Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Influence of chirality on the mesophase of side chain polymers with phenyl benzoate pendant groups

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To cite this Article Kozlovsky, Mikhail(2005) 'Influence of chirality on the mesophase of side chain polymers with phenyl benzoate pendant groups', Liquid Crystals, 32: 3, 401 — 405
To link to this Article: DOI: 10.1080/02678290500046249
URL: http://dx.doi.org/10.1080/02678290500046249

Liquid Crystals, Vol. 32, No. 3, March 2005, 401–406

Influence of chirality on the mesophase of side chain polymers with phenyl benzoate pendant groups

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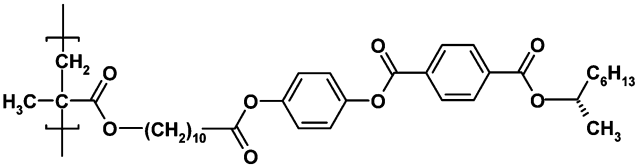
(*Received 30 June 2004; accepted 29 September 2004*)

To reveal the structure of an amorphous mesophase with a hidden liquid crystalline structure (ISm*) in a chiral side chain polymer, P8*M, its racemic isomer has been synthesized along with two more *RS*-copolymers with controlled enantiomer excess. The phase behaviour of the copolymers was studied comparatively by DSC and X-ray scattering. Optical rotatory dichroism was measured for thin films of P8*M and two homologue polymers, differing in the polymeric main chain, by the size of the chiral terminal group and by its absolute configuration. A helical superstructure with pitch of about 250 nm is indicated within the ISm* mesophase. Its structure as a short pitch TGB phase hase been proven conclusively.

1. Introduction

The effect of chirality on the phase behaviour of liquid crystals and, in particular, of liquid crystalline polymers can hardly be overestimated. The introduction of non-centrosymmetric moieties into nematic or tilted smectic structure causes the formation of helically twisted structures, and leads to such unique physical properties as selective light reflection, a large optical rotation and, in the case of smectics, ferroelectricity. Furthermore, it has been shown that even in the orthogonal smectic A phase, if it is built from chiral molecules, a discontinuous helical superstructure can organize itself through a lattice of screw disclinations, the twist grain boundary (TGB) phase [1–6].

We have previously reported an unusual phase behaviour in a chiral side chain polymethacrylate, P8*M [7]:



This shows a phase transition to the isotropic melt at 64°C (on heating), detected by various experimental techniques including DSC, X-ray diffraction, and broad line NMR. Below the transition point, the polymer forms a layered structure showing a well developed system of SAXS peaks. Moreover, CD and UV-Vis spectroscopy data give evidence of some helix-like superstructural ordering in the mesophase [8]. However, the 'isotropic smectic' mesophase, ISm*, of the polymer shows no birefringence in the visible wavelength range, in contrast to all known LC phases, so that the phase transition cannot be traced by microscopic observation.

To date, we have found the formation of an ISm* phase for a half-dozen chiral polymethacrylates and polisiloxanes, and for several series of related copolymers [9, 10]. Table 1 overviews the chemical structure and phase behaviour of various synthesized comb-like homopolymers, which carry chirally substituted side chains derived from asymmetric esters of terephthalic acid and hydroquinone, a structure which seems to favour formation of the ISm* phase.

The suggested extra short short pitch TGB-like phase [8] remains the only structural model which can yet explain the observed lack of birefringence in the ISm* phase. Actually, if the helical pitch is less than the visible wavelength range, the mesophase appears visually as amorphous and optically isotropic, while keeping the smectic ordering at the molecular dimensions of 1–100 nm. However, there have been no conclusive proofs to date for the existence of a helical twist in the mesophase with a pitch of 200–250 nm.

To confirm the suggested TGB structure of the ISm* phase in P8*M and related polymers, we have performed the two sets of chirality measurements reported below. First, the racemic form of the polymer P8$^{\pm}$M was prepared and studied, along with the completely chiral (*R*)-isomer P8*M, and two intermediate polymers with different value of enantiomer excess, *ee*.

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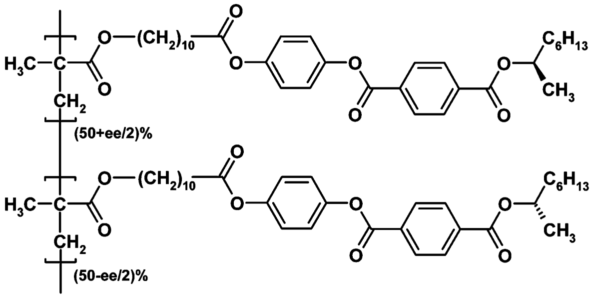
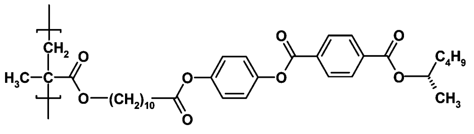
Liquid Crystals
ISSN 0267-8292 print/ISSN 1366-5855 online © 2005 Taylor & Francis Group Ltd
http://www.tandf.co.uk/journals
DOI: 10.1080/01411590500046249



Polymer	ee, %
P8*M ≡ CE100	100
CE60	60
CE25	25
P8$^{\pm}$M ≡ CE0	0

Second, the optical rotatory dichroism (ORD) was measured for P8*M both below and above the phase transition point, and compared with the same curves for two other homopolymers. For comparison purposes, the following polymers were chosen, which differ from P8*M by the polymeric main chain, by absolute configuration of the chiral centre, and/or by size:

P6*M *(S)*



P8*ST *(R)*

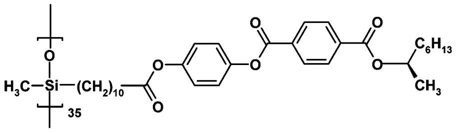
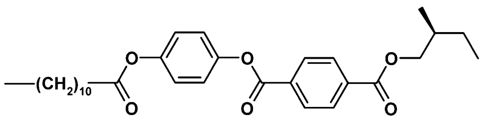
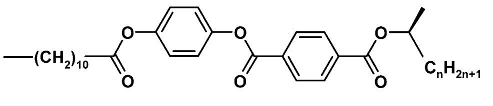
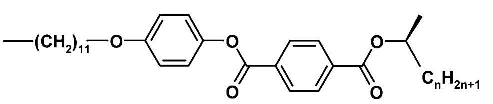
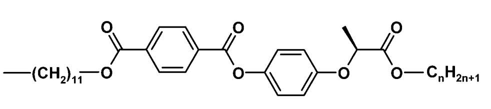


Table 1. Chiral homopolymers with side chains based on asymmetric esters of terephthalic acid and hydroquinone.

Polymer	Main chain	Side chain structure	*n*	Phase transitions/°C[a]
P5*A	Acrylate			Sm F* 77 Sm C* 97 I
P5*M	Methacrylate			g 40 Sm C* 74 Sm A 85 I
P4*A	Acrylate		2	Sm B 50 Sm C* 88 I
P4*M	Methacrylate		2	g 40 Sm C* 78 I
P6*M	Methacrylate		4	g 30 ISm* 53 I
P6*ST	Siloxane		4	Sm B 33 Sm C* 51 I[b]
P7*M	Methacrylate		5	g 30 ISm* 57 I
P7*ST	Siloxane		5	g 18 ISm* 54 I
P8*A	Acrylate		6	Sm B 55 Sm A 61 I
P8*M	Methacrylate		6	g 30 ISm* 64 I
P8*ST	Siloxane		6	g 25 ISm* 61 I
P8*S	Siloxane		6	g 24 ISm* 47 I (metastable) or g 24 Sm C* 43 Sm A 47 I (equilibrium)
PL4*A	Acrylate		4	g 10 I
PL4*M	Methacrylate		4	g 15 I
PL4*S	Siloxane		4	g 10 I
PL6*S	Siloxane		6	g 15 I

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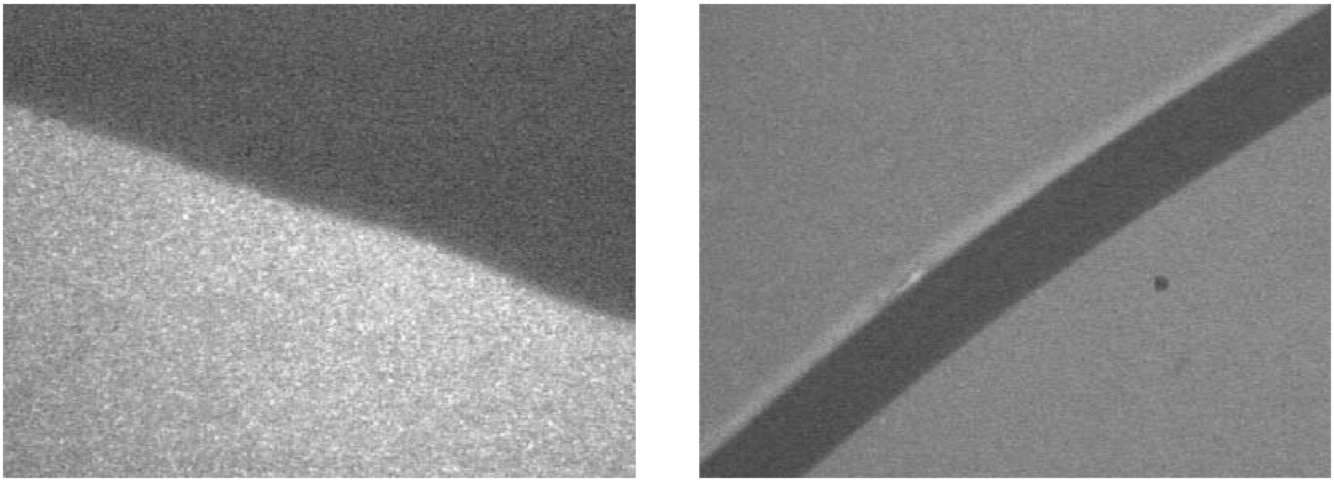
[a] On heating.

[b] For a sample annealed 24 h at 20°C.



(*a*) (*b*)

Figure 1. Polarizing microscopic textures of the polymer films: (*a*) racemic polymer P8 ± M, crossed polarizers; (*b*) chiral polymer P8*M (the angle between the polarizers reduced to 70° for better recognition of the phase border).

2. Experimental

The synthesis of all the homopolymers except the racemic one, P8$^{\pm}$M, has been described previously [7, 9]; the latter polymer was synthesized using the same procedure as for its chiral form P8*M, but starting from racemic *dl*-2-octanol.

DSC curves were recorded with a Perkin-Elmer DSC-7 calorimeter. X-ray scattering cuves from non-oriented polymer samples as 2 mm diam. capillaries were taken with a Stadi Stoe-2 diffractometer [11]. The peak positions and their widths at half-maximum level, $\Delta\Theta_{1/2}$, were estimated by fitting with a square root Lorentz function.

Samples for ORD measurements were prepared by pressing a polymer fragment between two 1 mm thick quartz glass plates at *c*. 75°C with further cooling, and the film thickness was calculated from sample weight and film area, taking for the polymer density the value $d=1.2$, typical for side chain LC polymers [12]. To avoid possible errors in the estimation of film thickness due to wedge configuration, only the very central part of the film was used for measurements. The typical thickness of the polymer film was 10–15 µm. The ORD measurements were carried out using a home-made set-up [13].

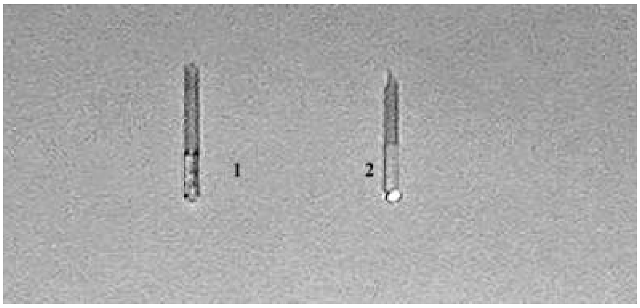


Figure 2. Optical appearence of the polymer CE25 (bulk sample) at ambient temperature in the ISm* phase (1) and in the Sm A phase (2).

3. Results and discussion

3.1. *Effect of enantiomer excess on the phase behaviour of P8*M*

The chiral polymer P8*M, and its racemic form P8$^{\pm}$M, exhibit quite different optical appearances at ambient temperature, as illustrated in figure 1. Both the completely chiral homopolymer P8*M, and its 'optically impure' isomer C60, form the transparent, visually non-birefringent ISm* phase; while the racemic polymer P8$^{\pm}$M forms a turbid birefringent texture identified as the conventional Sm A phase. Most interesting, however, is the phase behaviour of polymer CE25, having enantiomer excess of chiral centres in the *R*-configuration to those in the *S*-configuration as low as 25%. When cooled slowly (0.2 K min^{-1}) from temperatures above the transition point, the polymer forms the Sm A phase both in thin films and in bulk (the latter shown in figure 2); while quenching of the polymer at *c*. 20 K min^{-1} results in formation of the ISm* phase. It should be noted, however, that annealing of an ISm* sample of CE25 at 60°C (just below the transition point) for two weeks produces no change in its optical appearance towards the birefringent Sm A texture. To summarize, the polymer can appear, at any temperature below the phase transition, either transparent and optically isotropic (ISm* phase) or turbid and birefringent (Sm A phase), depending on the thermal prehistory

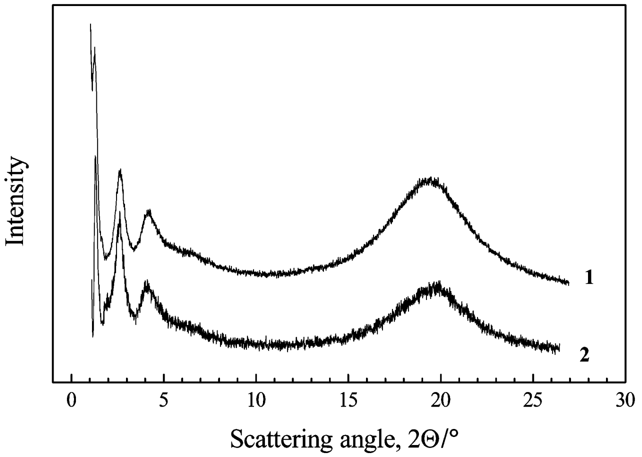


Figure 3. X-ray scattering curves at 40°C: (1) racemic polymer, P8$^{\pm}$M, Sm A phase; (2) chiral polymer, P8*M, ISm* phase.

of the sample. Similar ambivalent behaviour has been reported earlier for several photochromic copolymers based on P8*M [14].

X-ray data from P8*M and P8$^{\pm}$M reveal no remarkable difference, either in the shape of scattering profiles (figure 3), or in the values of layer spacing, d_2, and intralayer distance between neighbouring mesogenic groups, D (table 2). Taking into account the calculated length of the side chains, l=39.5 Å, we should note here that both polymers form a local bilayer SmA$_d$ structure with the main periodicity d_1~65 Å. However, it is difficult to study the corresponding X-ray peak in detail because of scattering of the incident beam. For that reason, the second order reflection with a much better defined position, d_2~33 Å, was selected for detail structural investigations.

The only systematic difference between the conventional Sm A phase and the 'isotropic smectic' state ISm*, observed in the X-ray data for the same material at the same temperature (CE25), is the width of the d_2 peak at half-height level, FWHM. The data of figure 4 confirm a less ordered smectic structure for the ISm* phase, as compared with the Sm A phase, and agrees well with data reported for the TGB phase of low molar mass compounds [6, 15].

Table 2. X-ray data for the optical isomers of P8*M at room temperature.

Polymer	Half-layer spacing, d_2/Å	Intralayer distance, D/Å
P8*M≡CE100 (ISm*)	31.7	4.52
CE60 (ISm*)	32.2	4.53
CE25 (ISm* state)	32.8	4.51
CE25 (SmA state)	32.4	4.52
P8$^{\pm}$M≡CE0 (Sm A)	33.0	4.54

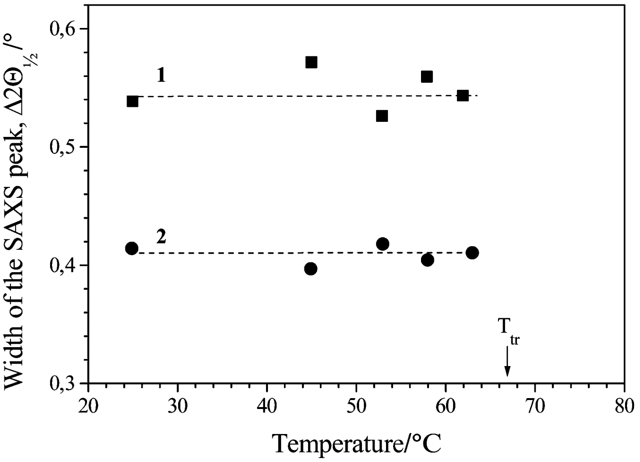


Figure 4. The width of the d_2 peak, FWHM, for CE25 in the transparent ISm* state (1) and in the turbid Sm A state (2), versus temperature.

To conclude this section, we note that some degree of chirality is necessary for the formation of the ISm* phase, although the threshold value of the enantiomer excess is surprisingly low, ⩽25%. In this connection we should note, however, that even racemic mixtures of low molar mass liquid crystals can deracemize spontaneously, forming separate left-handed and right-handed domains [16]. The supramolecular chiral structure of the ISm* phase is confirmed by ORD data presented in the next section.

3.2. *Optical rotatory dichroism of the ISm* phase*

Specific optical rotation data for an ISm* film of P8*M is presented in figure 5 (*a*), as a function of wavelength. The α value shows a 15-fold growth, on shortening the wavelength from red light (650 nm) to the near UV range (310 nm). The experimental conditions did not allow us to achieve the maximum α value, because of a too low transmittance of the film at the shorter wavelength range. Such a low transmittance may be related to either selective reflection or absorption by phenyl benzoate groups. However, the drastic drop of α at temperatures above the transition point proves conclusively that the rotation is caused not by molecular chirality but by a chiral supramolecular structure of the ISm* phase. The angular (in)dependence of the specific rotation in both phases, figure 5 (*b*) excludes any macroscopic orientation of the film sample and also confirms the intrinsic helicity of the ISm* structure.

The ORD curve for P8*M is plotted in figure 6, along with the data for two other ISm* polymers: polymethacrylate P6*M and polysiloxane P8*ST, which have the opposite absolute configuration of the chiral centre. As seen from the figure, the latter configuration determines

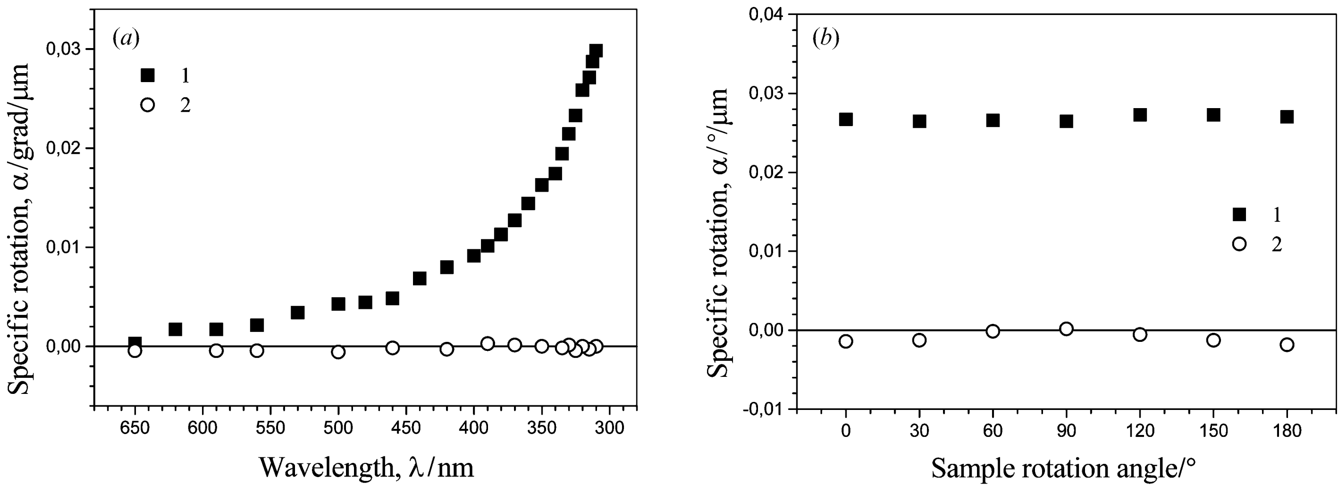


Figure 5. (*a*) Specific rotation of a P8*M film versus wavelength; (*b*) specific rotation of the film at 315 nm, versus sample rotation angle. Film thickness 7 μm; (1) ISm* phase at 20°C; (2) conventional isotropic melt at 80°C.

the sign of optical rotation as (−) for *S*-derivatives but (+) for *R*-derivatives; the derivative of 2-octanol (P8*M) shows a much higher rotating power than the homologous polymer derived from 2-hexanol (P6*M). Such a correlation is well known for the cholesteric and ferroelectric Sm*C phases of LC molecules [3–5].

The siloxane polymer P8*ST shows, however, a very large optical rotation with an absolute value exceeding by an order of magnitude the corresponding value for the methacrylic analogue. This fact may be explained by the higher flexibility of the polysiloxane main chain, which allows a much better organization of the mesogenic side chains in the complex short pitch TGB structure. We should note here also, that a vanishingly low but non-zero birefringence has been detected for the ISm* phase of P8*ST, estimated as $\Delta n \sim 0.004$ [9]. This bridges the optical properties of the ISm* phase of chiral polymers and those of a conventional TGB phase, which is known to be birefringent and to form well developed microscopic textures [15, 17].

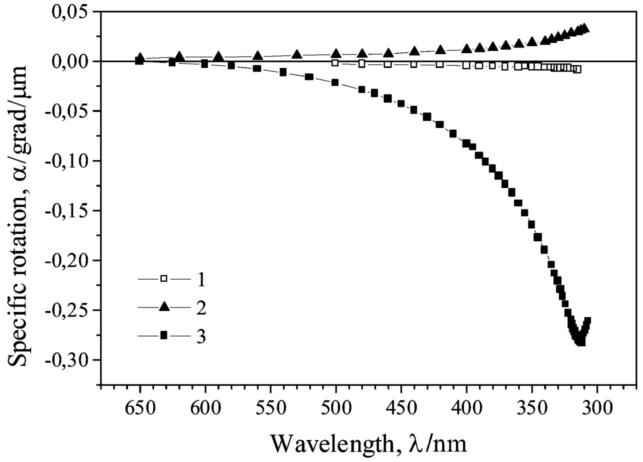


Figure 6. Specific rotation of ISm* films versus wavelength: (1) P6*M (S); (2) P8*M (R); (3) P8*ST (S).

Finally, by extrapolating curve 3 in figure 6 towards shorter wavelengths until reversal of the rotation sign, we obtain an estimate for the helical pitch in P8*ST as $p \sim 250$ nm, which agrees well with the suggested short pitch TGB structure.

4. Conclusions

This comparative study of P8*M isomers having different proportion of *R*- and *S*-monomer moieties, from the pure chiral polymer to the racemic polymer, provides evidence for the determining role of chirality in formation of the ‘isotropic smectic’ phase, ISm*. The ORD data for several ISm* polymers indicate the presence of a short pitch helical superstructure in this mesophase, with a periodicity of *c.* 250 nm. The combination of both sets of experimental data allows us to assert that the short pitch TGB structure for the unusual ISm* phase of chiral side chain polymers is completely confirmed. We should note here that these conclusions are strongly supported by our recent observation of selective reflection from ~0.6 μm thick spin-coated P8*M films in the near UV range with $\lambda_{max} \sim 240$ nm [18].

Acknowledgements

The author is greatly indebted to Prof. W.Haase (Institute of Physical Chemistry, Darmstadt University of Technology, Darmstadt, Germany) and Prof. H.-G.

Kuball (Institute of Physical Chemistry, University Kaiserslautern, Kaiserslautern, Germany) for their hospitality, valuable discussions, and support in chemical synthesis and X-ray measurements (WH) and ORD measurements (HGK). The assistance of Dr B.Helgee (Institute of Polymer Technology, Chalmers University of Technology, Göteborg, Sweden) in DSC measurements is also acknowledged. This work was supported by the Volkswagen Foundation (Germany), Project I 74 471, and by the Deutsche Forschungsgemeinschaft (DFG, Germany), project Re 923–8.

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