

Infrared Spectra of Poly(ethylene 2,6-Naphthalate) and Some Related Polyesters

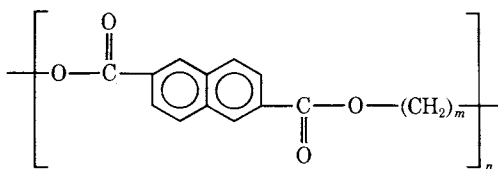
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Synopsis

Infrared spectra of some poly(methylene terephthalates) and some poly(methylene 2,6-naphthalates) were compared. To interpret the spectral changes during drawing and heat treatment, the concept of rotational isomerism of the $-\text{O}-(\text{CH}_2)_m-\text{O}-$ part, which was fairly successful in poly(ethylene terephthalate) (C_2T), was tried to apply to the polyesters other than C_2T . Also, the bands originated from a benzene ring and from a naphthalene ring were distinguished. Poly(ethylene 2,6-naphthalate) (C_2N) has some bands behaving differently from those of other polyesters. This would be due to the existence of certain intermolecular interactions arising from tight packing of the molecules in the crystal of C_2N .

INTRODUCTION

Poly(ethylene 2,6-naphthalate) (C_2N) is relatively well known among poly(methylene 2,6-naphthalates) with different numbers of methylene groups:



The properties and the crystal structure of C_2N have been discussed by several authors,¹⁻⁵ but its infrared spectrum has not been reported yet. On the other hand, the infrared spectrum of poly(ethylene terephthalate) (C_2T) whose repeat unit has a benzene ring instead of a naphthalene ring in the main chain has been the subject of extensive studies since the late fifties.⁶⁻¹⁰ Most spectral changes during drawing and heat treatment of C_2T were explained by a number of workers, except Liang and Krimm,⁸ in terms of rotational isomerism of ethylene glycol residue. It would be of interest to compare the spectra of various poly(methylene terephthalates) and poly(methylene 2,6-naphthalates) and to see if the spectral changes due to drawing or heat treatment in these polymers, particularly in C_2N , conform to the above interpretation in C_2T . The comparison of the spectra would also provide knowledge on the difference between the bands originating from a benzene ring and from a naphthalene ring.

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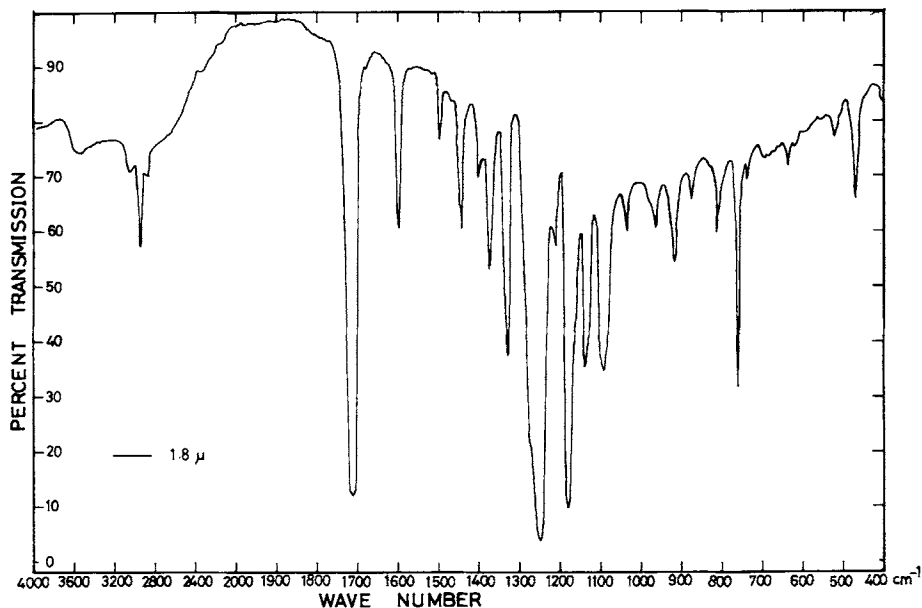


Fig. 1. Infrared spectrum of C₂N.

BANDS ASSOCIATED WITH —O-(CH₂)_m-O—

Infrared spectra in the range between 4000 and 400 cm⁻¹ were taken by means of a Japan Spectroscopic Co., Type IRA-2 spectrometer. The spectrum of C₂N is shown in Figure 1. Also, in Table I, all the bands of C₂T, C₃T [poly(trimethylene terephthalate)], C₄T [poly(tetramethylene terephthalate)], C₂N₁C₄N [poly(tetramethylene 2,6-naphthalate)], and C₆N [poly(hexamethylene 2,6-naphthalate)] are summarized.

As we will discuss below, the bands at 2965, 2910, 1477, 1453, 1370, and 1330 cm⁻¹ are considered to be related to the vibration of CH₂, and the bands at 1090 and 1044 cm⁻¹ may be associated with the vibration of C—O in ethylene glycol residue in C₂N.

The bands at 2965 and 2910 cm⁻¹ of C₂N correspond to the bands at 2950 and 2900 cm⁻¹ of C₂T and should be the antisymmetric and symmetric vibration of CH₂, respectively. By heat treatment, structures appear at 2990 and 2890 cm⁻¹ as shown in Figure 2. The spectra of C₃T, C₄T, C₄N, and C₆N have corresponding bands but do not show distinct structures as in C₂N upon heating. A spectrometer of high dispersion may be necessary to investigate these points further.

The bands around at 1470 and 1450 cm⁻¹ exist in all the polyesters concerned here. In C₂N, the σ band at 1477 cm⁻¹ intensifies and the π band at 1433 cm⁻¹ weakens by drawing or heat treatment, as shown in Figure 3. These bands may be assigned as CH₂ bending vibrations of trans and gauche configurations, respectively, as in C₂T. This assignment may be supported by the fact that there are two absorption bands between 1440 and 1470 cm⁻¹ in bis(β -hydroxyethyl) 2,6-naphthalate and diethyl 2,6-naphthalate, but that there are no absorption in this range in naphthalene and 2,6-naphthalic acid, which have no CH₂ group in the molecules. The 1477 cm⁻¹ band of C₂N shows much sharper σ polarization

TABLE I
 Infrared Spectra of Various Polyesters

C ₂ T		C ₃ T		C ₄ T		C ₂ N		C ₄ N		C ₆ N	
Fre- quency cm ⁻¹	Intensity polarization spectral change	Fre- quency cm ⁻¹	Intensity polarization spectral change	Fre- quency cm ⁻¹	Intensity polarization spectral change	Fre- quency cm ⁻¹	Intensity polarization spectral change	Fre- quency cm ⁻¹	Intensity polarization spectral change	Fre- quency cm ⁻¹	Intensity polarization spectral change
3650	vw	3650	vw	3630	vw	3650	vw	3610	vw	3610	vw
3560	vw	3550	vw	3550	vw	3550	vw	3550	vw	3540	vw
3440	w ⊥	3430	w ⊥	3420	w ⊥	3430	w ⊥	3400	w ⊥	3400	w ⊥
3055	w	3050	w	3050	w	3060	w ⊥	3050	w	3050	w
						3050	sh crys.			3030	sh
2950	m	2970	m	2950	m	2990	mw crys.	2940	m	2930	m
2900	mw	2900	mw	2880	mw	2910	w	2880	mw	2850	m
						2890	sh crys.				
1957	w	1950	w	1950	w	1950	w	1950	w	1950	w
1830	vw					1820	vw				
1715	vs ⊥	1715	vs ⊥	1715	vs ⊥	1715	vs ⊥	1715	vs ⊥	1715	vs ⊥
1615	w	1610	w	1610	w	1600	s	1600	s	1600	s
1575	m	1575	mw	1575	mw	1570	vw ⊥	1570	vw ⊥		
1508	m	1500	m	1500	m	1500	m	1500	m	1500	m
1475	w ⊥ +	1470	mw ⊥ +	1470	sh	1477	m ⊥ +	1460	m	1470	m ⊥
						1460	sh				
1450	m -	1450	m -	1450	m	1455	sh	1445	m	1450	sh
						1450	m -				
1400	s	1400	s	1440	sh ⊥	1440	sh	1400	m	1400	m
1380	mw crys.	1380	mw crys.	1400	s	1400	m	1400	m	1400	m
1365	mw -	1365	mw -	1380	ms	1370	ms -	1380	m	1365	ms
1337	s +	1340	s +	1350	mw	1337	s +	1340	ms	1340	s
						1332	sh crys.				
				1320	ms			1320	mw		

$\nu(\text{OH})$
 overtone $\nu(\text{C}=\text{O})$
 $\nu(\text{arom. CH})$
 crys. $\nu(\text{arom. CH})$ crys.
 $\nu_a(\text{CH}_2)$ crys.
 $\nu_a(\text{CH}_2)$ amorph.
 $\nu_s(\text{CH}_2)$ amorph.
 $\nu_s(\text{CH}_2)$ crys.

$\nu(\text{C}=\text{O})$
 arom. ring vibration
 arom. ring vibration
 arom. ring vibration
 $\delta(\text{CH}_2)$ trans

$\delta(\text{OH}_2)$ gauche

arom. ring vibration

$\gamma_w(\text{CH}_2)$ gauche

$\gamma_w(\text{CH}_2)$ trans

$\gamma_w(\text{CH}_2)$ trans

TABLE I (continued)

C ₂ T		C ₃ T		C ₄ T		C ₂ N		C ₄ N		C ₆ N	
Fre- quency cm ⁻¹	Intensity polarization spectral change	Fre- quency cm ⁻¹	Intensity polarization spectral change	Fre- quency cm ⁻¹	Intensity polarization spectral change	Fre- quency cm ⁻¹	Intensity polarization spectral change	Fre- quency cm ⁻¹	Intensity polarization spectral change	Fre- quency cm ⁻¹	Intensity polarization spectral change
1280		1280		1260		1270		1270		1270	
1250	vs	1260	vs	1240		1250	vs	1250	vs	1250	vs
1240		1240		1200	w	1210	m -	1210	m	1220	m
						1180	vs -	1180	vs	1180	vs
1172	w	1170	w	1170	w	1135	s -	1135	s	1135	s
1120	s	1120	s	1120	s	1090	s -	1090	s	1090	s
1100	vs	1100	vs	1100	vs	1044	w -	1040	mw	1090	s
1042	w	1040	w	1020	s	1005	m	1040	mw	1090	s
1022	s	1020	s	1020	s	1005	m	1040	mw	1090	s
988	vw +	970	m +	980	sh	984	m +	980	m	980	ms
				950	sh	984	m +	960	s	980	ms
973	m +	970	m +	930	ms	968	m -	940	s	970	m
				920	m +	968	m -	940	s	970	m

$\nu(=C-O) + \text{arom.}$
 $\nu(=C-O) + \text{arom.}$
 arom. ring vibration
 naphthalene ring
 vibration
 $\gamma_1(\text{CH}_2)$ gauche
 naphthalene ring
 vibration
 benzene ring vibration
 $\nu_s(\text{O}-\text{C})$ gauche
 $\nu_a(\text{O}-\text{C})$ gauche
 $\delta(\text{arom. CH in-plane})$

930	vw				930	m	⊥	+											$\gamma_r(\text{CH}_2)$ gauche $\delta(\text{arom. CH out-of-}$ plane)
895	sh		-		919	m	⊥	-		920	s	⊥							
873	ms	⊥		870	ms	⊥				875	vw								
	930	w	+		930	m	⊥	+											
	900	sh		-	919	m	⊥	-		920	s	⊥							
	875	ms	⊥		905	sh	⊥	crys.		875	vw								
					880	w		-											
					835	m	⊥	crys.											
848	m	+		840	m		+			820	m	⊥							$\gamma_r(\text{CH}_2)$ trans
										820	m	⊥							
					810	m		crys.											
					810	w		+											
					790	w													
					740	w	⊥	+											
					725	s	⊥												
					725	s	⊥			765	s	⊥							
					700	w	⊥			790	mw								
					680	vw				740	w	⊥							
					680	vw				690	vw								
					630	vw				650	vw								
					630	vw				640	m								
					580	w				620	w								
					580	w				580	w								
					550	w				555	sh	⊥							
					520	w				530	mw								
					500	mw				525	mw	⊥	+						
					480	w				480	ms	⊥	crys.						
					430	mw				470	ms		-						
					430	mw				470	ms	⊥							
					420	mw				440	sh								
					420	w				420	w								

ν = stretching; δ = bending; γ_w = wagging; γ_r = rocking; crys. = bands which exist only in crystalline state; + = bands which increase in intensity upon crystallization; - = bands which decrease in intensity upon crystallization.

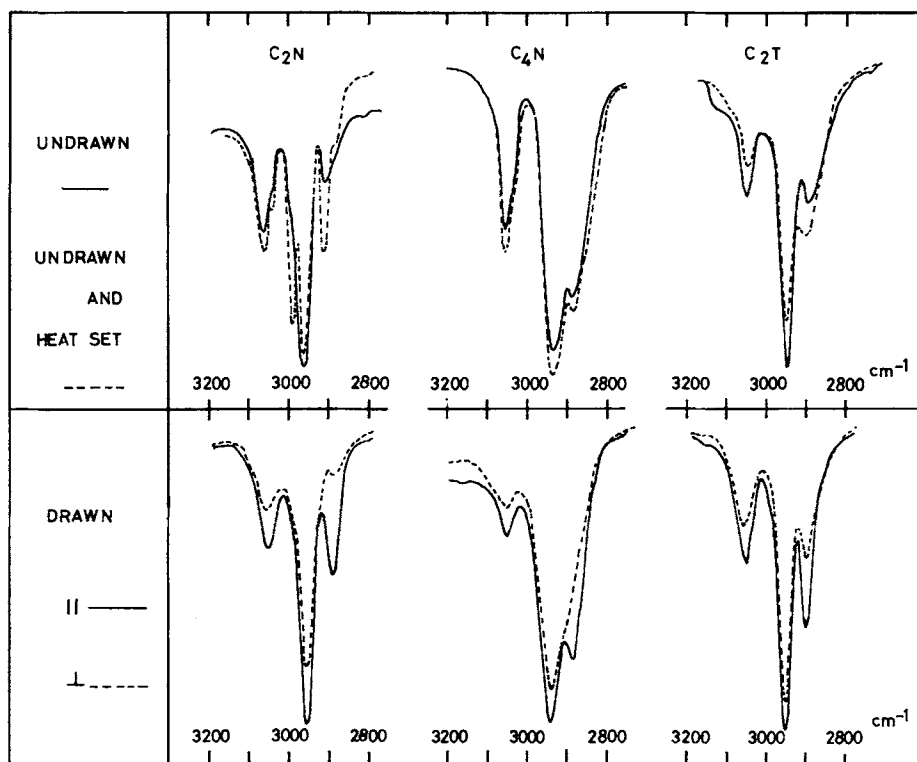
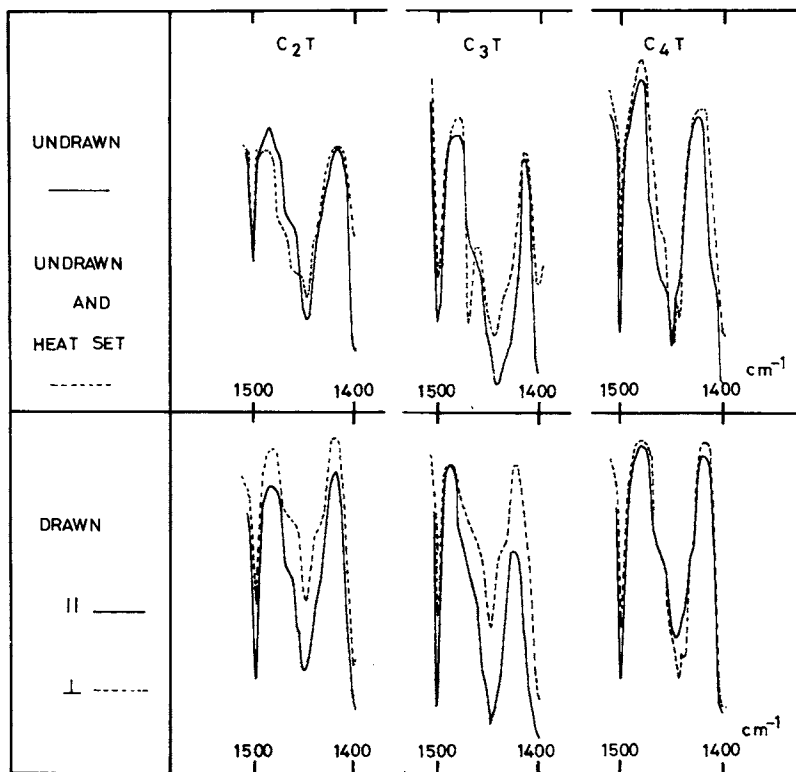


Fig. 2. Infrared spectra of some polyesters between 2800 and 3400 cm^{-1} .

than those of C_2T and other polymers, indicating that C_2N would take the trans configuration more easily. For C_4T , the 1470 cm^{-1} band is not distinct and does not increase in intensity by crystallization. According to Menčík,¹¹ C_4T crystals have methylene linkages arranged as GTT so that the polarization of the bands associated with methylene vibration in the crystals should be different from those of C_2T and C_2N . For C_4N , Watanabe,¹² in our laboratory, found the existence of two crystal forms: fully extended and contracted. So far, we have not succeeded in finding the difference in the infrared spectra of these two forms.

The CH_2 wagging vibrations of C_2N are assigned to the bands at 1370 cm^{-1} (gauche) and 1337 cm^{-1} (trans) as in C_2T . By heat treatment, the 1337 cm^{-1} band gives rise to a shoulder at 1332 cm^{-1} . The intensity change during crystallization is not as prominent for these bands as for CH_2 bending vibrations. For C_2T and C_3T , drawn and heat-treated samples show a relatively weak band at 1380 cm^{-1} . For C_4T and C_4N , three distinct bands always exist in this region: at 1380 , 1350 , and 1320 cm^{-1} for C_4T and at 1365 , 1340 , and 1320 cm^{-1} for C_4N . Thus, there are some variations in the spectra concerning the CH_2 wagging modes of different lengths of methylene groups.

The CH_2 rocking vibrations of C_2T were assigned to 848 cm^{-1} (trans) and 895 cm^{-1} (gauche) by Miyake.⁹ We tried arbitrarily to assign the band at 822 cm^{-1} of C_2N to CH_2 rocking vibration. But the behavior of this band is rather complicated, as shown in Figure 4. Namely, on drawing, the 822 cm^{-1} band shows sharp σ polarization and a band appears at 810 cm^{-1} with π polarization. On



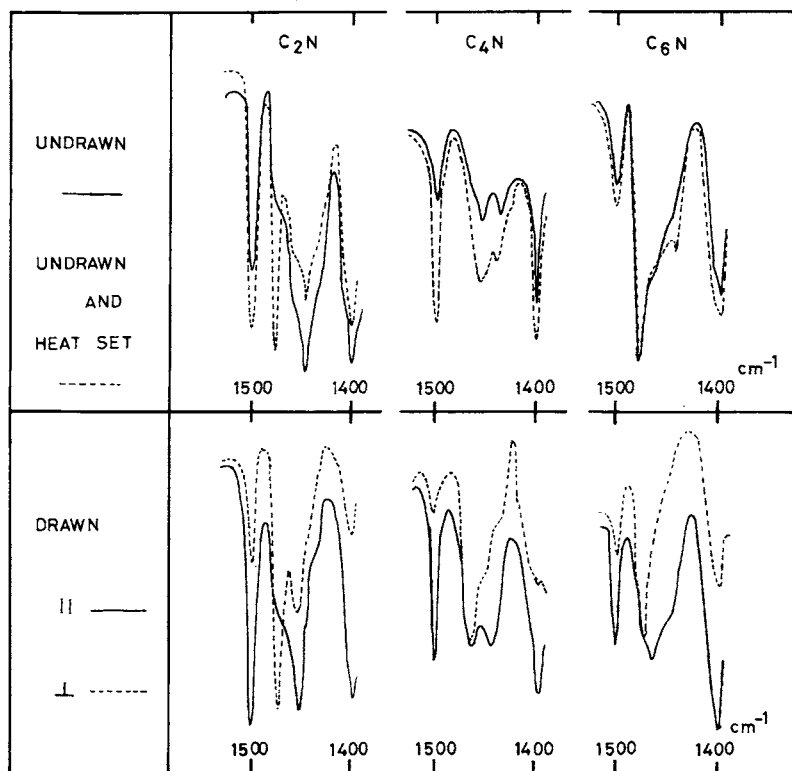
(a)

Fig. 3. Infrared spectra of some polyesters between 1400 and 1500 cm^{-1} .

heating either undrawn or drawn films, the 822 cm^{-1} band decreases in intensity and, instead, bands grow at 835 and 810 cm^{-1} . The 835 cm^{-1} band is of σ character. A band at 820 cm^{-1} exists in C_4N and C_6N , too, but it is a simple σ band and does not bring about 810 or 835 cm^{-1} bands upon crystallization. Thus, the bands that appeared at 810 and 835 cm^{-1} are characteristic of C_2N and probably originate from certain intermolecular interactions existing in oriented or crystalline states of C_2N , as discussed later.

The strong bands at 1090 cm^{-1} in C_2N , C_4N , and C_6N would correspond to the bands at 1100 cm^{-1} in C_2T , C_3T , and C_4T . They are of π polarization and decrease in intensity by heat treatment and may be assigned to the C—O symmetric stretching vibration of the gauche form. This assignment in case of C_2T was made by Miyake⁹ and others and differs from the views of Grime and Ward⁷ and some others; but it may be supported for C_2N by the fact that there is no intense absorption in the vicinity of 1100 cm^{-1} in the spectra of naphthalene and 2,6-naphthalic acid, which have no ethylene glycol residue, and that there is such an absorption in diethyl 2,6-naphthalate, bis(β -hydroxyethyl) 2,6-naphthalate, etc.

Although there are disagreements, Miyake⁹ assigned the band at 1042 cm^{-1} of C_2T to antisymmetric C—O stretching vibration of the gauche form. The weak band at 1044 cm^{-1} in C_2N would correspond to the above vibration of C_2T . Corresponding bands exist in C_3T and C_4N but are too weak to be seen in C_4T .

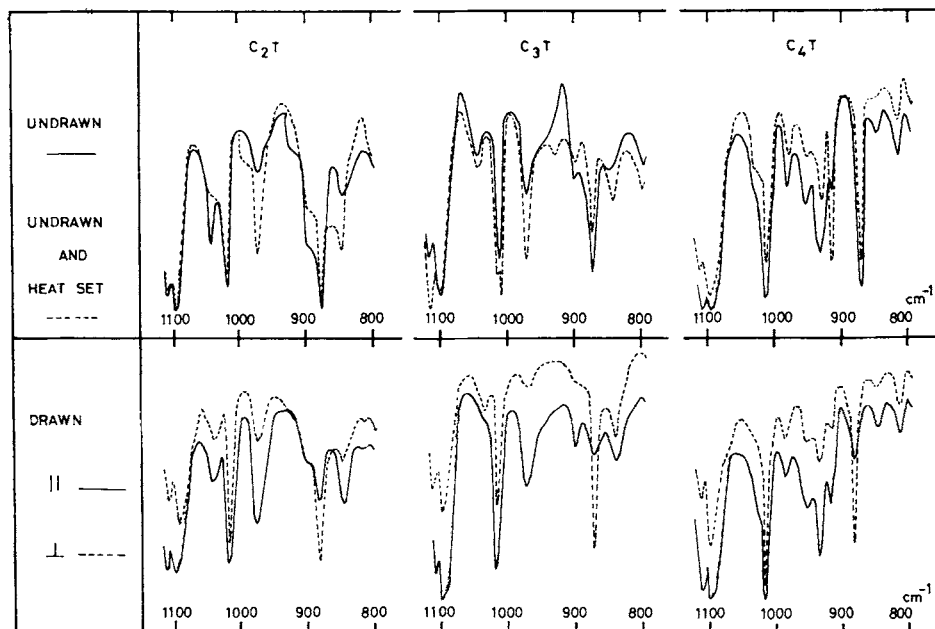


(b)

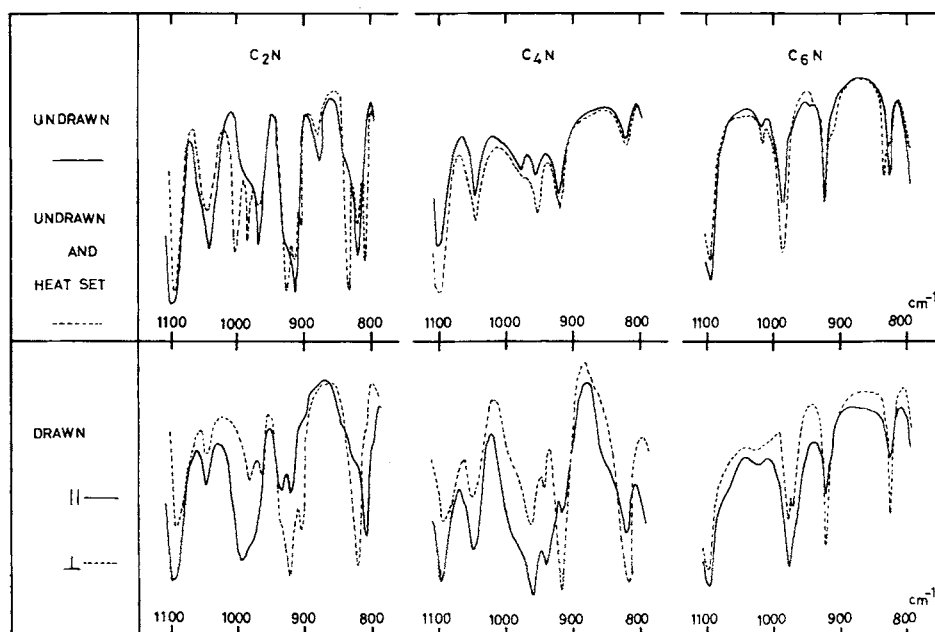
Fig. 3. (continued from previous page)

and C_6N . Making a couple with the 1040 cm^{-1} band, the parallel band at 973 cm^{-1} of C_2T was assigned to antisymmetric C—O stretching vibration of trans form by Miyake,⁹ although Liang and Krimm⁸ assigned it to a benzene ring vibration. The 973 cm^{-1} band exist in C_3T , but in C_4T it has a peak at 930 cm^{-1} with shoulders at 950 , 980 , and 920 cm^{-1} , which would throw some doubts on the assignment as C—O vibration. There are corresponding bands in C_2N , C_4N , and C_6N , but the spectral change of the 968 cm^{-1} band of C_2N is rather complex, as shown in Figure 4. On drawing, the shoulder at 984 cm^{-1} grows and both bands at 968 and 984 cm^{-1} show parallel dichroism. On heating, the original band decreases in intensity and a new band appears at 1005 cm^{-1} . The latter forms a distinct band for undrawn films, but is hidden behind the 984 cm^{-1} band for drawn films and has no perpendicular component. This behavior again must be related to some effects of intermolecular interactions under crystalline field characteristics to C_2N .

The origin of the intermolecular interactions which give birth to the new bands at 810 , 835 , and 1005 cm^{-1} is considered to be the close packing of molecules in the unit cells of C_2N . According to Menčík,¹ the unit cell of C_2N has dimension $a = 6.51\text{ \AA}$, $b = 5.75\text{ \AA}$, $c = 13.2\text{ \AA}$, $\alpha = 81^\circ 21'$, $\beta = 144^\circ 00'$, and $\gamma = 100^\circ 00'$. The projection of the molecules along the c axis is shown in Figure 5(a), and the projection normal to the plane of the molecule is shown in Figure 5(b). In contrast to the configuration of C_2T and C_4T , all the atoms of the polymer chain including O=C—O (except the hydrogens of CH_2) are coplanar in C_2N . This



(a)



(b)

Fig. 4. Infrared spectra of some polyesters between 800 and 1100 cm^{-1} .

plane is approximately ($\bar{4}30$) whose lattice distance is 0.88 Å. Therefore, the distance between the neighboring molecular planes perpendicular to the naphthalene ring is 3.54 Å. On the other hand, since the angle β is large, one of the C atoms of $-\text{CH}_2-\text{CH}_2-$ is just above a naphthalene ring, as seen from Figure 5(b). Considering that the van der Waals radius of a CH_2 is 2 Å and a half-

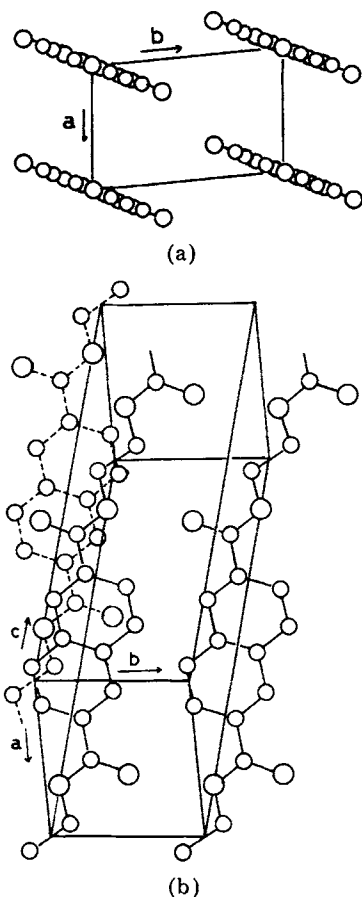
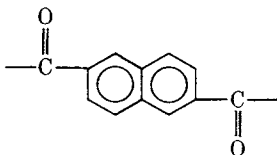


Fig. 5. Arrangement of molecules of C_2N in crystal (after Menčík): (a) projection along c axis. (b) projection normal to the plane of a naphthalene ring.

thickness of an aromatic ring is 1.7 \AA , the distance between a naphthalene ring and a hydrogen atom of CH_2 in the neighboring molecules is almost abnormally short, so that it is quite conceivable that interactions exist between these atoms in the crystalline state. Such tight packing does not seem to exist in C_2T ,¹³ C_4T ,¹¹ and C_4N ,¹² judging from the dimension of the unit cells or from the atomic arrangements in the crystal.

BANDS ASSOCIATED WITH



The σ band at 3060 cm^{-1} with a shoulder at 3050 cm^{-1} of C_2N may be safely assigned to ν (aromatic CH), although it is of parallel polarization in C_2T . The other C_mT and C_mN have this band at this region. Corresponding with the 875 cm^{-1} band of C_2T , C_3T , and C_4T , the band at 919 cm^{-1} in C_2N , C_4N , and C_6N

might be associated with an aromatic CH out-of-plane vibration. However, since the nearest band in the spectrum of naphthalene is at 955 cm^{-1} and compounds such as 2,6-naphthalic acid contain a band in this region, it may be better to consider the band due to O=C—O out-of-plane bending vibration. This band in C_2N is weakened on heating, and, instead, bands grow at 933 and at 905 cm^{-1} with σ polarization.

The bands at 765 cm^{-1} of C_2N , C_4N , and C_6N are very intense and of σ polarization and correspond to the 730 cm^{-1} band of C_2T , C_3T , and C_4T . The latter was a controversial one for a long time. First, Miller and Willis⁶ assigned it to a C—O—C bending vibration, but this was refuted by Grime and Ward⁷ since this band exists in terephthalic acid and other compounds containing no C—O—C linkage. Then, Miyake⁹ assigned it to the O=C—O out-of-plane bending vibration based on a number of spectra of the related compounds. However, in the spectrum of poly(ethylene terephthalate- D_4), the 730 cm^{-1} band shifts to 640 cm^{-1} so that the former does not seem to be associated, at least exclusively, with O=C—O bending. Thus, Grime and Ward⁷ and Liang and Krimm⁸ assigned the 730 cm^{-1} band to an aromatic CH out-of-plane vibration. Since naphthalene has a strong band at 780 cm^{-1} , we favor the assignment of the 765 cm^{-1} band of C_2N , C_4N , and C_6N to aromatic CH out-of-plane vibration.

The band at 470 cm^{-1} in C_2N , C_4N , and C_6N would correspond to the band at 430 cm^{-1} of C_2T which was assigned to aromatic CH out-of-plane bending by Liang and Krimm.⁸ This may be supported by the intense bands of naphthalene at 480 and 470 cm^{-1} . In C_2N , the behavior of the 470 cm^{-1} band is a little different from the others: upon heating, a band appears at 480 cm^{-1} . The 470 cm^{-1} band is of σ polarization, and the 480 cm^{-1} band is of π polarization.

Besides the bands described above, there are more bands related to aromatic ring vibrations at 1600 , 1570 , 1500 , and 1400 cm^{-1} . The strong σ bands at 1180 and 1135 cm^{-1} do not exist in terephthalate polymers and are characteristic for the compounds having a naphthalene ring.

The intense band at 1715 cm^{-1} is, of course, due to C=O stretching vibration. Its overtone appears around 3400 cm^{-1} .

The stretching vibration of =C—O can be assigned to the doublet at 1250 and 1270 cm^{-1} , which is the most intense in the spectrum. Since there is a strong absorption at 1265 cm^{-1} in naphthalene, the doublet may be partially associated with aromatic ring vibrations in addition to the =C—O stretching vibration.

In summary, among the poly(methylene 2,6-naphthalates), C_2N , C_4N , and C_6N have much in common in the infrared spectra, which also correspond fairly well to the spectra of C_2T , C_3T , and C_4T . However, at some frequencies, the spectral changes of C_2N show unique behavior owing to the existence of a characteristic crystalline field arising from the tight packing of the molecules in the crystal.

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