Polymers with rigid anisotropic side groups: 1. Side chain induced crystallinity in substituted biphenyl acrylates and methacrylates

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4-Hydroxy-4′-cyanobiphenyl and 4-hydroxy-4′-*n*-pentylbiphenyl have been converted into vinyl monomers by reactions with acryloyl and methacryloyl chlorides. All four new monomers were homopolymerized free radically to yield acrylic polymers which melt with decomposition at temperatures in excess of 200°C. Powder X-ray diffraction studies clearly show that the polymers are crystalline and suggest that the polymer backbones lie in essentially parallel planes contained within perpendicular smectic-like layers of the directly attached and rigid anisotropic side chain substituents. It is noteworthy that side chain ordering is sufficiently strong to overcome the normal conformational barriers associated with main chain methyl groups in the methacrylate polymers. Previous examples of this type of ordering have been restricted to acrylate polymers.

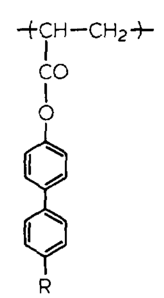
(Keywords: liquid crystal polymers; side chain induced crystallinity; biphenyl acrylates and methacrylates)

INTRODUCTION

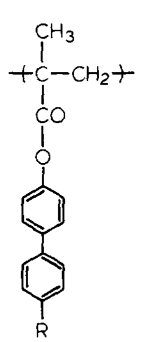
With the exception of ethylene and its fluorinated derivatives, vinyl monomers do not yield crystalline polymers unless there is a measure of configurational order in the vinyl polymer backbone[1]. Configurational order in vinyl polymer backbones arises mainly from specific mechanisms of polymerization or, occasionally, from the pronounced influence of bulky or chiral substituents.

During the last few years there has been growing interest in the synthesis and characterization of vinyl polymers in which the substituents may induce crystallinity by virtue of strong inter-substituent forces. The latter may have dipole or Van der Waals origins but side chain induced crystallization is now a well established feature of the polymeric state[2]. Substantial impetus to the characterization of side chain induced ordering in polymers is provided by the potential value of synthetic polymers having pendant mesogenic units, and exhibiting liquid crystal behaviour above the polymer glass transition temperature. Work in this field has been largely confined to the groups of Magagnini and Frosini in Italy, Finkelman and Ringsdorf in Germany, Plate and Shibaev in the U.S.S.R. and Blumstein in the USA. Two recent symposia reports[3,4] and review articles[5,6] provide convenient surveys of the results of these groups of workers and of techniques suitable for characterization purposes.

A number of compounds with anisotropic molecular structures are well known to exhibit liquid crystal behaviour. Of these, the 4,4′-disubstituted biphenyls, developed by Gray and collaborators[7] are important and very well characterized. In a series of papers we shall report on the synthesis and properties of acrylic and methacrylic polymers in which typical substituted biphenyls are attached to the polymer backbone by spacer groups of increasing molecular chain length. The work was stimulated in part by current interest in polymers exhibiting liquid crystal properties, and by the pioneering reports of Magagnini and collaborators[8] that poly(biphenylylacrylate) **1a** was partially crystalline and that the degree of crystallinity was independent of main chain tacticity[9].



1a, R = H
b, R = CN
c, R = $n\text{—}C_5H_{11}$



2a, R = H
b, R = CN
c, R = $n\text{—}C_5H_{11}$

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Crystallinity was not observed in polymers from biphenyl methacrylate **2a** although poly(p-cyclohexylphenyl acrylate) was crystalline[2].

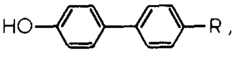
In the present paper we report on the synthesis, polymerization and characterization of similar acrylic and methacrylic homopolymers **1b,c** and **2b,c** in which the simple biphenylyl group is replaced by similar but more anisotropic biphenyl units with substituents (CN, n-C_5H_{11}) in the 4′-position.

EXPERIMENTAL

Materials

Benzene (A.R.) was dried over sodium wire and distilled on a vacuum line prior to use as polymerization solvent. Dimethylformamide (A.R.) was allowed to stand overnight over sodium hydroxide pellets and fractionally distilled. It was then passed over a column of Molecular Sieves (Linde, Type 4A), re-distilled and stored in the dark over Molecular Sieves. Methanol (A.R.) was used without purification. Azo-bis-isobutyronitrile was purified by two re-crystallizations from ethanol.

Monomer synthesis

Generally the polymerizable monomers were prepared from acryloyl and methacrylol chlorides (freshly distilled) by esterification with the appropriate substituted hydroxybiphenyl  R = CN, n-C_5H_{11}).

Alkenoyl chloride (5 ml) was added in one portion to a solution or suspension of the hydroxybiphenyl (5 g) in aqueous potassium hydroxide (50 ml, 20%) and dioxan (15 ml). The mixture was vigorously shaken and rapidly became hot. After ten minutes with occasional shaking, a further portion (5 ml) of alkenoyl chloride was added. The mixture was then allowed to cool naturally, with occasional shaking, and poured into water (50 ml). The resulting precipitate was filtered off, washed with cold water until neutral to litmus, and dried *in vacuo*. The crude product was dissolved in a minimum of chloroform and purified by chromatography on silica-gel using chloroform as eluant. Crystallization from ethanol gave the esters as colourless plates which showed single spots on thin layer chromatography and overall yields were 70–80% (based on biphenyl derivative). The monomers had all the expected i.r., n.m.r., and mass spectroscopic characterizations and, when examined under a polarising microscope (Nikon L-Ke with Mettler FP52 hot stage), gave the following melting points and phase transitions:

Monomers: **1b**, K 103°C N 129.3°C I; **2b**, m.p. 119°C; **1c**, m.p. 84°C; **2c**, m.p. 101°3. Thus only the cyanobiphenylyl acrylate **1b** exhibited any mesogenic behaviour, in agreement with an earlier independent report[10].

Polymer synthesis

Polymerizations were free radical and initiated thermally with azo-bis-isobutyronitrile. Typically 1:1 mixtures of solvent and monomer (containing initiator), were thoroughly outgassed by the conventional freeze-thaw technique before sealing and removing from the vacuum apparatus. Polymerization was allowed to proceed as indicated in *Table 1* before the mixture was poured into a ten-fold excess of methanol. Purification was accomplished by two further re-precipitations into methanol after which the polymers were dried *in vacuo*. Viscosity measurements were made in an Ubbelohde suspended level viscometer at 30°C (0.1 g polymer in 100 ml of the solvent indicated).

Thermal transitions in polymers

These were measured by means of a Perkin Elmer Differential Scanning Calorimeter, Model 2C.

For all four polymers there was no evidence of the usual glass transition behaviour. Rather, each polymer gave rise to a well marked, complex melting endotherm at temperatures above 200°C. The endotherms were not repeatable on the same sample and this was interpreted as the onset of significant thermal decomposition of the polymers.

X-ray diffraction studies

X-ray studies were performed with a Phillips PW 1020 Genvator Transmission apparatus. The Debye ‘pinhole’ technique was employed with a flat (Kodak No-Screen) film. FeK_α radiation was used with the sample placed at a distance of 80 mm. A small lead screen was placed at the centre of each film for protection from the main radiation beam. Polymers were examined as pellets made from films cast from 1–2% solution in DMF. Several films were cast and dried at room temperature *in vacuo* before being pressed together (13 ton/cm^2 for five minutes under vacuum) in order to form a pellet approximately 0.2 mm thick and 13 mm in diameter.

The spacings characteristic of the molecular organisation (d_1), the average distance between side groups (d_2) and any intermediate spacings were calculated using the Bragg Equation.

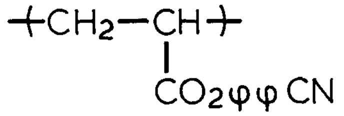
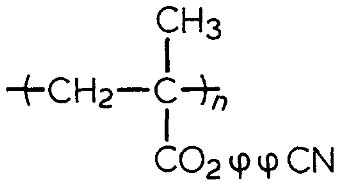
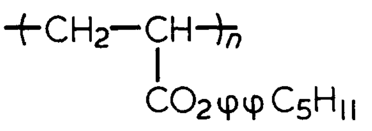
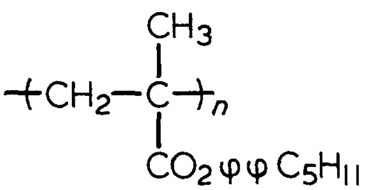
RESULTS AND DISCUSSION

Two new acrylic monomers **1b,c** and two new methacrylic monomers **2b,c** have been prepared and polymerized free radically. Despite the fact that the biphenyl substituents are very similar to small molecule analogues exhibiting liquid crystal behaviour, there is no real evidence for liquid crystal properties in any of the four new homopolymers. Rather the homopolymers all resemble typical crystalline polymers and are characterized (*Table 2*) by a complex melting process (with decomposition) at

Table 1 Polymerization of monomers

Monomer (conc. *M*)	Solvent	[AIBN] (10^3 M)	Temp. °C	Reaction time	Conversion %	[η] dl/g
1b (2.87)	benzene	4.87	80	20 min	84	1.62 (DMF)
1c (3.4)	benzene	4.87	70	20 min	75	0.74 (THF, 25°C)
2b (3.8)	DMF	2.85	85	7 h	87	0.55 (DMF)
2c (3.24)	benzene	2.43	80	84 min	82	0.15 (toluene)

Table 2 X-ray diffraction and d.s.c. data for biphenylyl acrylates and methacrylates

Polymer	Inner ring		Outer ring		Calculated length of anisotropic unit d(Å)	Onset of melting °C (d.s.c.)
	2θ	d_1 (Å)	2θ	d_2 (Å)		
 $+CH_2-\underset{CO_2\varphi\varphi CN}{CH}+$ (Poly-**1b**)	5.25	21.2	23.6	4.73	13.3	270
 $+CH_2-\underset{CO_2\varphi\varphi CN}{\overset{CH_3}{C}}+_n$ (Poly-**2b**)	5.35	20.7	22.7	4.91	13.3	240
 $+CH_2-\underset{CO_2\varphi\varphi C_5H_{11}}{CH}+_n$ (Poly-**1c**)	3.32	33.3	24.1	4.64	16.24	303
 $+CH_2-\underset{CO_2\varphi\varphi C_5H_{11}}{\overset{CH_3}{C}}+_n$ (Poly-**2c**)	4.11	27.0	23.8	4.70	16.24	232

temperatures in the 230°–300°C region. Glass transition temperatures could not be detected with the apparatus available and hence are assumed to involve highly hindered segmental motions. It is quite remarkable that these simple acrylates and methacrylates should show such high temperature behaviour in the absence of backbone stereoregularity.

The pioneering studies, including X-ray diffraction measurements, of Magagnini and collaborators[2] provide a basis for an explanation of the present data and for an extension of insight into side chain induced crystallization in vinyl polymers.

Magagnini *et al.*[2] showed that poly(p-biphenyl acrylate) (Poly-**1a**) was crystalline with an apparent $T_g = 110°C$ and $T_m = 280°C$. The crystallinity was deemed to arise via alignment of the rigid biphenylyl substituents as indicated later for Poly-**1c** in *Figure 2*.

Ordering of this kind would be similar to smectic ordering in low molar mass liquid crystal molecules and requires that the polymer backbone be significantly distorted from its normal random coil conformation. The proposed smectic-like order demands that the polymer backbone chains must lie in essentially parallel planes within the smectic-like layers. It is highly significant that the crystallinity of poly(p-biphenylyl acrylate) is independent of tacticity and that the corresponding poly(p-biphenylyl methacrylate) (Poly -**2a**) does not exhibit evidence of crystallinity[2]. These observations indicate that the highly unusual extended main chain, and essentially planar, conformation of poly(p-biphenylyl acrylate) is not significantly influenced by main chain configuration, and that the forces of attraction leading to smectic-like order are insufficient to overcome the additional main chain conformational barriers imposed by the methyl substituent in Poly-**2a**.

Figure 1 shows X-ray diffraction diagrams for the four new polymers studied in the present work. In all four cases there is a more or less sharp reflection at values of 2θ indicative of inter-chain spacings similar to those reported by Magagnini *et al.*[2,7] for the unsubstituted biphenylyl polymers. The sharp reflections arise from low angle scattering caused by smectic-like periodicity of the biphenylyl substituents. A broader, more diffuse, ring may be observed for all the polymers arising from wide angle scattering associated with amorphous material. *Table 2* summarizes the X-ray and d.s.c. data.

In contrast to the unsubstituted biphenylyl derivatives studied by Magagnini *et al.*[2], monomers and corresponding polymers used in the present work are inherently more anisotropic because of the additional substituent (CN, n-C_5H_{11}) located *para*- to the attached polymerizable functionality. It is to be expected therefore

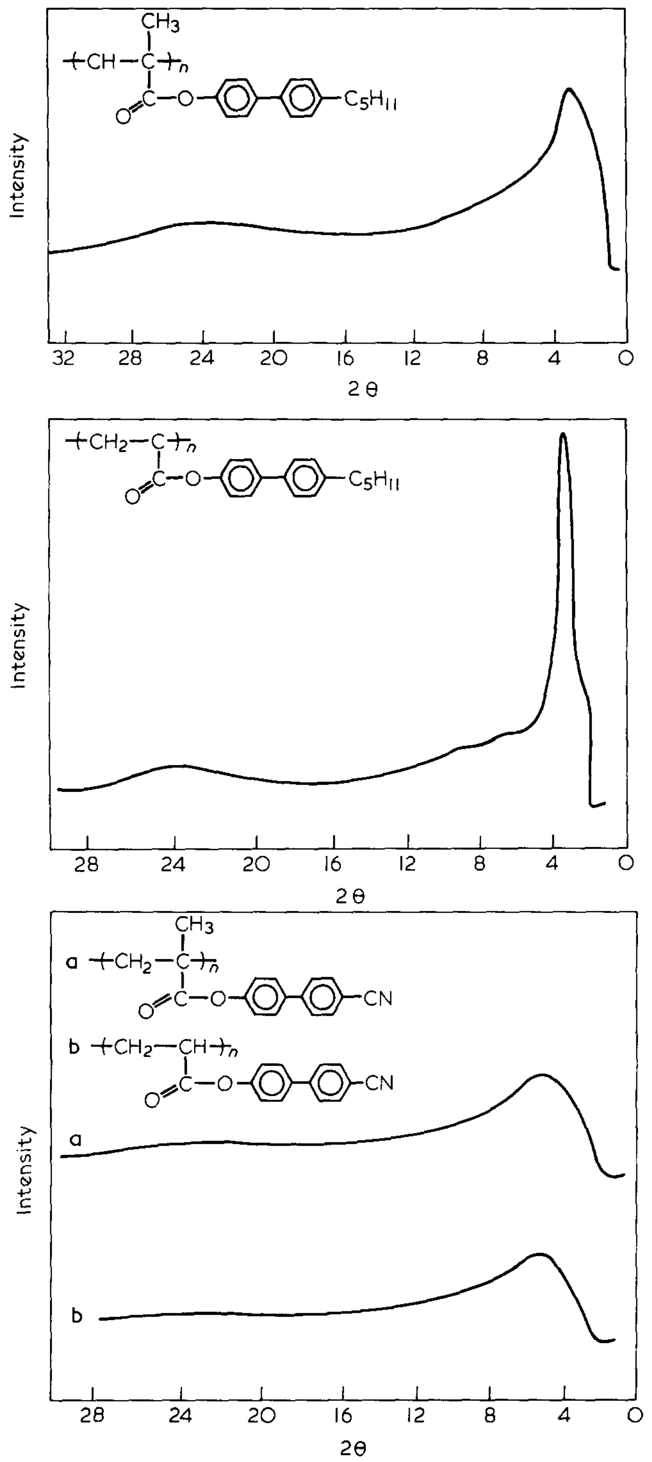


Figure 1 Powder X-ray diffraction diagrams (see experimental section for details)

that any side chain ordering phenomena will be enhanced. Clear evidence for this is provided by the fact that both methacrylate polymers (Poly-**2b,c**) exhibit order and crystallinity similar to that of the corresponding acrylates (Poly-**1b,c**). Obviously the additional anisotropy afforded by CN and n-C_5H_{11} groups is sufficient to overcome the extra conformational constraints (compared with acrylate polymers) imposed by the main chain methyl substituents.

Inspection of the data in *Table 2* suggests that the inter-chain spacing for poly(p-pentylbiphenylyl acrylate) (Poly-**1c**) corresponds approximately to the sum of the anisotropic group lengths and fits very well (see *Figures 2* and *4*(*a*)) the model of Magagnini.

In contrast, the inter-chain spacing for the corresponding methacrylate polymer (Poly-**2c**) (see *Figure 3*(*c*)), corresponds to a distance (d_1) less than the sum of the lengths of the two biphenylyl units ($d_1 = 1.8d$). Such a result could be readily explained, as indicated in *Figure 3*, either by a tilted smectic-like ordering *Figure* (*3a*), or an inter-chain overlapping of substituents within the smectic-like ordered array *Figure* (*3b*). Recent studies of smectic structures in small molecule mesogens based on cyano-biphenyls suggest[7] strongly that overlapping dipoles, as indicated by the molecular structure in *Figure 4b*, are to be anticipated. This is in contrast to the situation (*Figure 4a*) for the pentyl analogue—Poly-**1c**. X-ray analytical data for Poly-**1b** might then be explainable according to the model shown in *Figure 3b*. Similar considerations apply to interpretation of the data for the cyano-substituted biphenylyl methacrylate Poly-**2b**. Details of the smectic-like ordering in Poly-**2c** cannot be finalized on the basis of existing X-ray diffraction data but, as indicated in *Figure 3*, either a tilted or overlapping structure would be possible.

The side chain ordering imposed by anisotropic substituted biphenylyl substituents in acrylate polymers, originally demonstrated by Magagnini and collaborators[8] is thus confirmed and extended to methacrylate polymers. Interestingly perhaps the most vivid demonstration of this type of side chain ordering may be seen in the work of Krongauz and Goldburt[11] in which polymerization of a spiropyran methacrylate was shown to

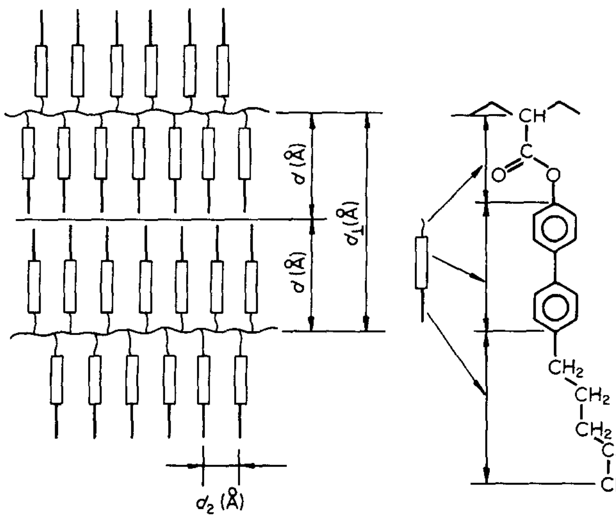


Figure 2 Schematic representation of ordering in Poly-**1c**

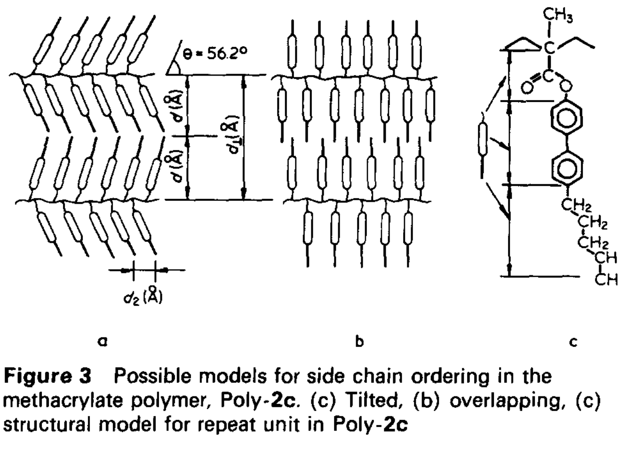


Figure 3 Possible models for side chain ordering in the methacrylate polymer, Poly-**2c**. (c) Tilted, (b) overlapping, (c) structural model for repeat unit in Poly-**2c**

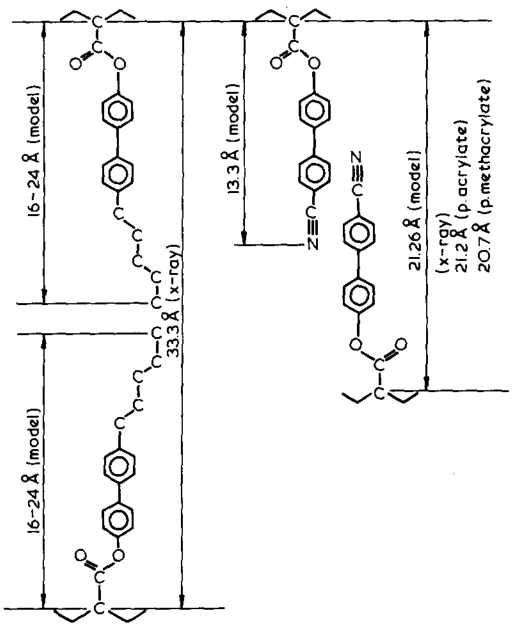


Figure 4 Structural models for end-on (a) and overlapping (b) anisotropic units

yield progressively more crystalline polymers with increasing conversion of spiropyran to ring opened, and highly polar, merocyanine.

CONCLUSIONS

Information as to the structures of the four new polymers prepared in the present work greatly complements and extends the original observations of Magagnini relating to poly(p-biphenylyl acrylate). Increasing the anisotropy in biphenyl side chains by means of suitable substituents greatly increases the propensity for smectic-type ordering of the rigid side chains. Polymer backbones are thought to lie in essentially parallel planes in a highly unusual conformation for acrylates and methacrylates.

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