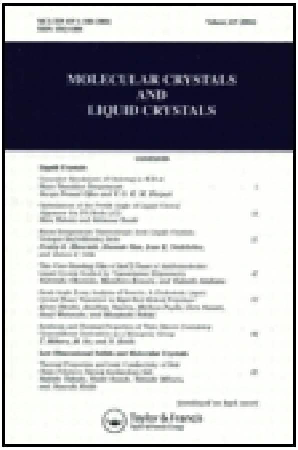

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New Thermotropic Polymers with Flexible Backbone and Mesogenic Side-Chains: Synthesis and Characterization

P. Robert [a], J-J. Villenave [a], M. Fontanille [a], J-M. Gilli [b] & P. Sixou [b]

[a] L.C.P.O. (U.A. C.N.R.S. et E.N.S.C.P.B.) Institut du Pin - 351, cours de la Libération-33405, Talence, cedex, France

[b] L.P.h.C. (U.A. 190 C.N.R.S.) - Parc Valrose, 06043, Nice, cedex, France

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NEW THERMOTROPIC POLYMERS WITH FLEXIBLE BACKBONE AND MESOGENIC SIDE-CHAINS : SYNTHESIS AND CHARACTERIZATION

P. ROBERT, J-J. VILLENAVE, M. FONTANILLE
L.C.P.O. (U.A. C.N.R.S. et E.N.S.C.P.B.)
Institut du Pin -
351, cours de la Libération-33405 TALENCE-cedex-France

J-M. GILLI, P. SIXOU
L.P.M.C. (U.A. 190 C.N.R.S.) - Parc Valrose -
06043 NICE-cedex-France

Abstract A new method to synthesize comb-like polymeric liquid crystals with flexible main chains through the chemical modification of a low molecular weight polybutadiene is described. Polarized light optical microscopy and differential scanning calorimetry allow the mesophases to be identified as S_A and their existence temperature range to be determined.

INTRODUCTION

Among the various approaches to synthesizing liquid crystalline side-chains polymers [1,2], those based on the chemical modification of macromolecules by functional mesogenic groups prove most suitable. A major advantage is the possibility of obtaining odd mesogenic materials [3] by merely working up average polymers. However, a drawback is the difficulty in reaching quantitative modification yields, on account of the reactivity lowering of each functional group by its vicinal homologues [4].

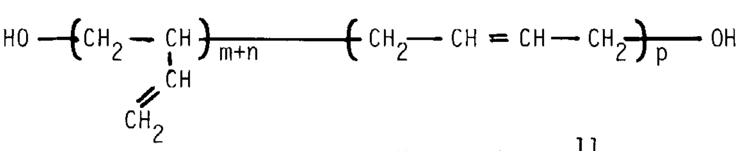
This disadvantage is likely to account for the weak number of basic polymers that have been used until now; the polyacrylates [5], polymethacrylates [6] and polysiloxanes [7-10] are most outstanding.

As we aimed at getting new families of comb-like mesogenic grafted polymers, we assumed that such backbones as issuing from the polymerization of conjugated dienes should be able to afford modified products displaying unusual properties. Then, a study of the modification of polybutadiene samples by mesogenic groups was undertaken; the reactive functions of the polymeric units were thus vinylic ones.

This paper deals with the method of synthesis developed as well as with the physicochemical characterizations of the liquid crystal polymers obtained.

SYNTHESIS OF MESOGENIC SIDE-CHAINS GRAFTED POLYBUTADIENES

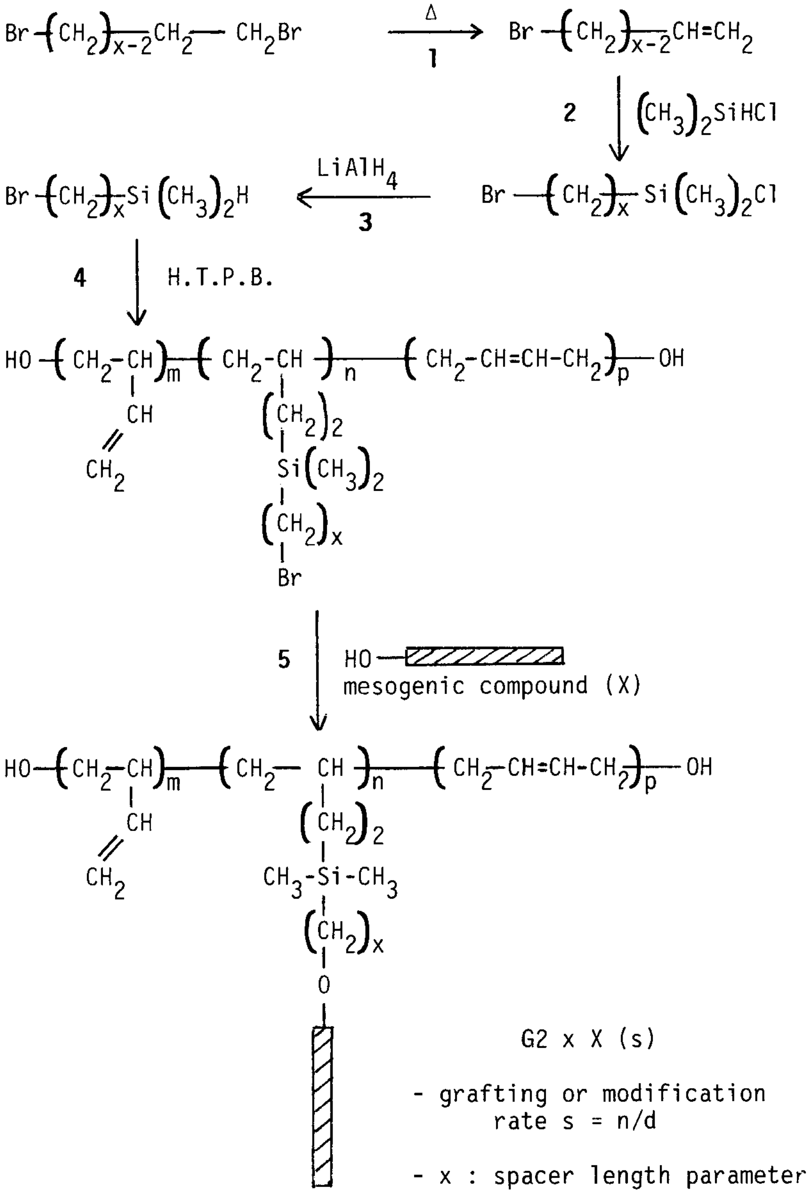
As raw material, we used an α , ω -hydroxy-polybutadiene (HTPB)[11] obtained from an anionic polymerization process; as such, it contains mainly 1,2 units. The characteristics of the basic polymer are reported hereunder



$$HO-\left(CH_2-\underset{\underset{CH_2}{\overset{\|}{CH}}}{CH}\right)_{m+n}-\left(CH_2-CH=CH-CH_2\right)_p-OH$$

HTPB : G 2000[11]

- average degree of polymerization $\overline{DP}_n = d = m+n+p \simeq 40$
- average molecular weight $\overline{M}_n \simeq 2000^n$
- 1,2 units rate $(m+n)/d \simeq 90\%^n$
- random distribution of 1,2 units (m+n) and 1,4 units (p) in the oligomer.



G2 x X (s)

- grafting or modification rate s = n/d

- x : spacer length parameter

FIGURE 1 . General reaction scheme

In the present study the terminal hydroxy groups of HTPB were not taken into account. However, they are of obvious interest since they allow the preparation of polyurethane-type elastomeric materials to be achieved through the reaction with multi-isocyanates.

The synthetic route is required to fulfil some conditions.

- Every stage must be complete in order to control the 'grafting rate' (s= n/d) more easily.
- The method must allow adjustable length spacers to be inserted between the mesogenic groups and the polymeric backbone.

To this end, we opted to grafting ω-bromoalkyl links on the vinylic double bonds of HTPB by means of hydrosilation reactions, and then to substituting ω-hydroxy mesogenic groups for the terminal bromine atoms. The general reaction scheme is described in figure 1.

Stage 1. Synthesis of ω-bromo-1-alkenes

The title compounds were prepared from commercially available α,ω -dibromides, reacting with hexamethylphosphoric triamide [12]. Fairly good yields were obtained with x from 4 to 7 starting dihalides. It should be noted that spacer length parameters (x) from 4 to 7 give spacer 'lengths' from 7 to 10 provided the silicon atom and the carbon atoms of the vinylic linkage are included.

Stages 2 and 3 . Hydrosilation of the ω-bromo-1-alkenes

Hydrosilation of the bromo vinylic compounds was performed with dimethylchlorosilane as reagent according to the catalytic ($H_2PtCl_6,6H_2O$) procedure generally described [13].

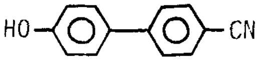
It should be observed that stage **3** of the synthetic pathway -i.e. the substitution of hydrogen atoms for bromine ones by reacting with $LiAlH_4$- aims to regenerate a hydrosilation reagent that can react with the vinylic double bonds of HTPB.

Stage **4**. Hydrosilation of HTPB

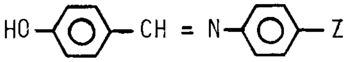
This stage is of major importance since the grafting rates (s = n/d) are actually settled by the trialkylsilane to HTPB ratio.

Stage **5**. Mesomorphic Group Grafting

Among the mesomorphous low molecular weight compounds used, the most interesting ones are likely to be :

-4-hydroxy-4'-cyano-biphenyl  : A

and

-Schiff's bases 

D (Z = cyano group) and E (Z = acetyl group),

prepared by reacting p-hydroxybenzaldehyde with the related substituted primary amines[14].

Substituting the mesogenic groups for the bromine atoms of the hydrosilated HTPB (while eliminating HBr) was carried out by means of solid - liquid phase transfer catalysis (K_2CO_3- butanone or toluene - catalytic amounts of tetrabutylammonium bromide).

The synthetic pathway thus obtained eventually yielded such products as those described in figure 1. We decided to identify them as G2x X (s), G2 standing for G2000 HTPB, x for the spacer length parameter, X for the mesogenic group (A,D or E) and (s) for the grafting rate. It should be noted that the preparation of G2x X (s) liquid crystal polymers is dealt with in a patent taken out by Rhône-Poulenc S.A. [15].

CHARACTERIZATION OF THE LIQUID-CRYSTAL POLYBUTADIENES

Analytical Techniques[16]

The phases behaviour of the synthesized products has been studied using Differential Scanning Calorimetry (D.S.C.). In most cases , the D.S.C. charts include a glass transition (at Tg) related to the polymeric backbone, and a clearance first-order transition from the mesophase to the isotropic liquid (at Tc) related to the grafted mesogens.

The samples have been scanned using a polarized light microscope provided with a heating stage. Fan-shaped textures with focal conics, which characterize smectic phases, were most often observed. However, it sometimes needed long-time annealings to obtain the characteristic textures or even to just observe birefringent shapes.

Results and Discussion

The results to be discussed are given in table 1.

Influence of the side-chains mesogenic substituents

The characteristic temperatures depend a little on the mesogens. Thus, using cyanobiphenyl (A) moieties allowed smectic A (SA) typical textures to be obtained, providing the grafting rates (s) are high enough, while using Schiff's bases (D or E, x being equal to 4) just resulted in scattering textures, even at high grafting rates. With the latter, very long-time annealings (up to several days) were needed to observe smectic needles.

TABLE 1 : Phases Behaviour Characteristic Temperatures (°C) of G2x X (s) Polymers.

		DSC[a]		Microscopy : birefringence range	
	s	Tg	Tc	Temp. ↗ [b]	Temp. ↘ [b]
G24A	0.18	-5	-	-	-
	0.44	0	-	-	-
	0.50	16	38.5	30-35	-
	0.75	15	75	80-84	75-72
	0.90	13	86	88-97	92-85
G25A	0.45	-3	42	-	-
	0.90	13.5	109	102-116	112-100
G26A	0.45	-4	32	-	-
	0.90	8.5	98	96-108	104-93
G27A	0.85	7	115	119-124	122-116
G24D	0.70	14	-	39-50	-
	0.85	-	-	57-66	-
G26D	0.80	12	102	101-111	98-92
G24E	0.85	20	-	85-110	100-90

temp.program. : [a]10°C/min., [b] 0.34°/min.

As expected, Tg, which is mainly related to the polymeric backbone, does not depend much on the grafted mesogen.

Influence of the Spacer Length

At a given grafting rate (s = 0.90) , G2xA samples are suited to study the influence of the spacer length parameter (x) on the transition temperatures.

The low decrease of Tg when x increases would be accounted for by a rise in the plasticizing power of the spacer[17].

With regard to Tc, as x increases from 4 to 5, 6 and 7, it starts increasing, then slightly decreases , and eventually increases again. This is in agreement with the 'even-odd effect" already observed with other mesogenic side-chain polymers[12].

The fan-shaped textures, with focal conics, that are observed whatever the spacer length parameter is, characterize a SA mesophase. However, it should be pointed out that, at the low x values, when the temperature range including Tc is high enough to induce a low viscosity of the polymer , broad fan-shaped textures appear nearly at once on slowly cooling the isotropic liquid.

Influence of the Grafting Rate (s)

At any grafting rate, G24A mesophases are SA ones but on the other hand, the temperature range in which the mesomorphism exists as well as the annealing necessary to obtain birefringent textures are closely related to the s values. At high s values (upper than 0.75), birefringence is observed quite at once while slowly cooling the liquid ; the stability range of the liquid crystalline phases is rather broad (more than 60 degrees). On the contrary, for s equal to 0.50, a several-day annealing merely allows scattering textures to be observed ; the mesomorphism temperature range is then much narrower (about 20 degrees). As the temperature range including Tc (38.5°C) is low, the polymer viscosity is high and the ordering of the mesogenic groups is likely to be hindered. It should be noted that no birefringence can be obtained for s lower than 0.50.

As regards Tg, it slightly decreases as s rises, which is consistent with the increasing mobility of the backbone.

CONCLUSION

The chemical modification of polybutadiene samples offers an enhanced versatility in studying the influence of much structural parameters on the phases behaviour of comb-like polymeric liquid crystal.

Furthermore, such important features as the possibility of cooling and freezing the mesophases down to temperatures lower than Tg, are likely to promise as wide application fields as those already described for the mesogenic side-chain polymers.

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