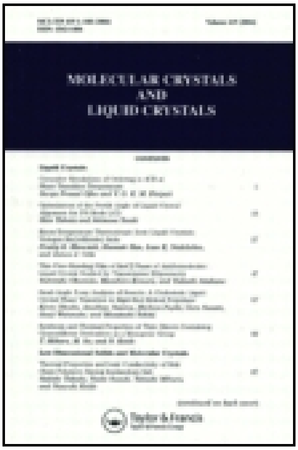


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Liquid Crystalline Side Chain Polymers Derived From Poly-acrylate, Poly-methyacrylate and Poly-α-chloroacrylate

Jean-Claude Dubois [a], Guy Decobert [a], Pierre Le Barny [a], Sophie Esselin [b], Claude Friedrich [b] & Claudine Noël [b]

[a] Thomson-CSF, L.C.R., Domaine de Corbeville, Orsay a, FRANCE

[b] ESPCI, Laboratoire de Physicochimie Structurale et Macromoléculaire, Paris, FRANCE

Version of record first published: 13 Dec 2006.

Mol. Cryst. Liq. Cryst., 1986, Vol. 137, pp. 349-364
0026-8941/86/1374-0349$20.00/0

LIQUID CRYSTALLINE SIDE CHAIN POLYMERS DERIVED FROM POLY-ACRYLATE, POLY-METHYACRYLATE AND POLY-α-CHLOROACRYLATE

Jean-Claude Dubois, Guy Decobert, Pierre Le Barny
Thomson-CSF, L.C.R., Domaine de Corbeville, Orsay, FRANCE

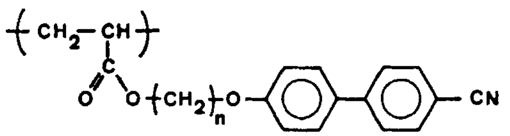
Sophie Esselin, Claude Friedrich, Claudine Noël
ESPCI, Laboratoire de Physicochimie Structurale et Macromoléculaire, Paris, FRANCE

INTRODUCTION

Interest in liquid crystalline side-chain polymers has grown tremendously in recent years because of their theoretical aspects and their potential applications.Over the past few years, a considerable research effort has been made in electro-optic display using nematic [1] [2] or smectic A [3] mesogenic side-chain polymers. On the other hand, non linear optical effects have been obtained with a nematic side-chain copolymer doped with a molecule exhibiting an extremely large molecular hyperpolarizability β [4] and poled with a D.C. electric field.

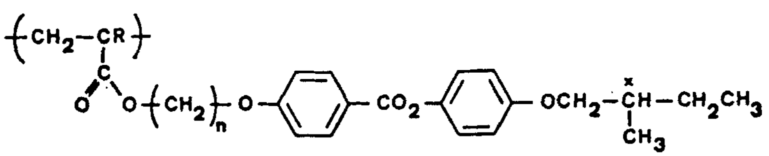
Difficulty in obtaining good orientation and mechanical hysteresis related to the semisolid character of the phase have delayed the use of smectic liquid crystals. However, interest in the synthesis of chiral materials exhibiting tilted smectic phases has increased considerably since the advent of a fast switching, bistable, electro-optical device based on their ferroelectric properties.

As part of a continuing effort to produce new materials suitable for applications, we have synthesized and studied two families of side-chain polymers, with the following general formulae:



(I)

where n= 2-6



(II)

where n=2, 6, 11

and R= H, CH_3, Cl

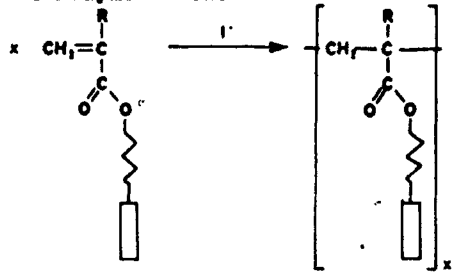
From the liquid crystal properties of low molar mass compounds, we expect nematic mesophases for polymers (1) and Ch, S_A and / or chiral tilted smectic phases for polymers (2).

SYNTHESIS

Liquid crystalline side-chain polymers are generally prepared by free radical polymerization of monomers having an activated double bond (acrylates, methacrylates or α-chloroacrylates) and bearing a mesogenic unit attached to the polymer backbone by flexible spacer groups.

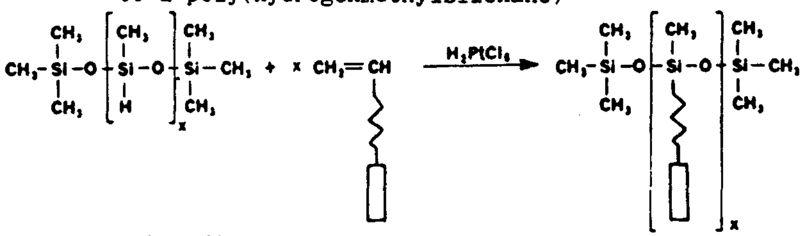
Another possible way is to modify reactive polymers such as poly(hydrogenmethylsiloxane) [5] [6], sodium polyacrylates [7] or sodium polyitaconates [8] by using suitable reactive mesogenic compounds (Figure 1).

Free Radical Polymerization

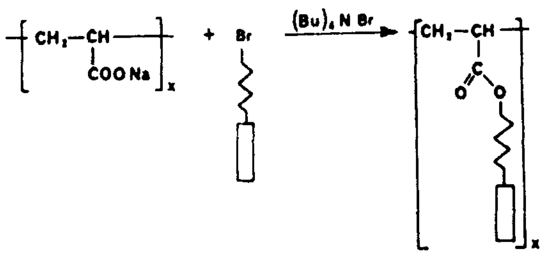


Chemical modification of a reactive polymer

- addition of vinyl substituted mesogenic molecule to a poly(hydrogenmethylsiloxane)



- esterification via Phase-Transfer catalysis



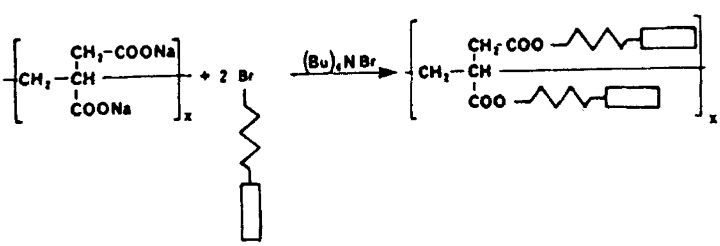


Figure 1. Synthesis of side-chain liquid crystalline polymers.

Polymer		Polymerization conditions				G P C	
Ref.	n	Solvent	$\frac{[\text{Monomer}]}{2\,[\text{AIBN}]}$	Reaction time (h)	Conversion %	$\overline{Mw}$	$\frac{\overline{Mw}}{\overline{Mn}}$
PO-2	2	C_6H_6	200	18	68	80 000	2,42
PO-3	3	THF	30	21	88	4 500	1.5
PO-4	4	THF	30	21	90	8 100	2
PO-5	5	C_6H_6	30.5	15	62	55 000	3.43
PO-6	6	C_6H_5Cl	152	15	62	62 000	3.38

TABLE I

Polymerization conditions
and average molecular weights of polymers (I)

Polymers (1) and (2) were prepared by free radical polymerization in solution with the use of azo-bis-isobutyronitrile as initiator. Purification was accomplished by two re-precipitations into methanol after which the polymers were dried in vacuo. Molecular heterogeneities and weight average molecular weights were determined by GPC using universal calibration (Table 1).

Synthesis of the corresponding monomers is described elsewhere [(9) (10) (11)]

RESULTS AND DISCUSSION

Transition temperatures in polymers were determined by means of a differential thermal analyser, Du Pont 1090.

The structure of the mesophases was identified both by optical microscopy (using a polarizing microscope Olympus BHA-P equipped with a Mettler FP5 hot stage) and X-ray investigations. X-ray diffraction patterns were recorded on flat films using Ni-filtered CuK_{α} radiation. Well-oriented samples were produced by drawing fibers out of the mesophase with a pair of tweezers.

POLYMERS (1) (TABLE 2)

Polymers of this family are essentially non crystalline in character. We may observe that Tg decreases as the length of the spacer increases because the mesogenic group is moved away from the skeleton and because of the effect of internal plasticizing.

There is no real evidence for liquid crystal properties in polymer PO-2. Rather, this polymer resembles typical semi-crystalline polymers. The D.S.C. trace is characterized by a marked glass transition at 84°C and a small endotherm at 113.5°C.

POLYMER	Tg		T		T		Tc	ΔH_c cal.g^{-1}
PO-2	84						113.5	0.36
PO-3	54				60[(b)]	S_{Ad}	82	0.11
PO-4	42			N			110	0.29
PO-5	35		75.3[(b)]	S_{Ad}	120	N	124.4	0.43[(a)]
PO-6	32	N_{re}	80	S_{Ad}	124.5	N	132	0.61[(a)]

TRANSITION TEMPERATURE (°C)

TABLE 2
Thermal Properties of Polymers (1)

(a) These values were determined from the unresolved peaks which correspond to the S_A/N and N/I transitions.Thus, the values of ΔH_c are lower than those tabulated.

(b) This transition does not appear by D.S.C. measurements on cooling.

Below this temperature no fluidity can be detected and no typical texture can be obtained. Above 113.5°C the polymer gives a clear isotropic fluid phase. By pressing over the cover slip, however, birefringence appears. This effect is observable up to 140°C and may be due to polymer alignment under stress. The X-ray diffraction patterns obtained with unoriented samples exhibit at large diffraction angles a diffuse broad ring which is related to the lateral interferences between the mesogenic cores and points out the lack of lateral periodic order. It corresponds to an average intermolecular spacing of approximately 4.4 Å. A second diffuse ring is seen at small angles. It corresponds to a distance of about 23 Å which is in excess of the length L of the side-chain in the fully extended conformation (L≃16.5 Å) but shorter than 2L. The X-ray diffraction patterns obtained with stretching oriented fibers do not exhibit Bragg reflexions and are similar to those obtained with nematic polymers. Note that the side-chains are parallel to the stretching direction.

Polymers PO-3 and PO-4 exhibit S_{Ad} phase and N phase, respectively.

By cooling down polymer PO-5 from the isotropic state, threaded and schlieren textures with disclinations of strength ± 1/2 appear first. Then, at about 120°C, a fan-shaped texture with focal conics is observed. X-ray diffraction patterns of a powder sample is consistent with a nematic mesophase at high temperature and a S_{Ad} mesophase at lower temperature. These results are not in agreement with those reported by SHIBAEV et al.[12]. Indeed, these authors have described polymer PO-5 as nematic from 40°C to 120°C.

A reentrant polymorphism N, S_A, N_{re} is observed with polymer PO-6 [9].

As observed with certain low molar mass cyano derivatives having S_{Ad} phases [13-15] polymers PO-3, PO-5 and PO-6 in the smectic A state exhibit a bilayer structure in which the side-

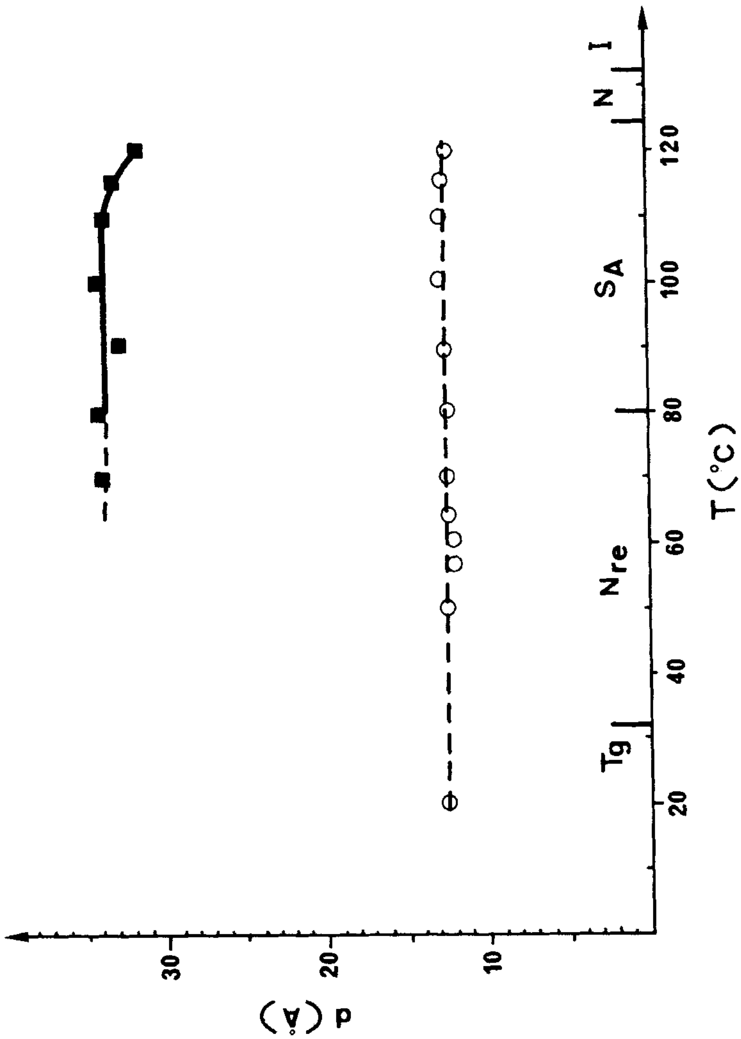


Figure 2. Thermal evolution of the modulation wave vectors in polymer PO-6 (----- diffuse rings).

POLYMER X	n	TRANSITION TEMPERATURE (°C) and MESOMORPHISM	ΔH_c $cal.g^{-1}$
H	2	$T_\beta(-5)$ Tg(65) S_C^* (110) S_A (146) I	1.08
H	6	$T_\beta(-18)$ Tg(15) Tm (46) S_A (87) I	2.09
H	11	$T_\beta(-15)$ Tg(32) Tm (59) S_A (108) I	2.99
CH_3	2	Tg(110)[a] S_A (155) I	2.03
CH_3	6	Tg(40) S_A (90) I	2.56
CH_3	11	Tg(~20)[a]Tm(58) S_C^*(90) S_A(106)I	3.09
Cl	2	Tg(97)[a]Tm(172) I	2.68
Cl	6	Tg(37) Tm(94) I	2.46
Cl	11	$T_\beta(-32)$ Tg(20)[a]Tm(62)S^*(86)[b](112)I	3.20

TABLE 3

Thermal Properties of Polymers (2)

a : Very small increase in heat capacity

b : Very small endotherm. No transition was detected by optical microscopy and X-ray diffraction.

chains are partially overlapped. In addition, X-ray investigations show a diffuse ring which is related to local monolayer fluctuations (Figure 2).

Partially bilayer and monolayer fluctuations are also present simultaneously in the nematic phase of polymer PO-4 and in the reentrant nematic phase of PO-6. When temperature decreases, only monolayer fluctuations remain.

POLYMERS (2) (TABLE 3)

Some of polymers (2) are essentially crystalline in character and their glass transition temperature cannot be determined with accuracy from the D.S.C. traces: only a very small and diffuse increase in heat capacity occurs. In contrast, dielectric measurements provide a simple and direct method of following the α-relaxation process (Table 4). All three series give the same type of glass transition vs. flexible spacer plot (Fig. 3). As for conventional polyacrylate and polymethacrylate series, lengthening the aliphatic spacer decreases the glass transition temperature. This behaviour arises from the plasticizing action of the spacer, cf., the similar explanation proposed to explain the decrease of Tg for poly(n-alkylacrylates) and poly(n-alkylmethacrylates). With reference again to Fig.3, the glassy to liquid mesophase transition is strongly shifted towards lower temperature as the flexibility of the polymer backbone is increased. This effect is clearly demonstrated for polymers (2) with n=2 and the following order of flexibility is obtained:

$$H > Me \simeq Cl$$

The acrylate polymer with n=2 exhibits both smectic A and C* phases. The X-ray diffraction patterns are characteristic of disordered lamellar structures: the outer ring is broad indicating a disordered arrangement of the molecules within the layers.

Polymer		Temperature of α relaxation (glass transition) at different frequencies (°C)			
n	R	1 Hz (DSC)	120 Hz	10^3 Hz	10^4 Hz
2	H	65	X	90	100
6	H	15	X	35	45
11	H	32	X	35	45
2	CH_3	110	X	145	170
6	CH_3	40	X	70	80
11	CH_3	20	X	58	75
2	Cl	97	X	X	X
6	Cl	37	X	X	X
11	Cl	20	55	60	65

X not determined

TABLE IV

Temperature of the glass transition of Polymers (2) at various frequencies

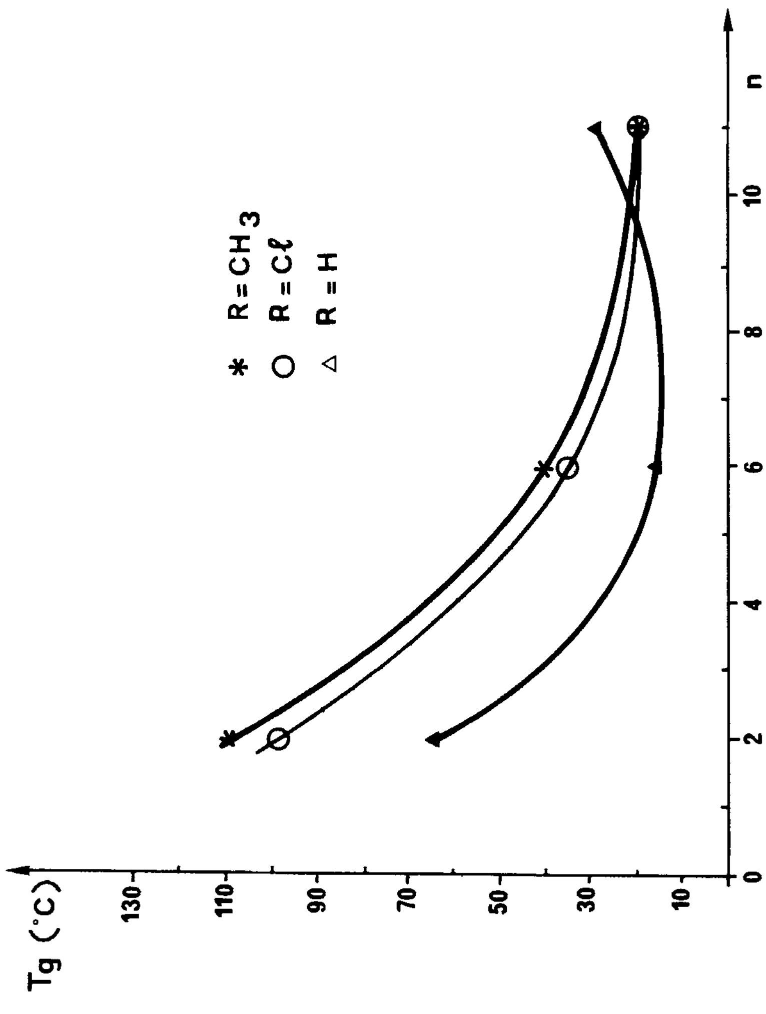


Figure 3. Tg as a function of (n) for polymer II (2,H).

Above 110°C, the layer spacings d vary only slightly (Fig.4) and correspond to a lamellar thickness of approximately 42.6 Å Thus, it is clear that, in the smectic A state, d is twice the length of the side-chain calculated from standard bond lengths and angles under the assumption of an all trans conformation of the molecule. This implies a form of bilayer structure. At about 110°C the value of d decreases with decreasing temperature but this decrease tapers off and at lower temperatures d ≃ 36-37 Å which is less than twice the side-chain length L. The diffraction patterns obtained using stretching oriented fibers indicate that the mesogenic side-chains are tilted with respect to the layer planes, as indicated in Fig. 4b.

If the number of methylene units is n=6 and n=11 **only** monolayer (d ≃ L) smectic A phases are observed.

All the polymethacrylates give smectic A phases. Again, for n=2, the polymer has a bilayer structure while for n=6 and n=11, the lamellar thickness corresponds to the length L of the side-chain in the fully extended conformation. It is worth noting that the polymer where R=CH_3 and n=11 also exhibits smectic C^*-like properties between 58°C and 90°C.

In contrast with the acrylate and methacrylate polymers of structure (2), the **α-chloropolyacrylates (X=Cl) with n=2 and 6** show no liquid crystal properties. On the other hand, the member of this series n=11 gives rise to a tilted smectic phase with a lamellar structure.

CONCLUSION

The study of liquid crystalline polyacrylates with terminally cyanobiphenyl-substituted side-chains allowed us to find a reentrant nematic phenomenon. Moreover, one of the polymers (PO-4) exhibiting only a nematic mesophase between 42° and 110°C is useful as host for SHG experiments.

(a)

(b)

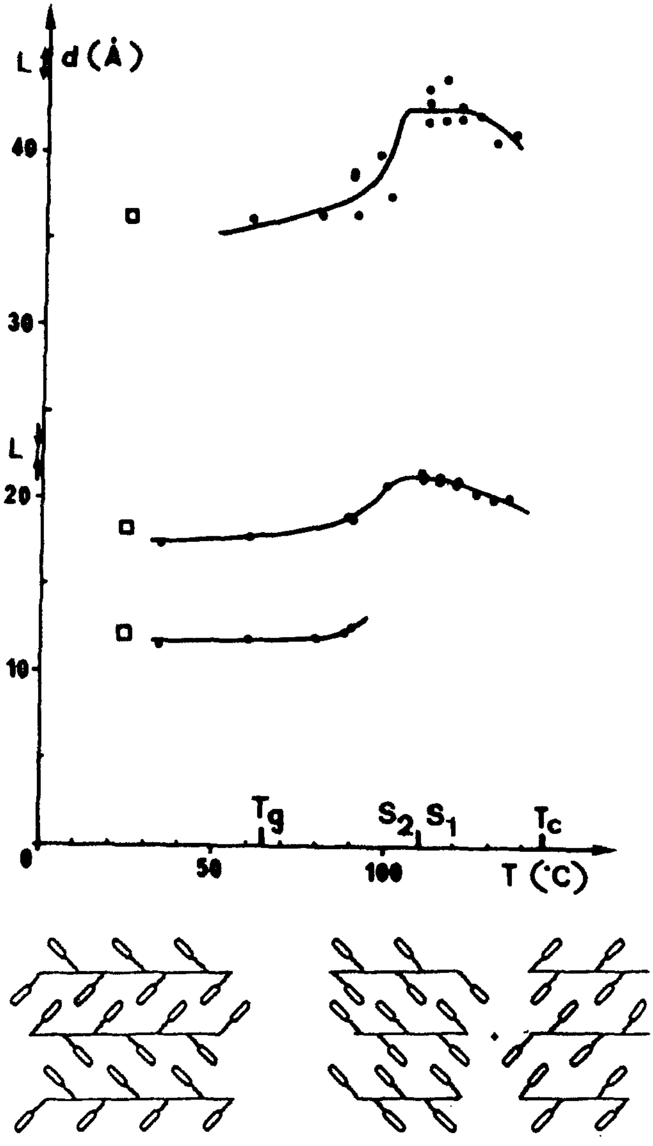


Figure 4 Polymer (2) where X=H and n=2.
a. d(Å) as a function of temperature.
b. Possible models for the smectic C*-like structure.

It is to be expected that the three side-chain polymers of structure (2) (X=H, n=2; X=CH_3, n=11 and X=Cl, n=11) which exhibit tilted smectic phases possess a spontaneous polarization and are ferroelectric. Such polymers may possibly be employed in different forms of application. However, preliminary experiments on the polymer where X=CH_3 and n=11 show that the difficulty is to obtain good orientation.

REFERENCES

1. H. Ringsdorf and R. Zentel, Makromol. Chem. 183, 1245 (1982)
2. H. Finkelmann, U. Kiechle and G. Rehage, Mol. Cryst. Liq. Cryst. 94, 343 (1983)
3. H.J. Coles and R. Simon, Polym.Sci.Technol. (Plenum), 28 (Polym.Liq.Cryst.) 351-368 (1985)
4. G.R. Meredith, J.G. Van Dusen and D.J. Williams, Macromolecules 15, 1385 (1982)
5. H. Finkelmann, G. Rehage, Makromol. Chem. Rapid Commun. 1, 131 (1980)
6. H. Finkelmann and G. Rehage, Makromol. Chem. Rapid Commun. 1, 733 (1980)
7. P. Keller,Macromolecules 17, 2937 (1984)
8. P. Keller, Macromolecules 18, 2337 (1985)
9. P. Le Barny, J.C. Dubois, C. Friedrich and C. Noël, Polymer Bulletin,in press
10. P. Le Barny, J.C. Dubois, C. Friedrich and C. Noël, to be published
11. G. Decobert, F. Soyer and J.C. Dubois, Polymer Bulletin 14, 179 (1985)
12. V.P. Shibaev, S.G. Kostromin and N.A. Plate, Eur. Polym. J. 18, 651 (1982)
13. F. Hardouin, A.M. Levelut, M.F. Achard and G. Sigaud,

J. Physique 80,53 (1983)

14. J.E. Lydon and C. Coakley, J. Physique Colloque 36, C1-45 (1975)
15. A.J. Leadbetter, J.C. Frost, J.P. Gaughan, G.W. Gray and A. Mosley, J. Physique 40, 375 (1979)
16. R.B. Meyer, L. Liebert, L. Strzelecki and P. Keller, J. Phys. Letters 36, 69 (1975)