

This article was downloaded by:

On: 26 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713926090>

Thermotropic liquid-crystalline polymers XXVI. Synthesis of comb-like polymers with oxygen containing spacers and a study of their phase transitions

S. G. Kostromin^a; V. P. Shibaev^a; N. A. Plate^a

^a Department of Chemistry, M. V. Lomonosov, Moscow State University, Moscow, U.S.S.R.

To cite this Article Kostromin, S. G. , Shibaev, V. P. and Plate, N. A.(1987) 'Thermotropic liquid-crystalline polymers XXVI. Synthesis of comb-like polymers with oxygen containing spacers and a study of their phase transitions', *Liquid Crystals*, 2: 2, 195 – 200

To link to this Article: DOI: 10.1080/02678298708086290

URL: <http://dx.doi.org/10.1080/02678298708086290>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Thermotropic liquid-crystalline polymers

XXVI. Synthesis of comb-like polymers with oxygen containing spacers and a study of their phase transitions

by S. G. KOSTROMIN, V. P. SHIBAEV† and N. A. PLATE

Department of Chemistry, M. V. Lomonosov Moscow State University,
Moscow 119899, U.S.S.R.

(Received 12 August 1986; accepted 1 November 1986)

Synthesis of new liquid-crystalline comb-like polymers with oxygen-containing spacers and mesogenic cyanbiphenyl groups is described. Liquid-crystalline homopolymers of acrylates and methacrylates, their copolymers and liquid-crystalline polysiloxane are obtained. It is shown that the incorporation of oxygen atoms in spacer leads to decrease of the clearing temperature. The mesophase types of the homopolymers and copolymers are determined.

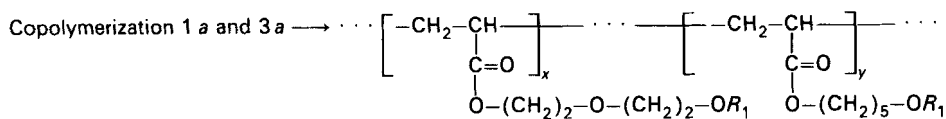
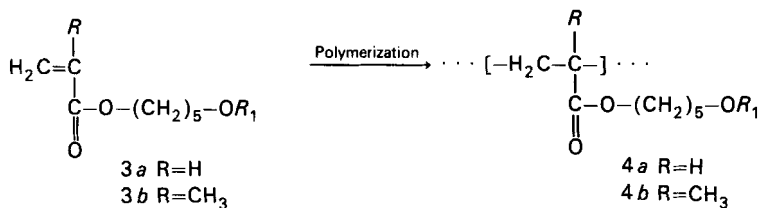
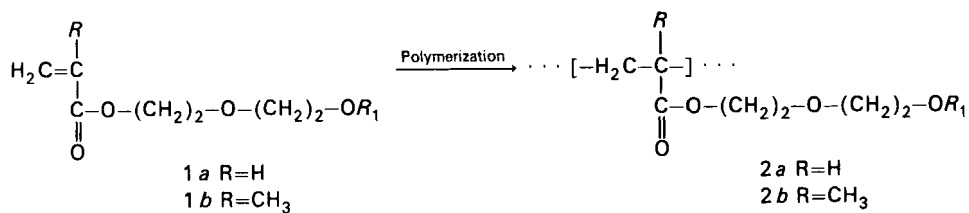
1. Introduction

One of the most important tasks in studying liquid-crystalline polymers is to examine the relations between their chemical structure and the properties of the mesophases. Extensive studies of comb-like liquid-crystalline polymers carried out in recent years have supplied a wealth of data on the influence of the structure of the mesogenic groups and the nature of the polymer main chain on the type and the properties of the mesophases [1, 2]. Thus at present a large number of chemical structures common among low molecular weight liquid crystals such as substituted biphenyls, phenyl benzoates, azobenzenes, and aromatic azomethines as mesogenic groups have been studied. Quite a variety of chemical structures have also been used as polymer main chains, for example, substituted polyacryl- and polymethacrylamides, polyacrylates, polymethacrylates, polychloro- [3] and polybromoacrylates [4], and polysiloxanes [2, 5].

The vast majority of liquid-crystalline polymers synthesized, however, contain the same polymethylene chains, $-(CH_2)_n-$ ($n = 1-14$), as groups linking mesogenic fragments with main chains (linking groups or spacer). A comparison of the data cited in [8, 9] shows that attempts to introduce benzene rings [6] or ester groups [7] into spacers has no significant effect on the temperature limits of the existence of the liquid-crystalline phases.

In this work, we have synthesized polyacrylates, polymethacrylates and polysiloxanes containing cyanobiphenyl mesogenic groups and ether fragments incorporated into the linking groups (see scheme 1). We have also studied the thermodynamic properties of the liquid crystal phases formed by these polymers and copolymers.

†KOSOVA, G. N., ROCHEV, V. YA., KOSTROMIN, S. G., and SHIBAEV, V. P., 1986, *Eur. Polym. J.*, **22**, 17 (paper XXV).

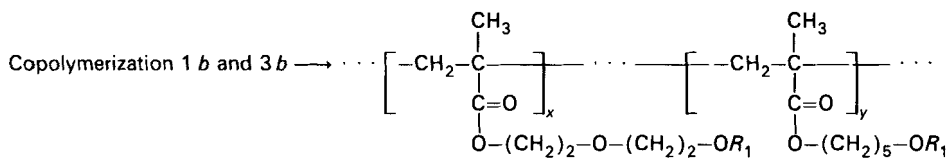


$$5a \ z = \frac{x}{x+y} \cdot 100 = 20$$

$$5b \ z = \frac{x}{x+y} \cdot 100 = 40$$

$$5c \ z = \frac{x}{x+y} \cdot 100 = 60$$

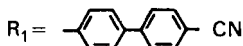
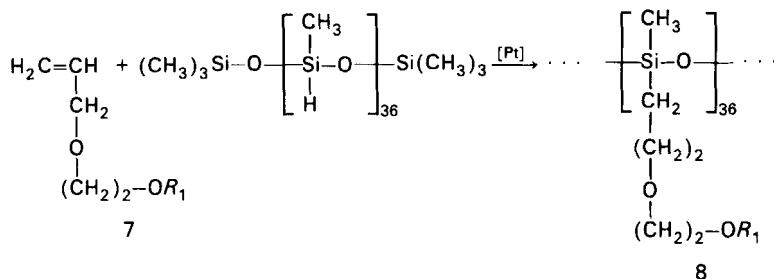
$$5d \ z = \frac{x}{x+y} \cdot 100 = 80$$



$$6a \ z = 20$$

$$6b \ z = 40$$

$$6c \ z = 60$$



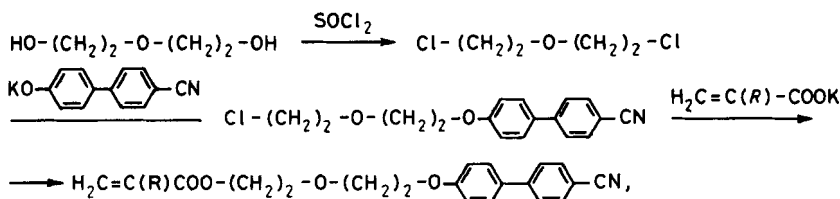
Scheme 1.

2. Experimental

The synthesis of polymers, copolymers and their structural formula notations are shown in scheme 1.

2.1. Monomers

Acrylate *1 a* and methacrylate *1 b* (see scheme 1) were prepared according to



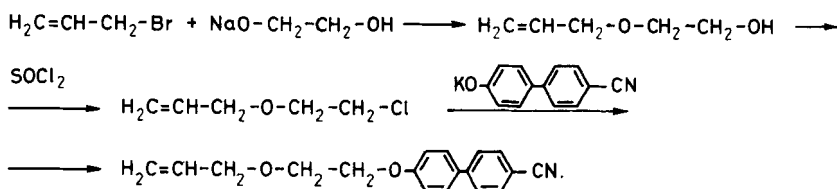
where $R = \text{H}$ (*1 a*) and $R = \text{CH}_3$ (*1 b*).

Bis- β -chloroethyl ether was made from diethylene glycol by the standard procedure, under the action of SOCl_2 . The product was sublimated under vacuum. B.p. 77–79°C/20 mm Hg. Yield 70–80 per cent.

β -[4(4-Cyano)diphenyloxy]ethyl- β' -chloroethyl ether was isolated from the reaction between bis- β -chloroethyl ether (2 mol) and the phenolate (1 mol) obtained by the action of potassium hydroxide on 4-hydroxy-4'-cyanodiphenyl. Details of the procedure were reported earlier [10]. The product was purified by chromatographing on columns with alumina (chloroform) and silica gel (benzene). A white crystalline substance with m.p. 59–61°C was obtained with a yield of 50–55 per cent.

Monomers *1 a* and *1 b* were prepared by reacting β -[4(4-cyano)-diphenyloxy]ethyl- β -chloroethyl ether with potassium acrylate or methacrylate in DMFA (115°C) [10] or HMFA at room temperature. The monomers were chromatographed on a column with silica gel (chloroform) and recrystallized from methanol, m.p. 61–62°C (*1 a*) and 63–64°C (*1 b*). Yield 50–70 per cent.

Monomer *7* was prepared following the scheme



Monoallyl ethyleneglycol ether was obtained as follows. Sodium metal (0.5 mol) was dissolved in 100 ml ethylene glycol, and allyl bromide (0.5 mol) was added drop-wise to the solution heated to 50°C. After the reaction finished (40 min), the precipitate (NaBr) was filtered off, and the liquid product was subjected to fractional distillation to isolate the fraction with b.p. 44–47°C/5 mm Hg. Yield 75 per cent.

(β -Chloro)ethyl allyl ether was prepared by the action of the corresponding alcohol on thionyl chloride in dry ether in the presence of pyridine. After the completion of the reaction the mixture was washed with water and sodium carbonate solution and dried over calcium chloride. Ether was distilled off, and the residue was subjected to fractional distillation under vacuum. B.p. 37°C/15 mm Hg. Yield 40 per cent.

The procedure for preparing monomer 7 was the same as for monomers 1 *a* and 1 *b*, except that the reagents were introduced in a 1 : 1 ratio. The product was a white crystalline solid. M.p. 69°C. Yield 40 per cent.

2.2. *Polymers and copolymers*

The synthesis of polymers has been described earlier [10]. Polymers 2 *a* and 2 *b* were prepared by a radical (AIBN) polymerization of the corresponding monomers in benzene solution. The polymerization was performed under argon at 60°C for 30 hours. The polymers were precipitated with methanol, three times reprecipitated from 1,2-dichloroethane into methanol, and dried until a constant weight was attained. Copolymers 5 *a* to 5 *d* and 6 *a* to 6 *c* were made in the same way. The composition of the copolymers was taken to be near that of the initial monomer mixture, because reacting monomers differed from each other in their chemical structure only insignificantly. The preparation of polysiloxane 8 followed the known procedure [11] according to which monomer 7 taken in excess (25 mol per cent) reacted with polyhydridimethylsiloxane in toluene in the presence of catalytic quantities of H_2PtCl_6 . The product was precipitated by methanol, several times reprecipitated from 1,2-dichloroethane into methanol, and dried under vacuum.

Polymers were studied using a MIN-8 polarization optical microscope equipped with a heating stage and a DSM-2 differential scanning microcalorimeter.

3. Results and discussion

Consider the properties of homopolymers 4 *a* and 4 *b* whose structural characteristics (mesogenic groups, main chain, the length of linking groups) are similar to those of polymers 2 *a* and 2 *b* with aliphatic spacers synthesized earlier. A comparison of these polymers gives the possibility to discount changes in the mesomorphic properties of the substances caused by changing the chemical structure of the spacers. The introduction of oxygen decreases substantially the ability of the polymers to form mesophases. Both polyacrylate 2 *a* and polymethacrylate 2 *b* do not give mesophases (cf. the table). To reveal the reasons for that, we have synthesized two series of copolymers, 5 *a* and 5 *d* and 6 *a* to 6 *c*, with successively increasing portions of units with oxygen-containing spacers.

It follows from the data presented in the table that the introduction of as little as 20 per cent of units containing oxygen into polymethacrylate 2 *b* to produce copolymer 6 *a* decreases substantially the degree of smectic ordering: the mesophase heat of melting is lowered by a factor of about 1.5. With higher portions, *z*, of oxygen units, the mesophase is still formed but T_{cl} is already only slightly higher than T_g . A further increase in *z* results in the formation of an amorphous polymer, i.e. it is likely to decrease T_{cl} below T_g (cf figure 1).

For polyacrylates 5, containing more flexible main chains and characterized by lower T_g s, the composition range where liquid crystal phases exist is broadened considerably from that found for polymers 6 (cf. figure 2). Copolymers containing up to 80 per cent oxygen units still exhibit mesomorphic properties. Decreasing *z* results in the appearance of two liquid crystal phases as well as a decrease in T_{cl} (cf. figure 2). The transition between these phases is accompanied by an enthalpy of transition of about 1.7–2.1 J g⁻¹. Melting of the high temperature mesophase is characterized by a very low enthalpy change of less than 0.2 J g⁻¹.

An X-ray study of the copolymers [12] enabled us to characterize both phases. The low temperature phase is similar to the smectic phase A of homopolymer 4 *a* [13], and the high temperature phase is a cybotactic nematic phase.

Glass temperature, phase transition points and heats of phase transitions for the polymers studied.

Polymer	Composition of copolymer, z (per cent)	$T_g/^\circ\text{C}$	Types of mesophases and phase transitions†	$\Delta H_1/\text{J g}^{-1}$	$\Delta H_{cl}/\text{J g}^{-1}$
2a	—	37	No mesophase	—	—
2b	—	65	No mesophase	—	—
4a	—	40	S _A 128 I	—	2.1
4b	—	60	S _A 129 I	—	6.3
5a	20	38	S _A 85 N 112 I	1.9	0.2
5b	40	38	S _A 76 N 102 I	0.9	0.2
5c	60	37	S _A 73 N 81 I	0.4	0.2
5d	80	37	S _A 71 I	—	0.5
6a	20	62	S _A 128 I	—	2.1
6b	40	62	S _A 87 I	—	2.1
6c	60	60	I	—	—
8	—	17‡	S _A 102 I	—	4.2

N, S_A, and I denote the nematic, smectic A, and isotropic phases, respectively; ΔH_1 is the enthalpy change at the S_A to N phase transition.

† Transition temperatures are given in $^\circ\text{C}$.

‡ Melting point of the crystalline phase.

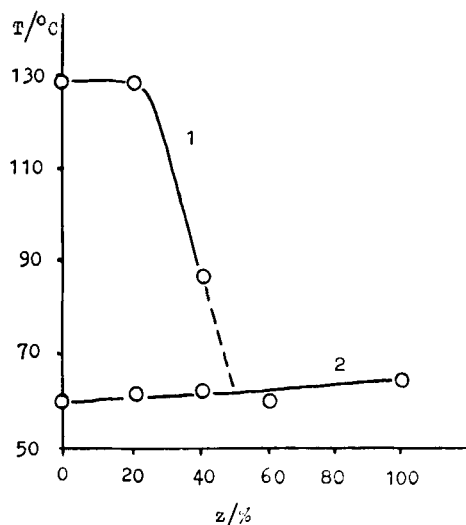


Figure 1. Clearing T_{cl} (1) and glass T_g (2) transition temperatures as a function of the copoly-methacrylates composition, z .

As with copoly-methacrylates, increasing z in the copolyacrylates results in a gradual decrease in the thermal stability of the mesophase and brings T_{cl} closer to T_g , which in this case also, makes the formation of a mesophase impossible. On going to polysiloxane polymer 8, these limitations are removed, and it forms a liquid crystal phase (cf. the table).

The combined data of this work permits us to conclude that the introduction of oxygen into the spacers makes it possible to reduce the upper temperature limit of the existence of mesophases substantially and sometimes, to obtain a smectic phase in addition to a nematic one even if the former is not characteristic for the corresponding

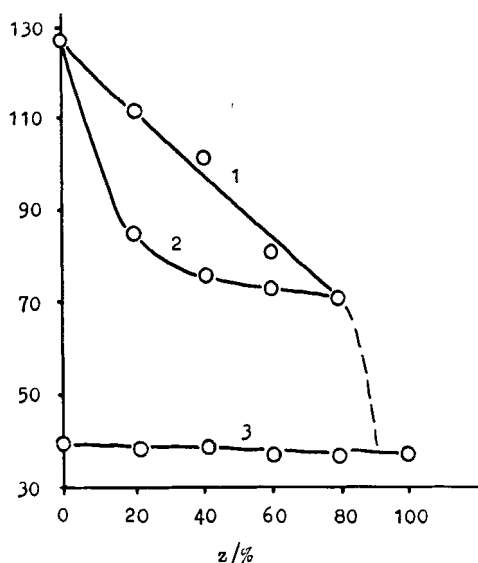


Figure 2. Clearing T_{cl} (1), S_A to N transition $T_{S_A N}$ (2) and glass T_g (3) points as a function of the copolyacrylates composition, z .

homopolymers with aliphatic spacers. Varying the nature of the spacers can therefore be regarded as an important means of controlling the structure and the properties of liquid-crystalline polymers.

We are grateful to B. Krüke (Martin Luther University, Halle, D.D.R.) for kindly providing the polyhydridimethylsiloxane.

References

- [1] SHIBAEV, V. P., and PLATE, N. A., 1984, *Adv. polym. Sci.*, **60/61**, 173.
- [2] FINKELMANN, H., 1984, *Adv. polym. Sci.*, **60/61**, 99.
- [3] ZENTEL, R., and RINGSDORF, H., 1984, *Makromol. Chem. rap. Commun.*, **5**, 393.
- [4] TSUKRUK, V. V., SHILOV, V. V., BLIZNYUK, V. N., LIPATOV, YU. S., KONSTANTINOV, I. I., and AMERIK, YU. B., 1982, *The 1st All-Union Conference on Liquid Crystal Polymers. Abstracts of Papers* (Chernogolovka), p. 19.
- [5] GEMMEL, P. A., GRAY, G. W., and LACEY, D., 1983, *Polymer Preprints*, **24**, 253.
- [6] FINKELMANN, H., RINGSDORF, H., SIOL, W., and WENDORFF, J.-H., 1978, *Makromol. Chem.*, **179**, 829.
- [7] CSER, F., NYITRAI, K., and HARDY, G., 1980, *Advances in Liquid Crystal Research and Applications*, Vol. 2, edited by L. Bata (Pergamon Press, Akademiai Kiado), p. 845.
- [8] FREIDZON, YA. S., SHIBAEV, V. P., KHARITONOV, A. V., and PLATE, N. A., 1980, *Advances in Liquid Crystal Research and Applications*, Vol. 2, edited by L. Bata (Pergamon Press, Akademiai Kiado), p. 899.
- [9] FREIDZON, YA. S., KHARITONOV, A. V., SHIBAEV, V. P., and PLATE, N. A., 1985, *Eur. Polym. J.*, **21**, 211.
- [10] SHIBAEV, V. P., KOSTROMIN, S. G., and PLATE, N. A., 1982, *Eur. Polym. J.*, **18**, 651.
- [11] FINKELMANN, H., and RECHAGE, G., 1980, *Makromol. Chem. rap. Commun.*, **1**, 311.
- [12] LIPATOV, YU. S., TSUKRUK, V. V., SHILOV, V. V., KOSTROMIN, S. G., and SHIBAEV, V. P., *Vysokomolek. Soedin.* (in the press).
- [13] TSUKRUK, V. V., SHILOV, V. V., LIPATOV, YU. S., KOSTROMIN, V. P., and SHIBAEV, V. P., *Liq. Crystals* (in the press).