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Oriented Polymer Growth in Thermotropic Mesophases

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ABSTRACT: Long-range order in polymers obtained through polymerization within mesomorphic and potentially mesomorphic media has been studied. Three representative monomers have been polymerized in mesomorphic and isotropic media and the properties of the polymers were investigated by means of X-ray and polarizing diffraction microscopy. *N-p*-Methacryloyloxybenzylidene-*p*-aminobenzoic acid (MBABA) was polymerized in its nematic state and in solution in DMF. In both cases a "locked in" nematic superstructure was observed. *N-p*-Butoxybenzylidene-*p*-aminostyrene (BBAS) was polymerized in bulk, in the nematic and isotropic states. Here again in both cases a "locked in" nematic superstructure was observed by X-ray diffraction. *p*-Methacryloyloxybenzoic acid (MBA) was polymerized in the isotropic bulk, in a nematic solvent, and in isotropic solvents. When polymerized in bulk, the polymer displayed pronounced crystallinity. A mesomorphic smectic superstructure appeared in films of the polymer cast from DMF, regardless of the method of polymerization, although none of the PMBA's studied are stereoregular. The results show on three examples that neither the presence of a mesomorphic matrix nor large amounts of cross-linking agent are necessary for the development and locking in of mesomorphic superstructure in polymers.

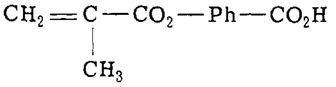
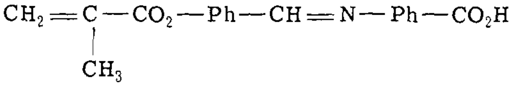
It was in 1963 that Herz, *et al.*,[1] succeeded in "locking in" the organization of the neat phase of the 11-sodium styrylundecanoate–water system through free radical polymerization. The reaction was carried out in the presence of a small amount of divinylbenzene used to cross-link the structure. A polymer was obtained with a molecular organization of a neat soap phase permanently locked in through cross-linking. Shortly thereafter, the locking in of the quasi-smectic organization of monolayers of polar monomer molecules adsorbed on montmorillonite was described by Blumstein, *et al.*[2] Here again a cross-linking agent (tetraethyleneglycol dimethacrylate) was used to stabilize the two-dimensional arrangement of monomer molecules. More recently Liebert and Strzelecki[3] obtained a number of anisotropic glasses by locking in the organization of different mesomorphic monomers. Polymeric glasses of nematic, smectic, and cholesteric symmetry were obtained. The authors stressed the necessity of using important quantities of cross-linking agents to avoid backcoiling of macromolecular chains with subsequent loss of order. Either bifunctional mesomorphic monomers were used, or mixtures of monofunctional mesomorphic monomers with at least 30 wt % of bifunctional monomers.

The locking in of mesomorphic superstructures through polymerization is analogous to locking in of molecular orientation through cooling. Such experiments have been described for different mesomorphic compounds by Chistyakov, *et al.*,[4] and more recently by Kessler and Lydon.[5] In both cases the long-range order in the glass was introduced through the quick depression of molecular motions, either through increase of the T_g (cross-linking) or direct freezing of the mesomorphic compound below its T_g. These facts suggest that the presence of a cross-linking agent may not always be necessary, provided the thermal motion of segments of the polymer, developing in the mesomorphic medium, is sufficiently depressed and that the polymer does not separate abruptly from the medium.

Polymerization within mesomorphic media has also been found to influence the degree of crystallinity of the resulting polymers. Such effects have been reported by Amerik and Krentsel[6] for poly(vinyloleate), by Hardy, *et al.*,[7] for cetyl vinyl ether, and by Perplies, Ringsdorf, and Wendorff[8] for a number of acrylic and methacrylic derivatives of Schiff bases.

The origin of the differences in supramolecular organization between polymers prepared in isotropic and mesomorphic media is unclear. There appears to be an interplay of three factors: (a) influence of the organization of the initial monomeric matrix (topotactic control); (b) strong interactions between side groups of the polymer, that is, the polymer's intrinsic tendency to organize; (c) possible influence of the matrix on the configuration of the polymer (topochemical control), which would in turn influence the supermolecular organization. We are attempting to discuss these questions on three representative examples. We would like to show evidence that anisotropic superstructures can be produced not only from systems displaying mesomorphism, but also from systems in which neither the polymer seg-

Table I
Phase Transitions of Monomers

Monomer	Structure	Transition[a]	Temp, °C
MBA	 $CH_2{=}C(CH_3){-}CO_2{-}Ph{-}CO_2H$	K → I	182
MBABA	 $CH_2{=}C(CH_3){-}CO_2{-}Ph{-}CH{=}N{-}Ph{-}CO_2H$	K → S_3 (?)	178
		S_3 → S_2	182
		S_2 → S_1	201
		S_1 → N	205
		N → I	?
BBAS	$CH_2{=}CH{-}Ph{-}N{=}CH{-}Ph{-}OC_4H_9$	K → N	83
		N → I	116

[a] K = crystal; S = smectic; N = nematic; I = isotropic liquid.

Table II
Polymerization of BBAS and MBABA

Monomer	Method of polymerization	Temp of polym, °C	T_g, °C	X-Ray, Å Low angle	X-Ray, Å Wide angle	Microscopic observations
MBABA	Bulk[a]	201				Nematic with birefringence unchanged until decomposition of polymer
	Bulk[b]		154		4.4	
	Bulk[a]	205				
	Isotropic solution in DMF[b]	120	87		4.4	
BBAS	Bulk[c]	83	55	23.2	4.35	Nematic with birefringence fading at 140°
	Bulk[c]	95[d]		23.2	4.35	

[a] *In situ.* [b] After removal of residual monomer and casting from DMF. [c] After removal of residual monomer. [d] Isotropic after a few per cent conversion to polymer.

ments nor the initial system are mesomorphic.

Experimental Section

Monomers. *N*-*p*-Butoxybenzylidene-*p*-aminostyrene (BBAS) was synthesized by condensation of *p*-aminostyrene with *p*-butoxybenzaldehyde. The method is described elsewhere.[9,10] *N*-*p*-Methacryloyloxybenzylidene-*p*-aminobenzoic acid (MBABA) was synthesized by condensing *p*-aminobenzoic acid with methacryloyloxybenzaldehyde. The method is described elsewhere.[9] The preparation of *p*-methacryloyloxybenzoic acid (MBA) was described previously.[11] All monomers were extensively purified by repeated recrystallization from various solvents.

Solvents. *p*-Heptyloxybenzoic acid (HBA) was recrystallized from acetic acid, methanol, and benzene. Transitions: K → S (91.5°), S → N (98°), N → I (146.5°). *o*-Ethoxybenzoic acid (EBA) was vacuum distilled at 172° (6 mm). Dimethylformamide (DMF) was distilled at 760 mm.

Polymerization. Bulk polymerizations of MBA and MBABA were carried out without initiators, the reaction taking only minutes at the high temperatures involved. Bulk polymerizations of BBAS and polymerizations in solution were carried out with benzoyl peroxide initiator at temperatures below 100° and *tert*-butyl perbenzoate initiator above 100°.

Properties of Monomers and Polymers. Phase transition temperatures of monomers and of polymers were determined by means of differential scanning calorimetry (Perkin-Elmer DSC-18) and polarizing microscopy. X-Ray diffraction from polymers and monomers was recorded by a flat plate camera at a sample-to-film distance of 7.38 cm for wide-angle patterns and 17 cm for small-angle patterns. The wavelength used was 1.54 Å. All samples were either powders or films and all diffraction patterns were recorded at room temperature. Films were prepared from polymer solution in DMF cast on a polyethylene plate and dried *in vacuo* at 80–90°. Specimens of polymers for polarizing microscopy were polished manually using an abrasive fine grade aluminum oxide powder. Glass transition temperatures were estimated from deformation tests performed with a Perkin-Elmer thermomechanical analyzer TMS-1.

Tacticities of poly(MBA) were determined on 10 wt % solutions of the polymer in *o*-dichlorobenzene after methylation. The methylation procedure of the polymer with methyltolyltriazene (MTT) was described elsewhere.[12] The 300-MHz nmr spectra provided a good resolution of the α-methyl triplet.

Results and Discussion

Table I gives the phase transition temperatures of the three monomers investigated in this study. The monomer BBAS is a mesomorphic Schiff base which displays a nematic mesophase; MBABA is a mesomorphic Schiff base with several smectic modifications as well as a nematic mesophase. Above 200°, MBABA polymerizes rapidly upon heating and we could not reliably measure the N → I transition temperature of this monomer. The third monomer listed in Table I, MBA, is a high-melting benzoic acid derivative which does not display a mesomorphic state, although it is capable of forming mixed smectic or nematic mesophases with lower melting smectic or nematic *p*-*n*-alkoxybenzoic acids.[13]

Conditions of polymerization of MBABA and BBAS are summarized in Table II, along with some properties of the resulting bulk polymers. The melt of BBAS was polymerized at the crystal → nematic transition temperature and also at 95°, within the nematic range of the monomer. At 95° the mesophase is destroyed shortly after onset of polymerization, which takes place thereafter within an isotropic melt. In both instances the X-ray pattern of the polymer is nematic[14] with diffuse rings at 4.35 and 23.2 Å. The total length of the monomer molecule, measured from a model,

Table III
Preparation of Poly(MBA)

Sample	Method of polym	Polym temp, °C	[Mo], mol/kg	Microscopic observations of polymer *in situ*
(1)	Bulk	188		Spherulites; side chains radial
(2)	Solution in nematic HBA	120	1.00	Birefringence until decomposition
(3)	Solution in isotropic HBA	150	1.00	Amorphous
(4)	Solution in isotropic EBA	120	1.00	Amorphous

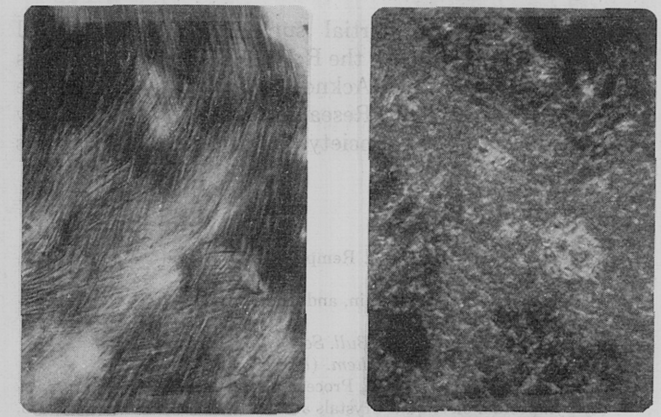


Figure 1. Poly(methacryloyloxybenzoic acid) precipitated from HBA "*in situ*." Photomicrograph between crossed polarizers: (left) at 120° (nematic) and subsequently heated up to 150°; (right) at 150° (isotropic).

Table IV
X-Ray and Pmr Characterization of Some poly(MBA's)

	X-Ray, Å		Tacticity		
Sample	Low angles	Wide angles	P_i	P_h	P_s
(1)	18.5	4.44	8.5	42.0	49.5
(2)	18.8	4.41	10.8	34.6	54.6
(4)	18.5	4.39	9.5	42.0	48.5

is approximately 23.5 Å, a value very close to that of 23.2 Å observed for the low-angle diffraction of the polymer. This indicates that the mesomorphic side groups are oriented perpendicular to the main chain. The X-ray diffraction data are supported by microscopic observations which also indicate that the nematic texture of the monomer appears to be locked in the polymer. The birefringence of the polymer begins to fade above 140°, that is some 20° above the nematic → isotropic transition temperature of the monomer. Progressive fading of the birefringence takes place over a temperature interval of some 10–15° and it may be due to the flow of the polymer, which has a relatively low T_g range and is not cross-linked.

Upon heating of MBABA at 205° in the nematic phase the polymer develops within minutes and a locked in nematic texture is observed *in situ* under the polarizing microscope. This texture persists up to the decomposition point of the polymer and it is also observed unchanged after dissolution in DMF, precipitation in methanol to remove residual monomer, and casting of a polymer film from DMF. The film of poly(MBABA) gives an X-ray pattern characteristic of a random nematic phase,[14] with one halo around 90 Å and one diffuse ring at 4.4 Å. This X-ray pattern is consistent with a nematic structure and confirms the microscopic observation. It is interesting to note that the same X-ray and microscopic results were observed when the polymer was prepared in isotropic solution in DMF, precipitated in methanol, and cast from DMF. The nematic order appears in the solid film irrespective of whether the polymer has been prepared in the mesomorphic bulk or isotropic solution. The glass transition temperature of poly(MBABA), however, appears to be strongly dependent on the method of polymer preparation (Table II), but at the present time we cannot propose a satisfactory explanation of this dependence.

The high value of T_g reflects the high rigidity of polymer segments as well as the network formation through hydrogen bonding. The mesomorphic order in this polymer appears to be due mainly to the strong interaction between side groups and an intrinsic property of their arrangement in concentrated solution. Bulk polymerization of MBABA in the smectic range, at 201°, also resulted in the locking in of the nematic structure, but because of the very narrow smectic S_1 interval of the monomer it was difficult to be certain that the polymerization did indeed take place in the smectic state of MBABA. Polymerization could have proceeded in a nematic medium and the lack of success in locking in a smectic arrangement at 201° may be due to fluctuation of temperature in a medium of very high viscosity where heat transfer is slow.

Table III summarizes the conditions of the preparation of poly(MBA) under various conditions as well as microscopic observations of polymers "*in situ.*" Bulk polymerization of MBA in the isotropic melt at 188° (sample 1) gives a polymer which in the microscope appears to have a spherulitic crystalline structure with radial packing of side chains. The T_g of this polymer is 110°. The polymer prepared from the nematic solution in HBA at 120° (sample 2) precipitates out of the mesophase as a highly birefringent phase with birefringence locked in until the onset of polymer decomposition (Figure 1, left). The polymer prepared in the isotropic melt of HBA (sample 3) and in the isotropic reference solvent EBA (sample 4) precipitates as an amorphous solid as witnessed by the lack of birefringence (Figure 1, right) and the absence of a sharp low-angle reflection.

It results from Table III that the organization of the matrix clearly influences the organization of the polymer as produced "*in situ*" (topotactic control of polymerization).

When polymers 1–4 are dissolved in DMF and solid films of poly(MBA) are cast from this solvent all of them develop a smectic superstructure. Table IV gives the X-ray diffraction results for polymers 1, 2, and 4, cast from DMF, as well as their tacticity. The films cast from DMF remain birefringent until decomposition of polymer.

Comparison of the X-ray data with the length of the chain measured from models indicates a layered smectic structure, with bilayers of molecules strongly tilted in the plane of the layers (45–47°). The angle of tilt appears to depend slightly on the conditions of preparation as is apparent from the sharp reflection at 18.5–19.5 Å (see Figure

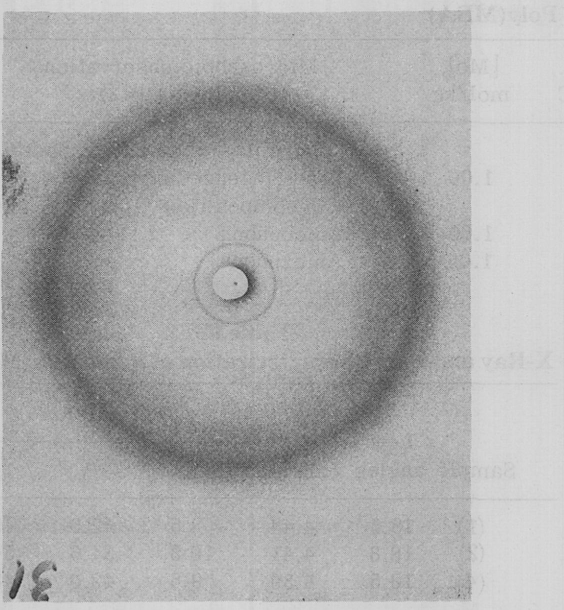


Figure 2. X-Ray diffraction photograph of a film of poly(methacryloyloxybenzoic acid) cast from DMF.

2), but the diffraction patterns are characteristic of smectic arrangements.[14] Table IV shows that these smectic superstructures are not the result of stereoregularity of the polymers, although poly(MBA) prepared within mesomorphic *p-n-* alkoxybenzoic acids appears to be formed of short stereoblocks, the structure of which is presently under investigation. This is an interesting point in so far as very little experimental data are available concerning the tacticity of macromolecules obtained within liquid crystalline media.

It appears therefore from our results that the orientation imposed upon the monomer molecules by the liquid crystalline matrix, in the case of polymerization within mesomorphic media (topotactic control), is only one of several factors leading to the development of mesomorphic superstructure in a polymer. Mesomorphic superstructures can be developed from isotropic solutions or in isotropic melts, provided specific interactions between polymer segments lead to ordered aggregation of segments. The role of a cross-linking agent is to counter the insufficient interactions between segments of the polymer and the mesomorphic matrix, which would normally lead to the "expulsion" of the polymer chain from the mesophase and its subsequent relaxation, and to increase the T_g of the network. Our results for three examples show that neither the presence of a mesomorphic matrix nor a large amount of cross-linking agent are necessary for the development and locking in of mesomorphic superstructures in polymers. It was also shown on one example that atactic polymers can also develop mesomorphic superstructures.

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