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LIQUID CRYSTAL BEHAVIOUR OF LINEAR COPOLYMERS—I

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Abstract—The molar volumes of some mesophasic linear homo- and copolymers have been measured as a function of temperature. Both the liquid crystal phase (nematic) and the isotropic liquid have been examined. The polymer chain is characterized by an alternating sequence of rigid groups and flexible spacers. The molar volumes measured for the liquid crystal phase give evidence for a substantially disordered conformation taken by the flexible spacers in the nematic phase. Analogies between homo- and copolymers are discussed.

INTRODUCTION

The possibility of obtaining linear polymers exhibiting mesophasic properties either in solution or in the molten state is well established. Actual observation of the liquid crystal phase in the molten state is limited, however, to those polymers with melting temperatures compatible with the thermodynamic stability of the mesophase and frequently with the chemical stability itself.

Polymers having completely rigid backbone chains are therefore hard to obtain in a mesomorphic, thermotropic state. On the contrary, polymers with molecular structure built up with alternating sequences of rigid portions and flexible spacers may show a mesophase in the molten state at convenient temperatures provided the flexible spacers are not too short.

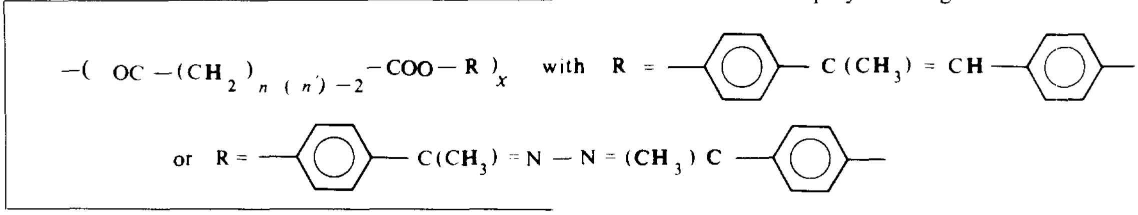
It has been shown how the thermal stability range of the mesophase of semi-flexible polymers forming a homologous series may depend on the length of the flexible part of the monomer unit [1].

Study of the mesophase of these polymers is equally interesting both in the molten state, within the appropriate range of temperature, and at room temperature. In fact in this latter condition, the polymers are semicrystalline (therefore biphasic) and investigation of the structure of the non-crystalline phase is of theoretical and possibly practical interest.

Direct study of the mesophasic homopolymers is frequently hampered on the one hand by too high melting temperatures and, on the other, by the presence at room temperature of variable amounts of crystalline phase. Random copolymers may offer adequate models in both cases.

A considerable widening of the thermodynamic stability of the mesophase (as a consequence of the depression of the melting temperature) may be achieved with polymers of homologous molecular structure by random insertion along the chain of flexible spacers of different lengths [2]. Furthermore, the mesophase can be quenched at room temperature with reduced crystallinity.

We have studied copolymers of general formula:



Copolymers containing equimolar amounts of flexible spacers of two different lengths normally exhibit the greatest melting point depression and their mesophase can be quenched at room temperature frequently with very low residual crystallinity.

The results of our study, based on DSC, X-ray diffraction and dilatometry, show that a copolymer of formula:

$$-\!\!(OOC-\!\!(CH_2)_{n(n')-2}-COO-R)\!\!-_x$$

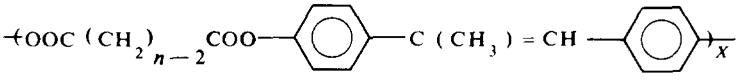
exhibits a mesophasic behaviour close to that shown by the homopolymer of formula:

$$-\!\!(OOC-\!\!(CH_2)_{(n+n')/(2)-2}-COO-R)\!\!-_x$$

provided n, n' and $(n + n')/2$ are all even or all odd.

EXPERIMENTAL

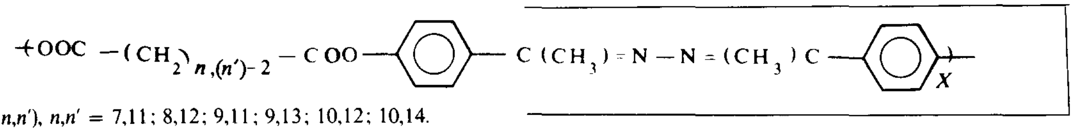
The following polymers have been prepared following standard procedures:

a) —


(OPA*n*) $n = 9, 10, 11, 12, 13$

(b) Copolymers of the same kind containing equimolar amounts of aliphatic groups of two different lengths: (CPA*n*,*n*′), *n*,*n*′ = 6,10; 7,11; 8,12; 9,13; 10,14.

(c) Copolymers of general formula:



(CPB*n*,*n*′), *n*,*n*′ = 7,11; 8,12; 9,11; 9,13; 10,12; 10,14.

For brevity, the polymers are indicated by the symbols given in parentheses.

Viscometry of chloroform solutions was performed at 26.00 ± 0.02° with an Ubbelhode viscometer. The extrapo-

Table 1. Experimental molar volumes as a function of temperature

Anisotropic liquid		Isotropic liquid		Anisotropic liquid		Isotropic liquid	
t	*V*	*t*	*V*	*t*	*V*	*t*	*V*
OPA9				CPA7,11			
176.0	348.8	191.5	359.5	140.8	341.7	199.2	361.0
176.8	349.5	206.5	363.3	145.8	342.5	200.0	361.0
180.5	350.1	217.5	365.7	155.7	345.1	211.0	363.8
181.0	350.8	227.5	368.2	165.5	347.4	212.7	364.2
189.0	352.4	238.8	370.7	175.5	350.3	219.7	365.9
189.4	352.4			185.5	352.6	221.2	366.2
189.7	353.3					230.7	368.3
196.7	354.7					232.2	368.7
$\sigma = 0.06$		$\sigma = 0.05$		$\sigma = 0.10$		$\sigma = 0.03$	
OPA10				CPA8,12			
185.1	366.2			142.5	354.3	194.1	378.1
190.2	368.3			160.5	359.8	205.3	381.1
195.1	369.9			170.0	362.2	214.1	383.1
199.7	371.2			171.0	362.5	223.2	385.5
201.5	371.7			179.6	364.7	233.8	388.2
206.1	373.2			180.0	364.8	244.3	390.6
214.9	375.2			189.2	367.5		
216.2	375.9			189.7	367.6		
				199.1	370.7		
$\sigma = 0.10$				$\sigma = 0.03$		$\sigma = 0.04$	
OPA11				CPA9,13			
160.7	380.0	190.2	394.2	148.2	377.2	182.5	392.6
165.4	381.6	197.3	396.1	155.5	379.3	190.0	394.6
165.8	381.4	205.0	398.1	162.8	381.4	198.6	396.9
169.0	382.5	214.8	400.2	170.1	383.6	206.0	398.6
171.2	383.0	220.5	401.6				
174.1	384.5						
178.2	385.9						
$\sigma = 0.10$		$\sigma = 0.03$		$\sigma = 0.03$		$\sigma = 0.04$	
OPA12				CPA10,14			
176.0	400.8	195.0	415.0	146.0	391.1	190.2	414.5
178.3	402.2	203.5	418.2	150.2	392.6	199.8	417.2
183.0	404.0	212.0	420.5	151.0	392.6	209.9	420.0
188.2	405.9	222.5	423.3	155.0	393.8	211.2	420.4
188.5	406.1			159.0	394.9	219.0	422.4
				160.5	395.5	220.0	422.6
				166.1	396.9	231.0	425.1
				170.2	398.4	231.5	425.4
				171.0	398.4		
				175.3	400.0		
				175.5	399.9		
				178.0	400.8		
$\sigma = 0.10$		$\sigma = 0.10$		$\sigma = 0.01$		$\sigma = 0.05$	
OPA13							
163.0	420.5	190.0	433.3				
165.2	421.7	195.5	435.3				
167.5	422.6	203.8	438.0				
170.5	425.7	215.5	441.6				
$\sigma = 0.10$		$\sigma = 0.06$					

t/°; V/cm^3 mol^{-1}; σ = square root deviation of V from the linear least squares fitting.

Table 2a. Comparison between calculated molar volumes of homo- and copolymers (OPAn and CPAn,n')*

Anisotropic liquid			Isotropic liquid			Anisotropic liquid			Isotropic liquid		
$n = 9$, $a = 0.272\,(3)$, $b = 301.2\,(6)$ $n = 7$, $n' = 11$ $a = 0.250\,(3)$, $b = 306{,}2\,(5)$			$n = 9$, $a = 0.237\,(1)$, $b = 314.1\,(3)$ $n = 7$, $n' = 11$ $a = 0.235\,(1)$, $b = 314.1\,(2)$			$n = 11$, $a = 0.334\,(9)$, $b = 326.1\,(15)$ $n = 9$, $n' = 13$ $a = 0.290\,(1)$, $b = 334.1\,(2)$			$n = 11$, $a = 0.242\,(1)$, $b = 348.2\,(2)$ $n = 9$, $n' = 13$ $a = 0.255\,(2)$, $b = 346.1\,(4)$		
	V			V			V			V	
t	hp	cp	t	hp	cp	t	hp	cp	t	hp	cp
140	339.3	341.2	170	354.5	354.1	140	372.9	374.8	160	387.0	386.9
150	342.0	343.7	180	356.8	356.5	150	376.3	377.7	170	389.4	389.5
160	344.7	346.2	190	359.2	358.8	160	379.6	380.6	180	391.9	392.0
170	347.5	348.7	200	361.6	361.2	170	382.9	383.5	190	394.3	394.6
180	350.2	351.2	210	363.9	363.5	180	386.3	386.4	200	396.7	397.1
190	352.0	353.7	220	366.3	365.9	190	389.6	389.3	210	399.1	399.7
200	355.6	356.2	230	368.7	368.2	200	392.9	392.3	220	401.6	402.2
210	358.3	358.7	240	371.1	370.6	210	396.3	395.1	230	403.9	404.8
$n = 10$, $a = 0.303\,(5)$, $b = 310.5\,(10)$ $n = 8$, $n' = 12$ $a = 0.2835\,(4)$, $b = 313.9\,(1)$			$n = 8$, $n' = 12$ $a = 0.249\,(1)$, $b = 329.9\,(2)$			$n = 12$, $a = 0.405\,(9)$, $b = 329.8\,(15)$ $n = 10$, $n' = 14$ $a = 0.3011\,(2)$, $b = 347.1\,(1)$			$n = 12$, $a = 0.299\,(5)$, $b = 357.0\,(10)$ $n = 10$, $n' = 14$ $a = 0.262\,(1)$, $b = 364.9\,(3)$		
140	352.9	353.6				130	382.4	386.3	180	410.8	412.0
150	356.0	356.5				140	386.5	389.3	190	413.8	414.6
160	359.0	359.3				150	390.5	392.3	200	416.8	417.3
170	362.0	362.1				160	394.6	395.3	210	419.8	419.9
180	365.1	365.0				170	398.6	398.3	220	422.8	422.5
190	368.1	367.8				180	402.7	401.3	230	425.8	425.1
200	371.1	370.7				190	406.7	404.3	240	428.8	427.7
210	374.2	373.5				200	410.8	407.3	250	431.7	430.4

* t/°C; V/cm^3 mol^{-1}. The molar volumes have been calculated using the formula: $V = a \cdot t + b$. The constants a and b have been obtained by linear least squares fitting of the experimental data. The standard deviation of a and b is given in parentheses and refer to the last figure. No experimental data have been measured for the isotropic phase of OPA10. hp = homopolymer, cp = copolymer.

Table 2b. Comparison between calculated values of molar volumes*

Anisotropic liquid			Isotropic liquid			Anisotropic liquid			Isotropic liquid		
$n = 10$ $a = 0.303\,(5)$, $b = 310.5\,(10)$			$n = 8$, $n' = 12$ $a = 0.249\,(1)$, $b = 339.9\,(2)$			$n = 13$ $a = 0.393\,(2)$, $b = 353.1\,(3)$			$n = 13$ $a = 0.250\,(1)$, $b = 383.9\,(2)$		
	V			V			V			V	
t	‡	†	t	§	†	t	∥	†	t	∥	†
140	350.8	352.9	180	374.0	374.7	140	408.6	408.1	160	423.3	423.9
150	354.5	356.0	190	376.8	377.2	150	412.3	412.1	170	425.9	426.4
160	358.3	359.0	200	379.5	379.7	160	415.9	416.0	180	428.7	428.9
170	362.1	362.0	210	382.2	382.2	170	419.4	419.9	190	431.3	431.4
180	365.9	365.1	220	385.0	384.7	180	423.1	423.8	200	434.0	433.9
190	369.0	368.1	230	387.7	387.2	190	426.6	427.8	210	436.7	436.4
200	373.5	371.1	240	390.5	389.7	200	430.2	431.7	220	439.4	438.9
210		374.2	250	393.1	392.2	210	433.9	435.6	230	442.0	441.4

* $t/°$; $V/\text{cm}^3\,\text{mol}^{-1}$.

† Calculated utilizing the least squares fitting of the experimental data (see note to Table 2a).

‡ Calculated subtracting, at the appropriate temperature, the molar volume of two CH_2 groups from the molar volume of OPA12 in the corresponding phase.

§ Calculated from OPA12 as indicated in ‡.

∥ Calculated adding the molar volume of two CH_2 groups to the molar volume of OPA11 at the corresponding temperature.

lated intrinsic viscosities ($[\eta]/\text{dl g}^{-1}$) are given in parentheses:

OPAn: $n = 9$ (2.30); $n = 10$ (2.40); $n = 11$ (2.30); $n = 12$ (2.90);
$n = 13$ (3.20).

CPAn,n′: $n,n' = 6,10$ (1.30); $n,n' = 7,11$ (1.10); $n,n' = 8,12$ (1.50);
$n,n' = 9,13$ (2.00); $n,n' = 10,14$ (3.00).

CPBn,n′: $n,n' = 7,11$ (1.00); $n,n' = 8,12$ (1.00); $n,n' = 9,11$ (2.10);
$n,n' = 9,13$ (1.00); $n,n' = 10,12$ (2.10); $n,n' = 10,14$ (0.90).

Molar volumes as a function of temperature were measured for OPAn and CPAn,n′ by volume dilatometry utilizing mercury as a filling liquid [3].

Prior to the preparation of the compacted samples for sealing in the dilatometer, the polymers were kept for 18–20 hr under vacuum (10^{-4} torr) at a temperature between 100 and 110°.

The volume changes as a function of temperature were monitored by weighing the mercury expelled from the dilatometer.

The thermotropic mesomorphism of most of the copolymers (the behaviour of polymers OPAn and CPB8,12 had already been investigated [1, 2]) was examined by DSC, polarizing microscopy and X-ray diffraction.

RESULTS AND DISCUSSION

The molar volumes experimentally found as a function of temperature are reported in Table 1. Most of the data, both for the liquid crystal phase and for the isotropic phase, were collected for undercooled phases. The reasons for operating in this way were the following: to reduce as much as possible the working temperature, particularly in the isotropic phase, in order to avoid errors due to chemical instability; to collect the data over a wide range of temperatures in order to reduce the uncertainty in the calculation of the temperature coefficient $\partial V/\partial t$; to avoid the temperatures at which the polymers are biphasic (i.e. isotropic + anisotropic liquid). Actually, a finite and frequently broad temperature interval for the isotropization transition is normal for the polymers because of the spread of the molecular masses. In any way, a non-linear dependence of molar volumes on temperature near the clearing point is observed also for low molecular weight compounds as a pretransitional phenomenon [4].

A comparison, at constant temperature, between the molar volumes of the copolymers and of the corresponding homopolymers is reported in Table 2a. The molar volumes have been calculated at each temperature utilizing a linear least-squares fitting of the experimental data. The matching of the calculated values is fairly good (the average square root deviation is $\Delta\bar{V} = 0.4\,\text{cm}^3\,\text{mol}^{-1}$ and $\Delta\bar{V}/\bar{V} = 0.001$) and it provides evidence, although not compelling, in favour of a close resemblance between the packing of homo- and copolymers in homologous phases.

The molar volumes as a function of n at fixed temperatures are reported in Fig. 1. A small but significant odd-even effect is observable in the sequence of values referring to the liquid crystal phase. The molar volumes of the "even" members of the group are somewhat smaller than those for the "odd" members.

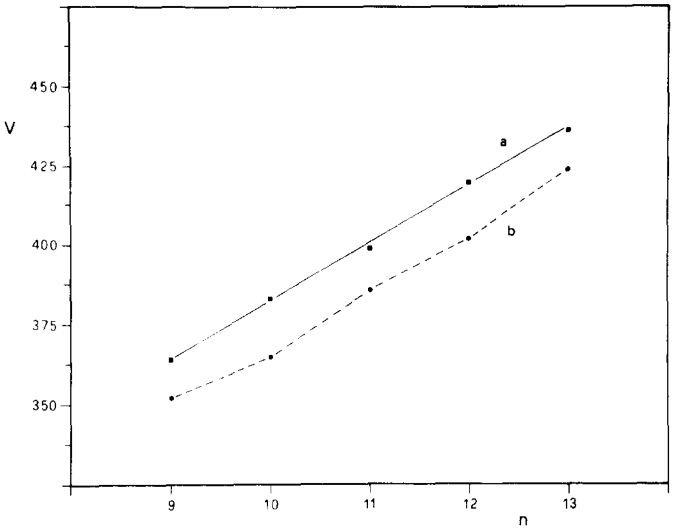


Fig. 1. Polymers OPAn: molar volumes (V/cm^3 mol^{-1}) as a function of n calculated for the liquid crystal phase: (b) at 180° and for the isotropic phase (a) at 210°. The value reported for the isotropic phase of OPA10 was calculated for the corresponding copolymer CPA8,12.

This feature is consistent with the odd-even alternation of the molar isotropization enthalpies observed for the same polymers; the even members show higher values.

The average value of $[\partial V/\partial n]_{180°}$ for the liquid crystal phase (taking separately into account even and odd members) is 18.5 cm^3 mol^{-1}. This coincides with the value of 18.4 cm^3 mol^{-1} obtained by extrapolating to 180° the experimental molar volumes of molten polyethylene reported in reference 5. (Table 2b shows some calculated values for comparison.) This could mean that the flexible polymethylene portions of the polymer chain behave, even in the liquid crystal phase, as if they were in a substantially random conformation. This conclusion, which must be taken with care because of the intrinsically low sensitivity of molar volumes to small conformational or packing modifications, is consistent with the observation that the molar isotropization entropies measured for the same sequence of homologous polymers are only slightly dependent on the length of the flexible spacers [1].

The thermodynamic data for the isotropization transition offer further evidence in favour of a rather close structural relationship between homo- and copolymers. Isotropization temperatures and molar entropic changes are reported in Table 3. The DSC analysis was extended to a second class of copolymers: CPBn,n'.

The pattern of the odd–even alternation of the thermodynamic quantities is the same for homo- and copolymers and the accordance between the data is particularly good for polymers of PBn type.

Rather convincing confirmation of this point is offered by the behaviour of copolymers CPB9,11 and CPB10,12. The first is a "pseudo-even" copolymer containing equimolar amounts of flexible spacers with $n = 9$ and $n' = 11$. The average stoichiometry corresponds to an "even type" homopolymer, namely OPB10. The isotropization temperature and molar entropy are, on the contrary, intermediate between the "odd-type" homopolymers OPB9 and OPB11.

{Ti(CPB9,11) = 525 K; [Ti(OPB9) + Ti(OPB11)]/2 = 520 K; ΔSi(CPB9,11) = 9.4 J mol^{-1} K^{-1}; [ΔSi(OPB9) + ΔSi(OPB11)]/2 = 9.4 J mol^{-1} K^{-1}}.

Equally good correspondence if found between the thermodynamic data for the "pseudo-odd" CPB10,12 and the average values obtained from OPB10 and OPB12: Ti(CPB10,12) = 529 K; [Ti(OPB10) + Ti(OPB12)]/2 = 531 K; ΔSi(CPB10,12) = 17.8 J mol^{-1} K^{-1}; [ΔSi(OPB10) + ΔSi(OPB12)]/2 = 18.0 J mol^{-1} K^{-1}.

Figure 2 shows the DSC heating curves for four different copolymers. Curves a and b refer to polymers of CPBn,n′ type not subjected to previous thermal treatment. Curves c and d refer to polymers of CPAn,n' type previously quenched in the liquid crys-

Table 3. Thermodynamic data relative to the isotropization transition

n n,n'	OPAn CPAn,n'		OPBn CPBn,n'	
	Ti	ΔSi	Ti	ΔSi
8	575	16.7		
6,10	562	12.4		
9	503	5.45	531	9.29
7,11	489	4.64	528	8.60
10	528	16.4	545	18.0
8,12	523	13.1	549	17.7
11	479	6.61	509	9.50
9,13	484	6.86	510	9.08
12	498	14.8	516	17.9
10,14	484	10.0	514	18.0

Ti/K, ΔSi/J mol^{-1} K^{-1}; σ(Ti)/Ti $\simeq$ 0.01 σ(ΔSi)/ΔSi $\leq$ 0.1

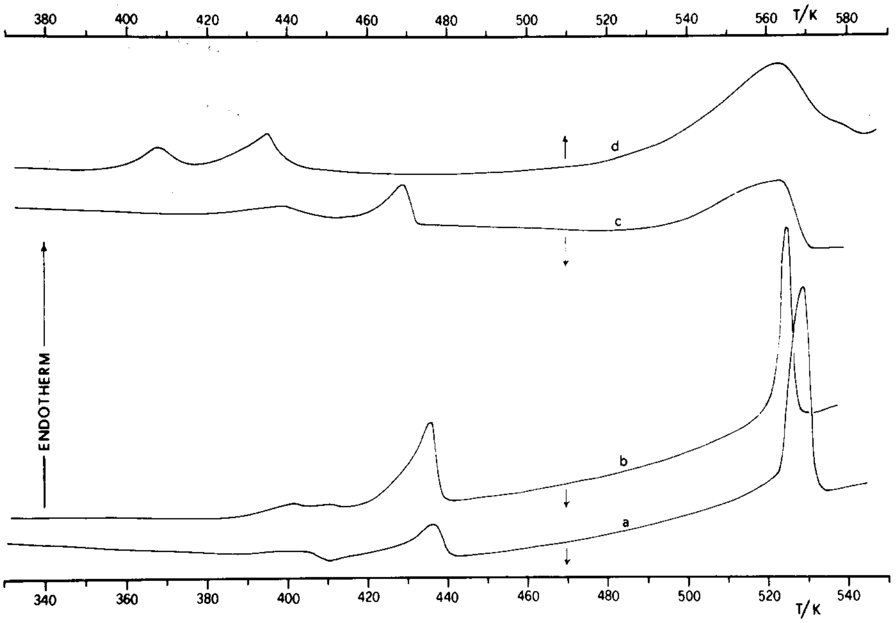


Fig. 2. DSC heating curves. Scanning rate 10 K/min. (a) CPB10,12; (b) CPB9,11; (c) CPA8,12, sample previously quenched from 450 to 273 K; (d) CPA6,10, sample previously quenched from 460 to 273 K.

tal phase. Since the high temperature endotherms are related to the isotropization of the mesophase, it is apparent that in all cases the samples have a very low content of crystal phase. The dominant phase should be considered at room temperature as a glassy nematic phase.

Figures 3 and 4 provide further evidence for this conclusion. Figure 3 shows the X-ray diffraction spectrum of CPA8,12 registered at 460 K, within the range of stability of the nematic phase. Figure 4 shows the diffraction spectrum of CPA8,12 registered at room temperature utilizing a sample previously quenched

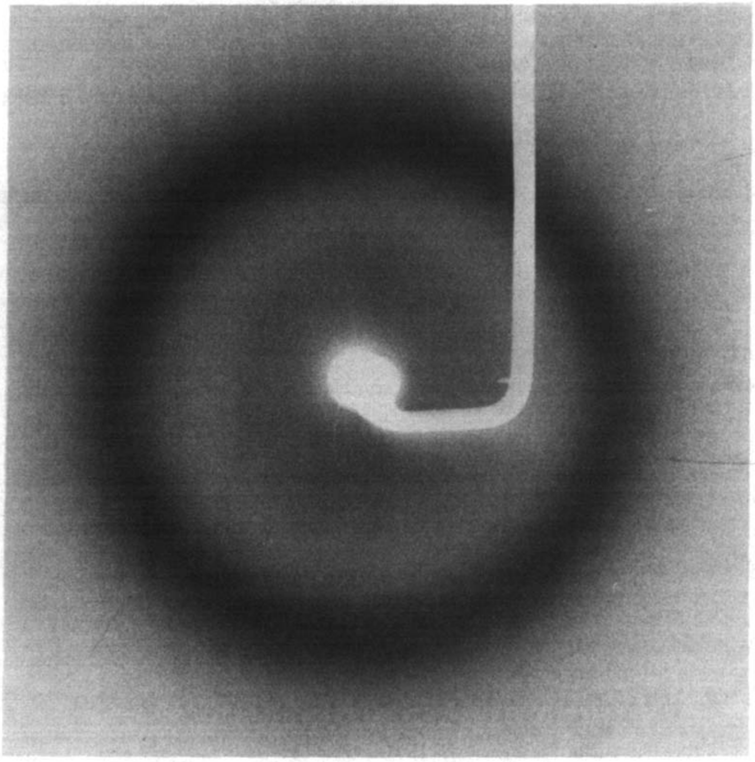


Fig. 3. CPA8,12: X-ray diffraction spectrum. $T = 460$ K, flat-film camera, CuKα radiation.

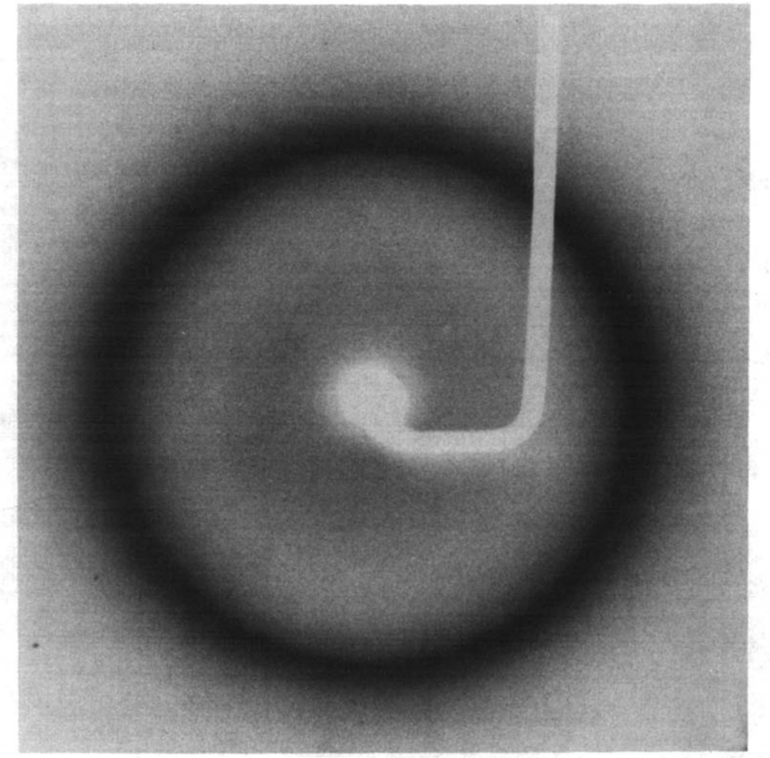


Fig. 4. CPA8,12: X-ray diffraction spectrum. Room temperature, flat-film camera, CuKα radiation. Sample previously quenched from 450 to 273 K.

from 450 K to 273 K. The nematic-like character of the spectrum is apparent.

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Riassunto—Sono state eseguite misure di volumi molari in funzione della temperatura per alcuni omo- e copolimeri lineari mesofasici. Sono state esaminate sia la fase liquido crystallina (nematica) che quella isotropa. Le catene polimeriche sono caratterizzate, dal punto di vista strutturale, da una sequenza alternata di gruppi rigidi e di spaziatori flessibili. Le misure di volume molare sembrano confermare l'ipotesi che nella fase nematica i gruppi flessibili siano sostanzialmente disordinati. Vengono inoltre discusse alcune analogie fra omo- e copolimeri.