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Smectic ordering in poly(4-maleimidocholesterylbenzoate), poly(6-maleimidocholesteryl-hexanoate) and alternating copolymers with styrene, α- and β-methylstyrene and phenylvinyl ethyl ether

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Summary

Poly(4-maleimidocholesterylbenzoate), poly(6-maleimidocholesterylhexanoate) and alternating copolymers with styrene, α- and β-methylstyrene and phenylvinyl ethyl ether are birefringent in polarizing optical microscope and show a sharp reflection at 1.49-1.73 nm and an amorphous halo at 0.55-0.57 nm. The absence of discrete reflections in WAXD indicates the smectic ordering, i.e. a frozen-in liquid crystalline phase. At lower angle a reflection at 3.53 nm appears for poly(4-maleimidocholesterylhexanoate-alt-styrene) thus indicating that the reflection at 1.71 nm is a 2nd order of the true periodicity of 3.5 nm for all studied polymers.

Introduction

N-Substituted polymaleimides belong to comb-like polymers which due to the rigid structure of planar succinimido group have tendency to partially smectic ordering. Many authors have shown that X-ray diffractograms of N-substituted maleimide polymers and copolymers show two diffraction maxima with characteristic interplanar spacings: d_1 which increases with the increase of the length of N-substituent, and d_2 which is independent on the length of N-substituent (1). The numerical values of d_1 and d_2 of poly-N-alkyl-maleimides have been determined by Cubbon (2,3), while the interplanar spacings of poly-N-alkyl (or aryl) substituted maleimide copolymers with α-methylstyrene were determined in our Laboratories (4). Recently we described the structural ordering of poly[4'-N(benzo-15-crown-5)maleimide] and of copolymer with α-methylstyrene. Similar to other homopolymers of long chain substituted maleimides, homopolymer which contains benzo-15-crown-5 group in side chain, shows a high tendency of smectic ordering (4). In the present paper we shall describe the structural ordering of poly(4-maleimidocholesteryl-benzoate) (PMIChBenz), poly(6-maleimidocholesterylhexanoate) (PMIChHex) and copolymers with styrene (St), α- and β-methylstyrene (MeSt) and phenylvinyl ethyl ether (PhVOEt).

Experimental

Materials

Monomers MIChBenz (I) and MIChHex (II) and corresponding homopolymers and copolymers are prepared according to the procedure described in ref. 5. The properties of

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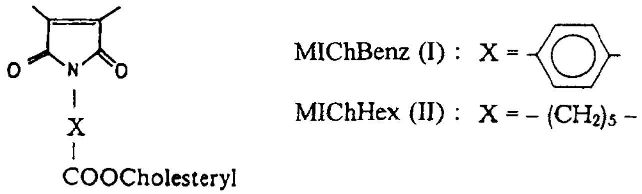
polymers are presented in Table 1. Homopolymers and copolymers are thermally stable in the region of transition temperatures. T_g's of polymers which contain flexible caproic acid esters are 15-30°C lower than those of benzoic acid esters, while the transitions at higher temperatures (T_{trans}) are 5-10°C lower for polymers which contain rigid aromatic ring in the side chain.



Apparatus

The texture of the liquid-crystal phases exhibited by the polymers were studied by polarizing microscopy using a Carl-Zeiss polarizing microscope equipped with a Linkam hot stage. X-ray diffraction experiments were performed by using Ni filtered CuK$_\alpha$ radiation and evacuated Statton cameras.

Differential scanning calorimetry was carried out on a Perkin-Elmer model DSC-2 with a scanning rate of 20°C/min^{-1} in nitrogen. The glass transition temperature was taken as the half-height of the corresponding heat capacity jump. The other transition temperatures were measured at the maximum of the peak. Thermogravimetric analysis was carried out on a Perkin-Elmer TGS-2 Thermogravimetric System in a nitrogen stream at a heat rate of 10°C/min^{-1}.

NMR spectra were obtained on a Varian EM 390 spectrometer. The copolymer composition was determined by NMR spectrometry and by elemental analysis.

Results and discussion

X-ray diffraction of monomers

X-ray diffraction of MIChBenz and MIChHex shows many reflections indicating highly crystalline materials as expected for low molecular weight compounds.

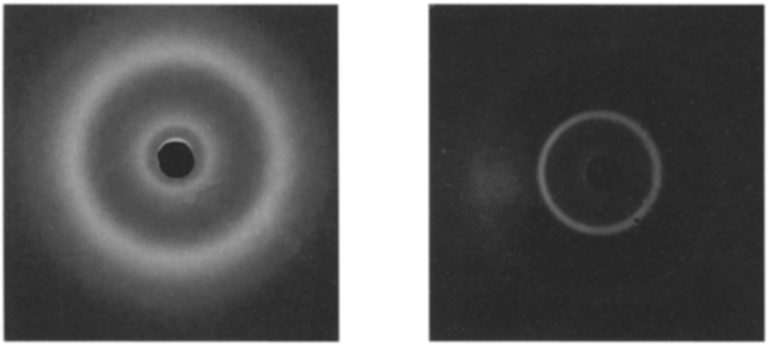
In the case of MIChBenz-monomer the lower angle reflections at 5.466, 2.678, 1.800 and 1.368 nm corresponded to 1st, 2nd, 3rd and 4th order of periodicity of 5.4 nm, what is consistent with the fall-off of the intensities with the increasing order of periodicity.

The same was also found in MIChHex, where reflections at 2.825, 1.421 and 0.943 nm are the 1st, 2nd and 3rd order of periodicity at 2.8 nm. Thus in MIChBenz the longest repeat value is 5.4 nm, while in MIChHex it is 2.8 nm. It indicates that the ratio of these values is 1:2, suggesting some doubling of the basic structural unit in MIChBenz. It may be the consequence of rigid structure of side chain in MIChBenz in comparison with the flexible side chain in MIChHex.

The structural ordering of homopolymers and copolymers

Monomers MIChBenz (I) and MIChHex (II) readily copolymerize with St, α-MeSt, β-MeSt and PhVOEt in toluene with AIBN as initiator yielding alternating copolymers.

The properties of polymers are presented in Table 1. Similar to the previously studied mechanism of copolymerization of homopolymerizable I and II with α-MeSt (5), the



1a 1b

Figure 1. WAXD pattern for: a) a sample of poly(MIChHex-alt-St) taken at a distance of ~50 mm; b) SAXD pattern of the same sample taken at a distance of ~200 mm.

Table 2. Spacing values of poly-MIChBenz (I), poly-MIChHex (II) and alternating copolymers

Polymer	Spacing values, d/nm 1)		
	Observed 2nd order reflection	Calculated 1st order reflection	Amorphous halo
Poly-I	1.50	3.00	0.55
Poly(I-alt-α-MeSt)	1.54	3.08	0.57
Poly(I-alt-β-MeSt)	1.61	3.22	0.56
Poly(I-alt-PhVOEt)	1.49	2.98	0.56
Poly-II	1.59	3.18	0.55
Poly(II-alt-St)	1.71	3.53 2)	0.55
Poly(II-alt-α-MeSt)	1.73	3.46	0.55
Poly(II-alt-β-MeSt)	1.67	3.34	0.55
Poly(II-alt-PhVOEt)	1.66	3.32	0.56

1) Measured spacing values of 2nd order reflections multiplied by two; 2) spacing value of directly observed 1st order reflection.

Table 2 shows the observed and calculated spacing values for examined specimens. It may be seen that in all cases the spacings occur at around 1.6 nm. It is reasonable to suggest that in all cases, as with poly-(MIChHex-alt-St) they are second orders and that the true periodicities are twice these spacings.

Despite the differences in composition of homopolymers and copolymers they all possess esterified planar cholesteryl group as a side chain connected to the main chain via either N-phenylmaleimide or N-pentamethylene maleimide link. Since according to the data in Table 2 all samples appear to show the same type of smectic structure, it is natural to look to the common structural features to account for these effects. Accordingly, it is reasonable to propose that the smectic ordering arises from layering of the side chain groups leading to a repeat of around 3.0-3.5 nm.

copolymerization of I with β-MeSt and PhVOEt and II with St, β-MeSt and PhVOEt at a molar ratio in the feed of 0.3/0.7 also gave alternating copolymers. The copolymer composition was determined by NMR spectrometry and by elemental analysis.

All of the polymers have been examined by polarizing optical microscopy and by X-ray diffraction and it was found that all homopolymers and copolymers exhibit very similar characteristics, which in view of their similar structure is not surprizing. In all homopolymers and copolymers the main chain represents the rigid succinimido group which is attached to cholesteryl group by rigid benzoate ester in poly-MIChBenz or by flexible spacer in poly-MIChHex. All are brittle indicating that they are below T_g and are birefringent thus suggesting either the presence of a crystalline phase or a frozen-in liquid crystalline phase. This issue is resolved by examination of X-ray diffraction pattern. An example of such a pattern is shown in Figure 1a for sample poly(MIChHex-alt-St).

Table 1. Polymerization conditions and properties of poly-MIChBenz (I), poly-MIChHex (II) and copolymers with St, α-MeSt, β-MeSt and PhVOEt; 0.3% AIBN in toluene at 70°C

Polymer	Conv.,% in 24 hrs	10^{-3}M.Wt Mw	Mn	Analysis, N% Found	Theor.	T_g°C	T_{trans}°C
Poly-I	96	53.5	23.7	2.47	2.39	215	327
Poly(I-alt-α-MeSt)	93	60.1	49.3	1.89	1.99	223	308
Poly(I-alt-β-MeSt)	90	66.8	32.8	2.25	1.99	212	317
Poly(I-alt-PhVOEt)	84	59.4	27.2	2.20	1.91	202	287
Poly-II	88	20.5	12.8	2.35	2.41	201	331
Poly(II-alt-St)	80	88.7	63.9	2.24	2.05	172	324
Poly(II-alt-α-MeSt)	73	94.5	50.5	1.94	2.00	200	321
Poly(II-alt-β-MeSt)	83	65.9	24.1	1.96	2.00	179	320
Poly(II-alt-PhVOEt)	68	45.6	28.0	2.03	1.90	170	322

Two features are noted in this pattern: an amorphous halo around 0.55 nm and one sharp reflection at a spacing of 1.7 nm. It is noteworthy that these features are common to all of the studied polymers (Table 2).

It is obvious that the scarcity of discrete reflections in Figure 1a precludes the presence of fully crystalline phases under such conditions, while the reflection at 1.7 nm has all the hallmarks of a smectic phase layer spacing. Further light on this problem is shed by repeating the same experiment but with a longer camera length to gain access to any reflections at lower angles which were previously obscured by the beam stop. The results of this experiment are shown in Figure 1b. Now a reflection at a spacing of 3.53 nm is also apparent; thus it becomes clear that the previous 1.71 nm is simply a 2nd order of the spacing of 3.53 nm. Hence it is established that the material displays smectic type ordering in a quenched glass with 3.53 nm being the true periodicity. Since the investigated samples are cast from solution in chloroform, it is proposed that the material developed the smectic type ordering either during or on the conclusion of solvent evaporation. However, the considerable amorphous halo indicates that higher level of ordering have not been possible during this process and hence the smectic phase exists in the glassy state.

However, it is also evident that the esterified cholesteryl unit is planar and it is therefore anticipated that there is some correlation between adjacent planes in these layers. It is proposed that the 0.55-0.57 nm spacing values of the amorphous halo represent the average separation of these groups similar to d_2 spacing values in other comb-like polymers (1,4,5).

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