Structural modifications of hexagonal crystalline polyoxymethylene. Infra-red and X-ray study

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Infra-red spectra and X-ray diagrams of polyoxymethylene samples prepared in various ways, of trioxane–dioxolane copolymers and of a polyoxymethylene–polydioxolane blend were obtained. With hexagonal crystalline polyoxymethylene (HCPOM), it is possible to prepare two forms, A and B, differing in their infra-red spectra; with copolymers, the maximum attainable content of form A rapidly decreases with increasing content of oxyethylene units in the chain. Form A could not be prepared in the polyoxymethylene–polydioxolane blend. Infra-red spectra of the two forms, A and B, of HCPOM differ in the vibrational interactions of neighbouring chains; these interactions are large in form A and small in form B. The possible structures of the A and B forms of HCPOM are discussed.

(Keywords: polyoxymethylene; copolymers of trioxane–dioxolane; infra-red spectrometry; X-ray diffraction; physical structure)

INTRODUCTION

According to the method of preparation, two types of hexagonal crystalline polyoxymethylene (HCPOM) can be obtained, which can be mutually interconverted by thermal treatment, dissolution and subsequent crystallization, pressing, milling, etc.[1-3] These two forms differ insignificantly in melting point, and powdered samples of both forms yield identical X-ray diffraction patterns[1]. Also the Raman spectra of these forms are almost identical[2]. However, pronounced differences between the two forms are observed in the infra-red spectra, where strong bands in the two forms are shifted by as much as 85 cm^{-1}. Therefore the generation and mutual transformation of these two forms can be conveniently studied by infra-red spectroscopy.

The form with characteristic infra-red bands around 228, 903 and 1098 cm^{-1} has been designated as A, the form with characteristic bands around 233, 988 and 1128 cm^{-1} as B[1,2]. These bands were assigned to vibrations of symmetry A_2 of the linear group of the monomer unit[2,4].

From analysis of X-ray measurements it is known that the HCPOM chains form a helix, of periodicity 9/5 as given by Tadokoro *et al.*[5], later refined to 29/16 by Carazzolo[6]. In later X-ray studies, the structure 9/5 was always considered for the sake of clarity (see e.g. ref. 7). In oriented samples of HCPOM with various contents of forms A and B, two types of weak reflections were found, assigned to two different types of deformation of regular helices[7]. These different deformations are explained by the authors as a consequence of various intermolecular ordering.

In spite of great effort, the structural parameters causing the difference between the A and B forms of HCPOM could not be safely determined, and the large differences in the positions of some bands in the infra-red spectra of the A and B forms have not been explained. In this work we have made an attempt to solve this problem by the measurement and analysis of infra-red spectra and X-ray diagrams of nascent and modified samples of 1,3,5-trioxane–1,3-dioxolane (TO–DO) copolymers, of polyoxymethylene (POM) and of mixtures of polyoxymethylene with polydioxolane (PDO). The composition and sequence distribution of the copolymers was determined by ^1H n.m.r. spectra.

EXPERIMENTAL

Synthesis

TO and DO (Fluka) were dried by refluxing in the presence of benzophenone over metallic sodium or sodium–potassium alloy, respectively, and then distilled under argon atmosphere before use (b.p. of TO, 112–114°C; b.p. of DO, 75–76°C). Nitrobenzene (Fluka) was dried with phosphoric anhydride and vacuum distilled (b.p. 93–94°C/2660 Pa). $BF_3O(C_2H_5)_2$ (British Drug Houses) was vacuum distilled (b.p. 42–43°C/1995 Pa); it was applied in the form of nitrobenzene solution, except in DO homopolymerization where ethyl ether solution was used.

TO homopolymer (POM—sample 1) and TO–DO copolymers (samples 2–5) (see *Table 1*) were prepared by polymerization in nitrobenzene with $BF_3O(C_2H_5)_2$ as catalyst, by stirring under argon for different time

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Table 1 Experimental conditions of cationic polymerization and copolymerization of 1,3,5-trioxane and 1,3-dioxolane, melting temperatures of homo- and copolymers and mole fractions of structural units from ^{1}H n.m.r. spectra

Sample no.	Initial conc. in nitrobenzene solution (mol l^{-1})			Polym. temp. (°C)	Polym. time (min)	Yield (%)	Melting range (°C)	Mole fractions from ^{1}H n.m.r.						
	TO	DO	Catalyst					f_M^a	f_{MMM}^b	$f_{MME+EMM}^b$	f_{EME}^b	f_{MEM}^b	$f_{M_t}^c$	f_D
1	2.0	0.0	1×10^{-2}	50	120	81	170–180	(1)	(1)	(0)	(0)	(0)	1	0
2	1.7	0.85	5×10^{-2}	25	120	66	140–147	0.93	0.80	0.12	0.01	0.07	0.92	0.08
3	1.0	1.0	1×10^{-2}	50	180	10	138–147	0.86	0.51	0.30	0.04	0.14	0.84	0.16
4	1.5	1.5	2×10^{-2}	50	9	20	137–144	0.82	0.48	0.29	0.05	0.18	0.78	0.22
5	1.0	2.0	2×10^{-2}	50	60	9	46–47	0.74	0.33	0.33	0.08	0.26	0.65	0.35
6[d]	0.0	bulk	1.4×10^{-1}	25	4320	80	47–51	(0.5)	(0)	(0)	(0.5)	(0.5)	0	(1)

[a] Mole fraction of M units
[b] Mole fractions of M- and E-centred triads
[c] Mole fractions of M_t and D units

$$f_{MMM}+f_{MME+EMM}+f_{EME}+f_{MEM}=f_M+f_{MEM}=f_{M_t}+f_D=1 \qquad f_{M_t}=\frac{f_M-f_E}{f_M}$$

[d] Bulk polymerization of DO with catalyst concentration in moles per litre DO.
The values in parentheses are by definition

intervals. POM (sample 1) and the copolymer with the lowest content of DO (sample 2) precipitated in the nitrobenzene solution during polymerization. After 2 h, polymerization was stopped with triethylamine and the polymers obtained were filtered; the residual monomers, solvents, triethylamine and catalyst were washed out with methanol and ethyl ether. The polydioxolane (PDO) homopolymer fraction in sample 2, if any, is soluble in methanol and ethyl ether as well. The POM homopolymer fraction in sample 2 was removed by treatment with alkali in water/ethanol mixture as described previously[8]. Copolymer samples with higher DO content (samples 3–5) were soluble in nitrobenzene. They were precipitated by pouring the polymerization reaction mixture into a large volume of methanol containing ammonia and the methanol solution was kept at −40°C overnight to precipitate the copolymer completely. Precipitated copolymers were filtered and washed with cold methanol at low temperature (−40°C).

The homopolymer of DO (PDO—sample 6) was prepared by bulk polymerization of DO at room temperature using $BF_3O(C_2H_5)_2$ as catalyst. The polymer obtained was washed with cold methanol and vacuum dried.

The experimental conditions of cationic polymerization and copolymerization of TO and DO, the yields of the polymer, melting points determined by optical microscopy, and copolymer composition obtained by ^{1}H n.m.r. spectroscopy are given in *Table 1*.

^{1}H n.m.r. spectra

The ^{1}H n.m.r. spectra of the copolymers were measured at room temperature with 5% w/v solutions in $CDCl_3$ (CEA) (samples 3, 4, 5—*Table 1*) or at 80°C with 5% w/w solutions in *p*-chlorophenol (Merck) (sample 2—*Table 1*), using Varian XL-200 and Jeol PS-100 spectrometers, respectively.

Infra-red spectra

The i.r. spectra were measured with samples in powder form as obtained by the above described polymerization. The samples were mulled with nujol and measured between CsI windows (nascent state) or were milled for 15 min in liquid nitrogen and pressed for 10 min with KBr (Merck) (about 0.3 mg of sample/300 mg of KBr, $p\simeq1$ GPa) to form pellets, or were melted at temperatures exceeding the melting point on KBr windows and cooled in air to form a film. The blend of POM–PDO was prepared by melting of a 1:1 mixture at 190°C in an ampoule under argon for about 3 min and cooled in air, milled under liquid nitrogen and pressed. The reference samples of POM and PDO were subject to the same procedure. Infra-red spectra were measured with a Perkin–Elmer 580 B infra-red spectrometer connected on-line with a Tracor TN 4000 spectrum analyser. For samples measured in nujol mull, the nujol spectrum was digitally subtracted. Band intensities were evaluated by determining maximum absorbance by the baseline method, and the bands at 900 and 935 cm^{-1} were separated assuming Lorentzian shape. For consideration of the spectra of TO units, in samples containing DO units, absorption of DO units was digitally subtracted.

X-ray diffraction

X-ray diffraction was measured using the automatic diffractometer Syntex $P2_1$, with Cu K_α radiation and carbon monochromator. The diffracted radiation was recorded by a scintillation counter. Scattering by the crystalline and amorphous phases of the polymer was separated in the diffraction patterns. Crystallinity *c* was determined from the integral scattering intensities of the crystalline (I_c) and amorphous (I_a) phases ($c=I_c/(I_c+I_a)$). Measurements were made with nascent powdered samples and with samples pressed at room temperature between smooth steel plates.

Powder diffraction patterns of homopolymers of the structural forms A and B were also obtained by means of the flat-film camera. The sample of form A was prepared by the method described in ref. 1a. Cu K_α radiation was used.

RESULTS

^{1}H n.m.r. spectra of the copolymers

^{1}H n.m.r. spectra of TO–DO copolymers exhibit a singlet at 3.66 ppm assigned to oxyethylene (E) units, and a multiplet at 4.8 ppm assigned to oxymethylene (M) units. From the integrated intensities of these two groups,

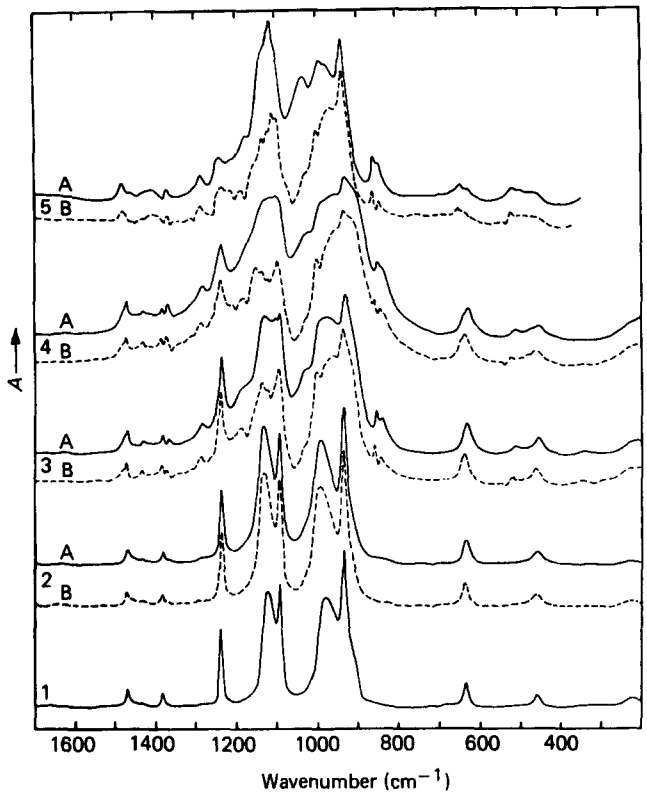

Figure 1 Infra-red spectra of nascent samples (see *Tables 1* and *2*): curve 1, HCPOM (sample 1); curves 2–5, TO–DO copolymers (samples 2–5); ———, measured spectra; – – –, PDO absorption subtracted

the fractions of M and E units, f_M and f_E, were determined (see *Table 1*).

The absorption about 4.8 ppm exhibits fine structure corresponding to the sequences[9] MMM, EMM + MME and EME. In agreement with ref. 10 we have found that the E units in the chain are always isolated, similarly as in PDO, so that the fraction of E units, f_E, is equal to the fraction of E-centred triad, f_{MEM}. The fractions of the triads MMM, MME + EMM, EME and MEM are given in *Table 1*.

In studies of the microstructure of TO–DO copolymers it was found[11,12] that the sequences formed can be well described by means of a combination of oxymethylene units M_t and dioxolane units D, where all M_t units originate from trioxane molecules. Therefore in *Table 1* the molar composition of the copolymers expressed in M_t and D units is also included.

Infra-red spectra of nascent samples

In *Figure 1* (curve 1) the spectrum of the nascent homopolymer POM is presented. It is a spectrum of the B form of HCPOM[1,2]. The figure further shows that the spectra of nascent copolymers (*Figure 1*, curves 2A–5A) do not exhibit the characteristic pair of bands at 903 and 1098 cm^{-1} assigned[1,2] to the A form of HCPOM (compare with curve 1 in *Figure 2*). The copolymers exhibit bands of oxyethylene (E) units, the intensity of which increases in proportion to their content. The most pronounced of these bands lie at 850, 1030 and 1140 cm^{-1}. These bands are also the most pronounced bands in the spectrum of PDO (see *Figure 4*, curve 2). By digital subtraction of the PDO spectrum from the spectra of the copolymers, difference spectra corresponding to polyoxymethylene sequences of the copolymer chain were obtained (*Figure 1*, curves 2B–5B). From *Figure 1* it can be seen that the spectra of both nascent HCPOM samples and of the copolymers exhibit well pronounced absorptions at 1130–1150 and 980–1000 cm^{-1} which have been assigned to the B form[1,2] in HCPOM. These bands are most prominent in the spectra of POM homopolymer and of the copolymer with the smallest content of E units (samples 1 and 2); with increasing content of E units in the chains, these bands are gradually broadened. The intensity in the maximum of the band at 1239 cm^{-1}, corresponding according to ref. 13 to the concentration of regular helices proportional to the content of the crystalline fraction in pure POM, decreases with increasing content of E units in the chains; in sample 5, containing 26 mol% of E units, this band almost disappears (see *Figure 1* and *Table 2*).

Infra-red spectra of modified samples

The spectra of samples milled in liquid nitrogen and pressed in KBr pellets are shown in *Figure 2*. A comparison of this figure with *Figure 1* reveals that the spectrum of POM and the spectra of TO–DO copolymers with up to 20 mol% of E units have changed by mechanical treatment. The sample of POM homopolymer exhibits an infra-red spectrum of the A form, and also sample 2 exhibits well pronounced bands at 900 and 1100 cm^{-1} assigned to the A form of HCPOM[1,2]. With a further increase of the content of E units in the chain, the intensity of the band at 900 cm^{-1} decreases very rapidly, and the composite band at 1100 cm^{-1} shifts to higher wavenumber. Sample 5 does not show any band of form A at 900 cm^{-1}. The highest reached value $R^{900/935}$ (intensity ratio of the band of the A form of POM at 900 cm^{-1} and of the band at 935 cm^{-1}, the intensity of

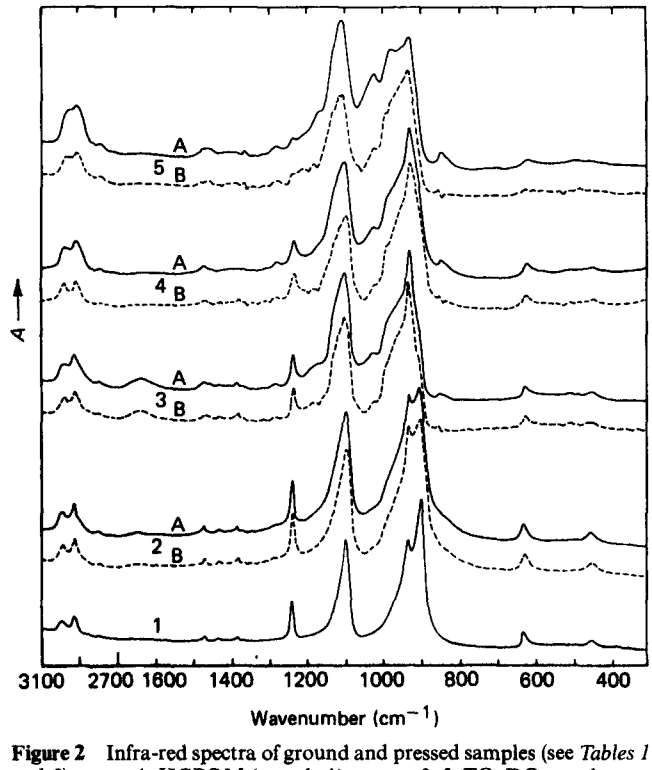

Figure 2 Infra-red spectra of ground and pressed samples (see *Tables 1* and *2*): curve 1, HCPOM (sample 1); curves 2–5, TO–DO copolymers (samples 2–5); ———, measured spectra; – – –, PDO absorption subtracted

Table 2 Structural parameters of HCPOM, PDO and TO–DO copolymers

	Type of statistics						
	Bernoulli (M_t,D)		Markov I (M_t,D)				
Sample[a]	W_1^9 [b]	W_2^9 [c]	W_1^9 [b]	W_2^9 [c]	c[d]	$R^{900/935}$ [e]	$R^{1239/935}$ [f]
1	1	1	1	1	0.9	1	1
2	0.85	0.71	0.87	0.75	0.8	0.6±0.1	0.9±0.1
3	0.54	0.13	0.38	0	0.7	0.1±0.1	0.8±0.1
4	0.35	0	0.33	0	0.6	0.1±0.1	0.5±0.1
5	0.10	0	0.13	0	0.3	0 ±0.1	0.3±0.1
6	0	0	0	0	0.7	–	–
Blend 1+6	–	–	–	–	0.3	0 ±0.1	0.6±0.1

[a] See *Table 1*
[b] Calculated content of segments in sequences longer than eight units according to respective statistics
[c] Calculated content of segments in pairs of sequences longer than eight units according to respective statistics
[d] Crystallinity of polymers from X-ray diffraction
[e] Relative intensity ratio of i.r. bands near 900 and 935 cm^{-1} attained after mechanical treatment
[f] Relative intensity ratio of i.r. bands near 1239 and 935 cm^{-1}

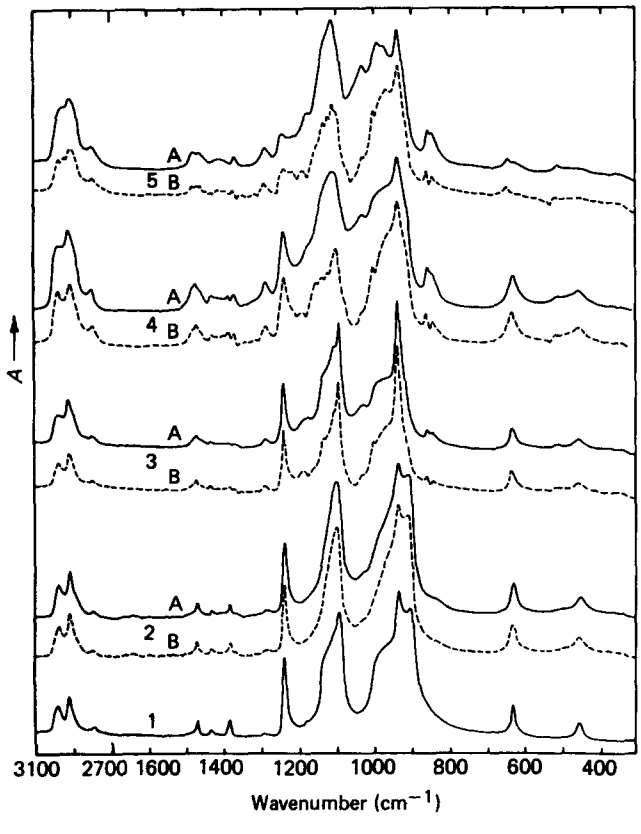

Figure 3 Infra-red spectra of melted and cooled samples (see *Tables 1* and *2*): curve 1, HCPOM (sample 1); curves 2–5, TO–DO copolymers (samples 2–5); ———, measured spectra; – – –, PDO absorption subtracted

which is proportional to the content of POM sequences in the chain[2]) is shown in *Table 2* for samples modified by milling and pressing. Also in the difference spectra, corresponding only to the polyoxymethylene part of the samples (*Figure 2*), the rapid attenuation of the band of the A form of POM at 900 cm^{-1} with increasing content of E units can be observed in mechanically modified samples. Moreover in these difference spectra, in the ranges about 985 and 1135 cm^{-1} where characteristic bands of the B form of POM are found[1,2], bands appear with intensity increasing with growing content of E units in mechanically treated samples. In POM homopolymer, the corresponding bands disappear by mechanical treatment. In the copolymer with the highest content of E units (sample 5), the intensity of these bands does not change by mechanical treatment (compare the curves in *Figures 1* and *2*). Similarly as in nascent samples, the intensity of the 'crystalline' band at 1239 cm^{-1} also decreases with increasing content of E units in samples modified by milling and pressing.

Changes in crystallinity of the polymer are accompanied by changes of intensity, shape, and within about ±10 cm^{-1} even of positions of infra-red bands characteristic of the A and B forms. However, these changes are several times smaller than the basic frequency differences of the characteristic bands of the two forms.

Spectra of samples modified by melting of the polymer on a KBr window and cooling in air, together with spectra obtained by digital subtraction, are shown in *Figure 3*. In the spectra of all these samples, characteristic bands of form B can be observed in the ranges 1130–1150 and 980–1000 cm^{-1}. POM (sample 1) and the copolymer with a small content of E units (sample 2) contain additional distinct bands at 900 and 1100 cm^{-1} characteristic of form A. The intensity of the band at 1239 cm^{-1} decreases with increasing content of E units similarly as in nascent polymers and in mechanically treated samples. The spectra of various samples prepared by cooling of the melt in air can be constructed from the spectra of the nascent sample of type B and of the corresponding sample modified by milling and pressing.

Infra-red spectra of the POM–PDO blend

The spectra of the blend of POM (sample 1) with PDO (sample 6) (component ratio about 1:1), of PDO and of POM are shown in *Figure 4*; all samples were melted, cooled, milled and pressed in the same way. The spectrum of the blend of POM with PDO, after digital subtraction of the PDO spectrum, is also shown in the figure. It appears that after this kind of physical treatment, absorption intensity at 900 cm^{-1}, corresponding to the A type structure of POM, is drastically attentuated in the blend as compared to pure POM subject to the same kind of treatment. The spectrum of POM in the treated blend obtained by digital subtraction corresponds to the infra-red spectrum of the B form of HCPOM (compare curve 3 in *Figure 4* with curve 1 in *Figure 1*).

The band at 1239 cm^{-1} is quite pronounced in the spectrum of the blend (see *Figure 4* and *Table 2*).

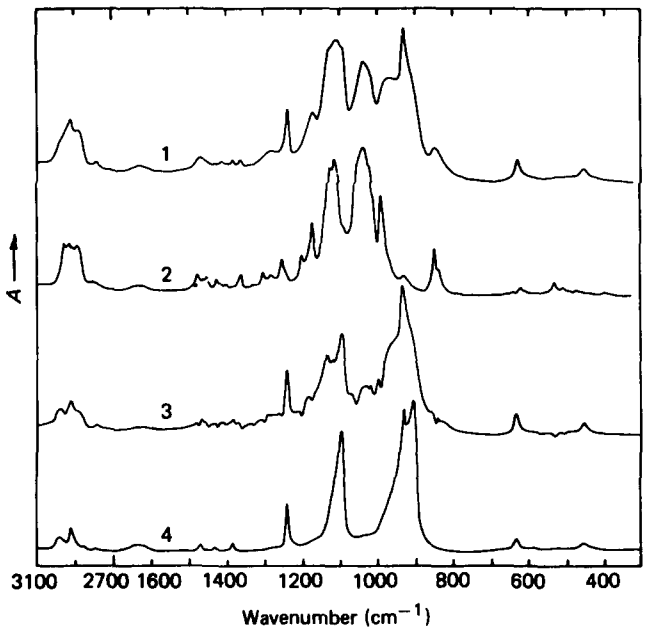

Figure 4 Infra-red spectra of melted, ground and pressed samples (see *Tables 1* and *2*): curve 1, blend POM + PDO (sample 1 + sample 6) ~1:1; curve 2, PDO (sample 6); curve 3, POM in blend (difference 1 − 2); curve 4, pure POM (sample 1)

X-ray diffraction

The diffraction patterns of POM powder samples of type A and B exhibit a number of narrow crystalline reflections. The crystalline structure of these samples is very well developed, with a crystallite size of about 12 nm. For both forms of POM, the crystalline reflections in the range of $2\theta < 50°$ were indexed according to the published structure of HCPOM[14] and their relative intensities were compared. It was found that, within the obtained resolution, the diffraction patterns are identical. It should be noted that, with the studied powder patterns, very small differences such as published in ref. 7 could not be detected.

Crystallinity values as determined by X-ray diffraction for powder samples of POM, TO–DO copolymers, PDO and the POM–PDO blend are given in *Table 2*. It appears that the crystallinity values in copolymer samples decrease with increasing content of E units in the chain. Within experimental error, the crystallinity values of the pressed samples did not differ from those of the samples in the nascent state. In the blend prepared by melting of a mixture of POM and PDO, crystallinity is greatly reduced as compared to the pure polymers (see *Table 2*).

DISCUSSION

Structure of A and B forms of HCPOM

Differences between the A and B forms of HCPOM may be caused by (a) defects of helix structure[1,2], (b) some difference of helix structure in forms A and B, or (c) difference in mutual ordering of the helices[15]. Let us examine to what extent each of these possibilities conforms with the results of infra-red, Raman and X-ray studies of POM and of TO–DO copolymers, and of infra-red and X-ray studies of the POM–PDO blend.

(a) Assuming that the differences between A and B forms are caused by helix defects, then the results of infra-red spectral analysis indicate intact helix structure in form A and defect helix structure in form B, because in TO–DO copolymers the tendency to generation of form A decreases with increasing content of E units. As samples of form B HCPOM of very high crystallinity (~95%) can be prepared, the defects of helix structure would have to be very small. To evaluate helix defect formation in oxymethylene chains due to copolymerization, use was made of ^{1}H n.m.r. analysis. As, according to refs. 10–12 the microstructure of TO–DO copolymers can be described by Bernoulli or first-order Markov statistics based on M_t and D units, the diad populations $f_{M_tM_t}$, f_{M_tD} and f_{DD} were calculated from the populations of M-centred and E-centred triads[9] (*Table 1*), yielding the corresponding chain growth probabilities[16] p_{M_tD} and p_{DM_t} of first-order Markov statistics. All these values were used to determine the content of sequences of M_t units of length sufficient for POM helix formation (nine M_t units) by means of the relation[17,18]:

$$W_1 = f_{M_t}(1) - \sum_{m=2}^{q-1} w_{M_t}(m) \tag{1}$$

where

$$w_{M_t}(m) = m p_{M_tD} p_{M_tD}^2 p_{M_tM_t}^{m-1} / (1 - p_{M_tD} p_{DM_t})$$
$$f_{M_t}(1) = p_{M_tD} p_{M_tM_t} (1 + p_{M_tD}) / (1 - p_{DM_t} p_{M_tD}) \tag{2}$$

The values W_1 for $q = 9$, corresponding to the maximum possible content of 9/5 helices in the copolymer, are given in *Table 2*. This table shows that the values of the maximum attained content of form A ($R^{900/935}$) in the series of samples 1 to 5 decrease much more rapidly than corresponds to the population of segments (W_1^9) suitable for 9/5 helix formation, irrespective of which type of statistics we use. This indicates that the effect of copolymerization on the infra-red spectrum of HCPOM does not agree with the assumption that form B of HCPOM corresponds to 9/5 helix structure with some defects, as formulated in our previous papers[1,2]. Also the finding that form A of HCPOM is not formed in POM–PDO blends cannot be brought into agreement with the assumption that the differences between forms A and B are due to helix defects.

(b) If forms A and B of HCPOM differ by helix structure, then according to X-ray diffraction these differences would have to be very small. In infra-red spectra, the differences between forms A and B are manifested by a shift of three bands of A_2 symmetry[2,4]—two of these bands are very strong and the shifts are considerable—whereas the other bands of the A and B forms of HCPOM differ very little in their positions. It is improbable that such a specific change of infra-red spectra could take place in consequence of a very small change of helix structure.

(c) In order to find out how the mutual positions of chains could affect the infra-red spectra of TO–DO copolymers, we have calculated the population W_2^9 of segments in pairs of neighbouring helices containing nine or more oxymethylene units, by means of the relation[18]:

$$W_2 = f_{M_t}(1) - 2\sum_{m=2}^{q-1} w_{M_t}(m) \tag{3}$$

valid for a system of parallel chains with a sequence

population governed by Bernoulli or first-order Markov statistics. Here $f_{M_t}(1)$ and $w_{M_t}(m)$ are defined by relations (2). The populations of W_2^9 helix pairs formed by nine monomer units are given in *Table 2* for various copolymers. The table reveals that the maximum content of form A in the copolymers corresponds fairly well to the population of neighbouring pairs of 9/5 helices, in any of the tested statistics. Also the infra-red spectra of the POM–PDO blend are compatible with the assumption that the differences in the infra-red spectra of the A and B forms of HCPOM are caused by interactions of neighbouring chains.

If we accept the assumption (c), explaining the differences between the spectra of A and B forms of HCPOM by interchain interactions, then measurements of the infra-red spectra of the blend as well as of the TO–DO copolymers indicate that these interactions take place in form A, and do not take place in form B. In the blend POM–PDO, crystallinity is strongly reduced (see *Table 2*), indicating that the POM chains are really separated in the blend.

Let us now analyse assumption (c) on the basis of vibrational spectra of POM. POM is formed by chains with large dipole moments, and in HCPOM the helices, and consequently also the C–O bonds in neighbouring chains, lie in parallel orientation[14]. Therefore a large intermolecular interaction of the transition moments of vibrational motions can take place[19]. It may be assumed that in the A form of HCPOM, changes of the original unperturbed band positions of noninteracting helices can take place as a consequence of interactions of transition dipole moments of the vibrations with frequencies 903 and 1098 cm^{-1} (C–O skeletal stretching plus CH_2 rocking of symmetry A_2) in neighbouring chains.

A similar interaction also can take place in orthorhombic crystalline POM (OCPOM)[20], where the bands of the C–O skeletal stretching plus CH_2 rocking vibrational mode lie at a practically equal position as in the A form of HCPOM[21], irrespective of the small shifts of many bands caused by different helix structure (2/1).

As in OCPOM intermolecular interactions are not manifested in Raman spectra[4], it is not surprising that the Raman spectra of the A and B forms of HCPOM in the range above 200 cm^{-1} are also equal.

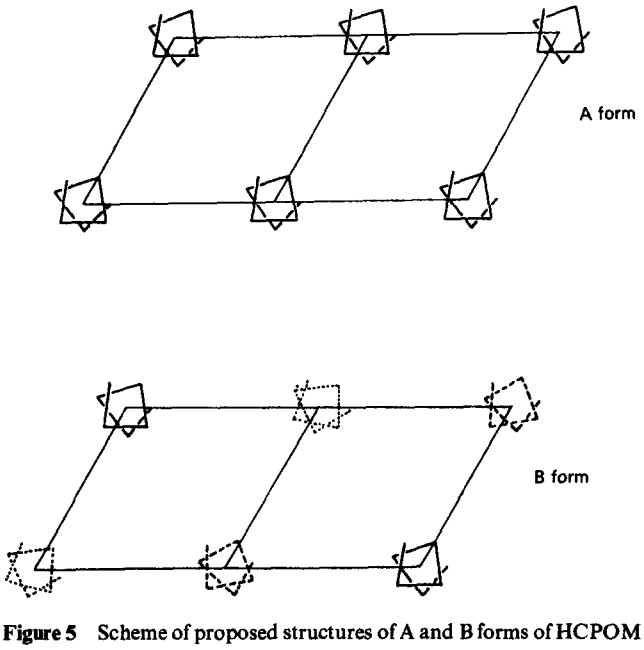

Figure 5 Scheme of proposed structures of A and B forms of HCPOM

Let us now observe in greater detail the behaviour of the band at 1239 cm^{-1} in HCPOM. This band was characterized by Tadokoro *et al.*[13] so that the existence of regular POM helices is needed for its appearance. In POM, the existence of helices is often connected with the existence of crystallinity: the band at 1239 cm^{-1} is strong in both A and B forms of HCPOM with high crystallinity; in copolymers its intensity decreases together with crystallinity at increasing concentration of E units in the chains; and in melts this band does not appear at all[1b]. However, the formation of helices does not necessarily lead to the formation of a crystalline lattice, as revealed by the measurements of the POM–PDO blends where the band at 1239 cm^{-1} is rather strong in infra-red spectra, while crystallinity measured by X-ray diffraction is low (see *Figure 4* and *Table 2*). Evidently the polyoxymethylene helices are well developed in the POM–PDO blend, in spite of the low crystallinity of the sample.

Further information on the structure of the A and B forms of POM can be obtained from a comparison of analysis of infra-red spectra and X-ray diffraction patterns.

The X-ray powder patterns of HCPOM of type A and B do not differ within the attainable resolution, and their structure corresponds to the published structure of HCPOM[14]. Depending on the history of the polymer, infra-red spectra indicate a continuous range of mixtures of A and B structures, including pure forms A and B. Therefore two types of structures must exist, clearly differentiated in the whole volume of the sample. The differences between the A and B forms of HCPOM cannot be explained by defects caused by parallel shifts of the helices, e.g. by a shift by one C–O bond, as proposed by Fawcett[15]. As these shifts would have to take place in a considerable part of the sample volume, they would have to be manifested on the X-ray diffraction patterns. In case of a defined shift by one bond, the unit cell would be increased, having to contain a minimum of two chains, contrary to the single chain in the unit cell of HCPOM. For random chain shifts, the nonequatorial reflections on the diffraction pattern would be diffuse or would disappear altogether. None of these effects has been observed in the diffraction patterns.

The small energy requirement of the transition between forms A and B and the observed large amplitudes of thermal vibrations of the C and O atoms about the helix axis ($\sim 16°$)[14] indicate the possibility of structural change by chain rotation (twist). A chain twist would not markedly affect the diffraction diagram, while the change of the transition dipole angles of vibrational modes could profoundly change the vibrational spectra[19]. An example of possible structures of the A and B forms of HCPOM differing by partial chain rotation is shown in *Figure 5*. In the A form of HCPOM, all C–O bonds are parallel, in the B form the parallelism of these bonds in nearest neighbours is removed.

After the completion of this work, there appeared a publication[22] based on X-ray diagrams of oriented HCPOM samples interpreted by the existence of conformational defects spaced regularly at intervals of 18 monomer units. We have measured the infra-red spectra

Table 3 Conditions of formation of A and B forms of HCPOM and their mutual transformations

A	B
Rapid cooling of the melt[3,23]	Slow cooling of the melt[3,23]
Rapid evaporation of the solvent from concentrated solution in DMF, precipitation[3]	Slow crystallization during cooling of dilute solution in DMF[3]
Simultaneous polymerization of TO in solution and crystallization of the resulting POM (growth of the chains on the surface of POM crystallites)[24]	Successive polymerization of TO in solution and crystallization of the resulting POM (growth of the chains on the POM segments projecting into the solution)[24]
Solid-state polymerization[23]	Polymerization in PMMA matrix[3]
Transformation from B by grinding and pressing[1]	In homogeneous blends remains also after grinding and pressing (this work)
By heating just below the melting point, both pure forms are transformed into the mixture	
A ⟶ A+B ⟵ B	

of unoriented samples prepared in an analogous way and we have found that the heating described in ref. 22 leads to an increase of the content of form B of HCPOM which could therefore be identified with the structure proposed by Saruyama and Miyaji. The presence of the proposed regular defects in itself could not explain the effects of copolymerization and of blend formation on infra-red spectra, but it might be the cause of the mutual twist of the chains thus making impossible the interaction of transition dipoles of the vibrational modes between neighbouring chains.

Generation and mutual transformations of the A and B forms of HCPOM

The conditions of generation and of the mutual transformations of the A and B forms of HCPOM are summarized in *Table 3*. The circumstance that the heating of pure A or B forms of HCPOM just below the melting point always leads to the formation of mixtures of A and B forms of HCPOM, together with the fact that the melting points of both forms are very near to each other, indicate that both forms are almost equally energetically favoured.

The effect of thermal treatment on the formation of forms A and B of HCPOM from melts and solutions[3,23] indicates that the structures with mutual angular orientation of chains similar to the A form are already preformed in concentrated solutions and melts. This is in agreement with our observation[1b] that the infra-red spectra of POM melts (lacking the band at 1239 cm^{-1} sensitive to regular helix formation) have a broad band in the range about 900 cm^{-1} where the strong characteristic band of the A form of HCPOM is found. Slow cooling of the melt or of a dilute solution leads to crystallization and a change of the mutual orientation of the chains inducing generation of form B.

The effect of polymerization procedure on the structure of HCPOM[24] indicates that the generation of forms A or B of HCPOM is also affected by the neighbourhood of the growing polymer end.

CONCLUSIONS

All cited results indicate that the differences between the infra-red spectra of the A and B forms of HCPOM are caused by interactions of transition dipoles of vibrational modes of neighbouring molecules. The interactions are strong in the A form of HCPOM due to parallel orientation of C–O bonds in neighbouring chains, and they are weak in the B form of HCPOM. The decreased intermolecular interactions of transition dipoles in the B form of HCPOM are caused by mutual twist of chains in the crystal lattice; this may concern either whole chains or, owing to conformational defects, only parts.

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