, mode 12 is characterized by a strong Raman line [24] which appears at 753 cm^{-1} in the Raman spectrum of the trisubstituted dianhydride, BTDA. The assignment of mode 12 agrees well with vibrational assignments of asymmetric trisubstituted phenyl groups performed by Sarma [21] and Dunkers and Ishida [24].

The band at 637 cm^{-1} in the amorphous polyimide spectrum and 635 cm^{-1} in the crystalline polyimide spectrum is attributed to mode 6b in *para*-disubstitution. Characteristic of mode 6b in *para*-disubstitution is a medium Raman line [25], which is found at 646 cm^{-1} in the Raman spectrum of the disubstituted aromatic diamine, DMDA. This assignment is also within the interval Varsanyi [19] gives for mode 6b in *para*-disubstitution ($610\text{--}650\text{ cm}^{-1}$).

In asymmetric trisubstitution, mode 13, classified as a radial skeletal C–X stretching vibration, is assigned to the 1209 cm^{-1} band in the amorphous polyimide spectrum. The trisubstituted aromatic model compounds A and B also display this band (compound A, 1210 cm^{-1} ; compound B, 1211 cm^{-1}). This assignment also agrees with that given by McMurry and Thornton [26] who give a range of $1195\text{--}1210\text{ cm}^{-1}$ for this vibrational mode in asymmetric trisubstitution.

Another radial skeletal, C–X stretching vibration for asymmetric trisubstitution is mode 7b, which is situated at 968 cm^{-1} in the amorphous polyimide spectrum. The other trisubstituted aromatic materials display this band in their spectra as well (compound A, 970 cm^{-1} ; compound B, 971 cm^{-1} ; BTDA, 965 cm^{-1}).

Out-of-plane bending vibrations

The aromatic out-of-plane bending vibrations include the out-of-plane skeletal vibrational modes 4, 16a and the C–H out-of-plane bending modes 10a, 10b, 11, and 17a. Ring bending mode 4 for the trisubstituted phenyl group is attributed to the band at 684 and 682 cm^{-1} in the amorphous and crystalline polyimide spectra, respectively. The band also appears in the spectra of the other trisubstituted aromatic materials (compound A, 687 cm^{-1} ; compound B, 682 cm^{-1} ; BTDA, 687 cm^{-1}). The interval given for this mode by Varsanyi [19], $680\text{--}740\text{ cm}^{-1}$, and by Colthup *et al.* [22], $685\text{--}735\text{ cm}^{-1}$, incorporates this assignment.

The band at 585 and at 584 cm^{-1} in the amorphous and crystalline polyimide spectra is assigned to mode 16a in asymmetric trisubstitution. The spectra of the other trisubstituted aromatic materials exhibit this band as well (compound A, 584 cm^{-1} ; compound B, 584 cm^{-1} ; BTDA, 593 cm^{-1}). Varsanyi [19] places mode 16a in the range $470\text{--}620\text{ cm}^{-1}$ for asymmetric trisubstitution.

For the *para*-disubstituted phenyl group, the C–H out-of-plane bending modes include 17a, 10b, and 11. In the crystalline polyimide spectrum, mode 17a appears at 961 cm^{-1} , while mode 10b appears at 939 cm^{-1} . Mode 11, which has an identical absorption for asymmetric trisubstitution and *para*-disubstitution [19], is assigned to the band appearing at 828 cm^{-1} in the amorphous polyimide spectrum and at 822 cm^{-1} in the crystalline polyimide spectrum. These assignments agree well with those given by Colthup *et al.* [22] (17a, 961 cm^{-1} ; 10b, 940 cm^{-1} ; 11, 817 cm^{-1}).

For the asymmetric trisubstituted phenyl group, modes 10a, 10b, and 11 correspond to C–H out-of-plane vibrations. Mode 11, as mentioned before, is identical for asymmetric trisubstitution and *para*-disubstitution. However, mode 10a for asymmetric trisubstitution appears at 928 cm^{-1} in the amorphous polyimide spectrum and at 924 cm^{-1} in the crystalline polyimide spectrum, while the amorphous component of mode 10b found at 864 and at 871 cm^{-1} for the crystalline component. These assignments also agree well with those given by Colthup *et al.* [22] (10a, 929 cm^{-1} ; 10b, 868 cm^{-1}).

Non-cyclic group vibrations

One of the most distinguishable bands of the BTDA–DMDA polyimide from the non-cyclic groups involves the benzophenone carbonyl group. The carbonyl stretching absorption band, with its relatively constant position ($1870\text{--}1540\text{ cm}^{-1}$) and relative freedom from interfering bands, makes it one of the most identifiable bands in infrared spectra. Conjugation of the carbonyl group with a phenyl group brings the absorption frequency into the $1685\text{--}1666\text{ cm}^{-1}$ region with further reduction in frequency possible with additional conjugation [27]. The benzophenone carbonyl stretching vibration in the

BTDA–DMDA polyimide absorbs at 1673 cm^{-1} in the amorphous state and 1655 cm^{-1} in the crystalline state. This spectral shift has been explained by increased conjugation upon crystallization as a result of intramolecular rotation about the benzophenone carbonyl [15].

Vibrational bands from the ether groups are also observed in the BTDA–DMDA polyimide spectrum. An alkoxy group on an aromatic ring typically yields two correlatable bands at $1310\text{--}1210$ and $1050\text{--}1010\text{ cm}^{-1}$ [22]. The aryl alkyl ether asymmetric stretching vibration appears at 1248 and 1252 cm^{-1} in the amorphous and crystalline spectra of the polyimide, respectively. This absorption band is also seen in the spectra of the other aromatic ether materials (compound B, 1249 cm^{-1} ; DMDA, 1243 cm^{-1}). The aryl alkyl ether symmetric stretching vibration is assigned to the band at 1045 and 1041 cm^{-1} in the amorphous and crystalline polyimide spectra, respectively. The spectrum of model compound B displays this band at 1031 cm^{-1} , while the spectrum of the diamine, DMDA, exhibits this band at 1038 cm^{-1} .

Methyl and methylene deformation bands are also evident in the BTDA–DMDA polyimide spectrum. The methyl asymmetric deformation band at 1470 cm^{-1} in the spectrum of model compound B and at 1469 cm^{-1} in the spectrum of the diamine, DMDA, is probably overlapped in the polyimide spectrum with the trisubstituted aromatic mode 19b. The methylene symmetric deformation band appears at 1464 and 1462 cm^{-1} in the amorphous and crystalline polyimide spectra, respectively. The methylene group in the spectrum of the diamine, DMDA, gives rise to a band at 1459 cm^{-1} .

The CH stretching vibrations of the alkane groups in the polyimide also appear in the infrared spectra. The methyl asymmetric stretching band is located at 2966 and 2963 cm^{-1} in the amorphous and crystalline polyimide spectra, respectively, while the methyl symmetric stretching band is found at 2872 cm^{-1} in both the amorphous and crystalline polyimide spectra. These assignments also agree very well with that of Silverstein *et al.* [27] who assigns the methyl asymmetric stretch to a distinctive band at 2962 cm^{-1} and the methyl symmetric stretch to a distinctive band at 2872 cm^{-1} . The peak at 2837 cm^{-1} in the spectrum of compound B is characteristic of a methoxy group attached to a phenyl ring [22]. The asymmetric stretching of the methylene group appears at 2930 and 2927 cm^{-1} in the amorphous and crystalline polyimide spectra, respectively. This assignment also agrees with that given by Silverstein *et al.* [27] who attributes a band at $2926 \pm 10\text{ cm}^{-1}$ to the methylene asymmetric stretching vibration.

CONCLUSIONS

A systematic analysis was conducted on the infrared spectral bands of the BTDA–DMDA polyimide. Vibrations characteristic to the *para*-disubstituted phenyl ring, the asymmetric trisubstituted phenyl ring, the imide ring, the benzophenone carbonyl group, as well as the ether and alkane groups were identified.

Acknowledgements—The authors gratefully acknowledge the financial support for this research from the National Science Foundation Center for Molecular and Microstructure of Composites (CMMC).

REFERENCES

- [1] A. N. Krasovskii, N. P. Antonov, M. M. Koton, K. K. Kalnin'sh and V. V. Kudryavtsev, *Polym. Sci. U.S.S.R.* **21**, 1038 (1979).
- [2] S. V. Serchenkova, M. V. Shablygin, T. V. Kravchenko, M. N. Bogdanov and G. I. Kudryavtsev, *Vysokomol. soyed.* **A18**, 1863 (1976).
- [3] P. R. Dickinson and C. S. P. Sung, *Macromolecules* **25**, 3758 (1992).
- [4] R. W. Snyder, B. Thomson, B. Bartges, D. Czerniawski and P. C. Painter, *Macromolecules* **22**, 4166 (1989).
- [5] T. J. Hsu and Z. Liu, *J. Appl. Polym. Sci.* **46**, 1821 (1992).
- [6] I. Y. Kardash, D. Y. Likhachev, M. B. Krotovich, N. V. Kozlova, I. L. Zhuravleva, Y. S. Bogachev and A. N. Pravednikov, *Vysokomol. soyed.* **A29**, 1364 (1987).

- [7] T. Matsuo, *Bull. Chem. Soc. Jpn.* **37**, 1844 (1964).
- [8] H. Ishida, S. T. Wellinghoff, E. Baer and J. L. Koenig, *Macromolecules* **13**, 826 (1980).
- [9] H. Ishida and K. Kelley, *Polymer* **32**, 1585 (1991).
- [10] W. H. Tsai, F. J. Boerio and K. M. Jackson, *Langmuir* **8**, 1443 (1992).
- [11] A. Y. Strunnikov, N. V. Mikhailova and A. V. Sidorovich, *Polym. Sci. U.S.S.R.* **32**, 1 (1990).
- [12] A. I. Koltsov, Y. G. Baklagina, B. M. Ginzburg, L. N. Korzhavin, M. M. Koton, N. V. Mikhailova, V. N. Nikitin and A. V. Sidorovich, *J. Polym. Sci.* **C42**, 867 (1973).
- [13] L. A. Laius, *Vysokomol. soyed.* **A16**, 2101 (1974).
- [14] V. P. Pshenitsyna, L. G. Kazaryan, Y. G. Lur'ye, M. L. Lebedinskaya and V. V. Kouriga, *Vysokomol. soyed.* **A14**, 628 (1972).
- [15] H. Ishida and M. T. Huang, *J. Polym. Sci. Polym. Phys. Ed.*, in press.
- [16] J. T. Young, W. H. Tsai and F. J. Boerio, *Macromolecules* **25**, 887 (1992).
- [17] S. Z. D. Cheng, M. L. Mittleman, J. J. Janimak, D. Shen, T. M. Chalmers, H. Lien, C. C. Tso, P. A. Gabori and F. W. Harris, *Polym. Int.* **29**, 201 (1992).
- [18] R. A. Dine-Hart and W. W. Wright, *Makromol. Chem.* **143**, 189 (1971).
- [19] G. Varsanyi, *Vibrational Spectra of Benzene Derivatives*. Academic Press, New York (1969).
- [20] J. H. S. Green, D. J. Harrison and W. Kynaston, *Spectrochim. Acta* **27A**, 807 (1971).
- [21] T. V. K. Sarma, *Appl. Spectrosc.* **40**, 936 (1986).
- [22] N. B. Colthup, L. H. Daly and S. E. Wiberley, *Introduction to Infrared and Raman Spectroscopy*, 3rd edn. Academic Press, New York (1990).
- [23] A. R. Katritzky, *Quart. Rev.* **13**, 353 (1959).
- [24] J. Dunkers and H. Ishida, *Spectrochim. Acta*, in press.
- [25] F. R. Dollish, W. G. Fately and F. F. Bentley, *Characteristic Raman Frequencies of Organic Compounds*. Wiley, New York (1974).
- [26] H. L. McMurtry and V. Thornton, *Analyt. Chem.* **24**, 318 (1952).
- [27] R. M. Silverstein, G. C. Bassler and T. C. Morrill, *Spectrometric Identification of Organic Compounds*, 4th edn. Wiley, New York (1981).