Polymer Bulletin 28, 243–250 (1992)

Polymer Bulletin

The behaviour of styrenes *p*-substituted with a liquid crystalline side group under anionic polymerization conditions

Bernd Zaschke*, Susanne Zelder, Heinz Altmann, and Manfred Arnold

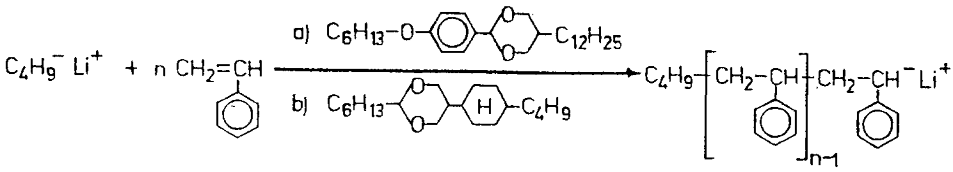
Institut für Technische Chemie, Martin-Luther-Universität Halle-Wittenberg, Schlossberg 2,
O-4020 Halle/Saale, Federal Republic of Germany

SUMMARY:

The synthesis of p-alkyloxymethylstyrenes and p-alkyloxystyrenes with 4,4'-disubstituted-biphenyl or 2,5-disubstituted-1,3-dioxane groups as side chains are described. The phase behaviour of both the monomers and polymers obtained by free radical polymerizations is investigated.
The monomers are not suitable for "living" anionic polymerizations because of the side reactions which occur as competitive reactions to the normal chain growth. The benzylic ether group of the alkyloxymethylstyrene was splited under the influence of the anionic centres. A metalation of the phenyl ring of the styryl group was observed for alkyloxystyrenes.

INTRODUCTION

Liquid crystalline side chain polymers based on acrylates, methacrylates and polysiloxanes (1-4) have attracted much attention, but only a few publications appeared about the synthesis and the properties of LC side chain polymers with stiff polystyrene backbone. RINGSDORF et al. (5) but also ATTARD and KARASZ (6) described the synthesis of such LC-polystyrenes using polymer analogous reactions. In this paper the synthesis of such macromolecules by free radical polymerization of styrene monomers containing biphenyl or 2,5-disubstituted-1,3-dioxane side groups is described.
In preliminary tests it could be detected that "living" anionic polymerization reaction of styrene (solvent: benzene/THF, initiator: n- butyllithium) is not hindered by presence of low molecular weight liquid crystals (Scheme 1).



Scheme 1: Anionic polymerization of styrene in presence of low-molar-mass mesogens

It can be concluded from Scheme 1 that our styrene-monomers substituted in p-position with the same structure units can be

---

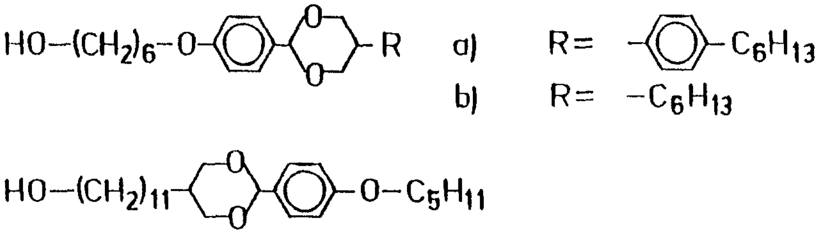
*Corresponding author

polymerized by "living" anionic polymerization. This allows the synthesis of liquid crystalline side chain block copolymers consisting of an amorphous A-block and a liquid crystalline B-block. So far such LC-block copolymers were prepared by adding of mesogene groups to one block component of an AB-blockcopolymer by polymer analogous reactions (7-10) or by "living" group transfer polymerization reaction of a LC-monomer (11).

SYNTHESIS OF MONOMERS

The alkyloxymethylstyrenes 4 (Scheme 3) were synthesized by etherification of the terminal OH-groups of the compounds (see Scheme 2) with p-chloromethyl-styrene [CMS]. Because of the aliphatic nature of the OH-groups satisfactory yields of products could be received only if the alcoholate was synthesized by using potassium hydride and if the reaction with CMS was carried out in the presence of a crown ether and catalytic quantity of potassium chloride. The alkyloxystyrene 7 was prepared in a three-step-reaction (ef. Scheme 4).

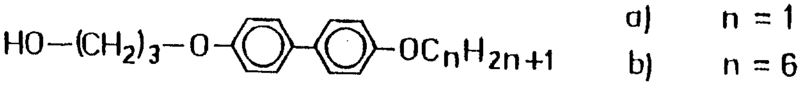
Scheme 2: 2,5-disubstituted-1,3-dioxane (1,4,12,13)



1

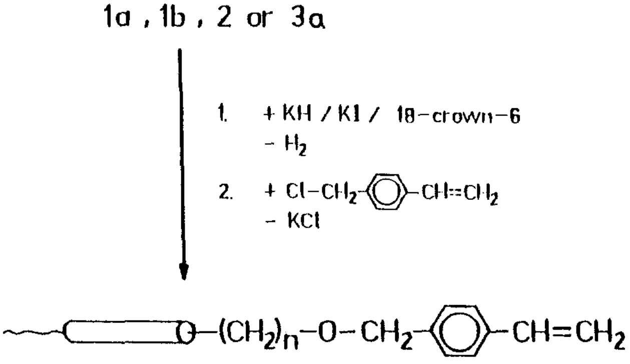
2

4,4'-disubstituted biphenyl (2,3)



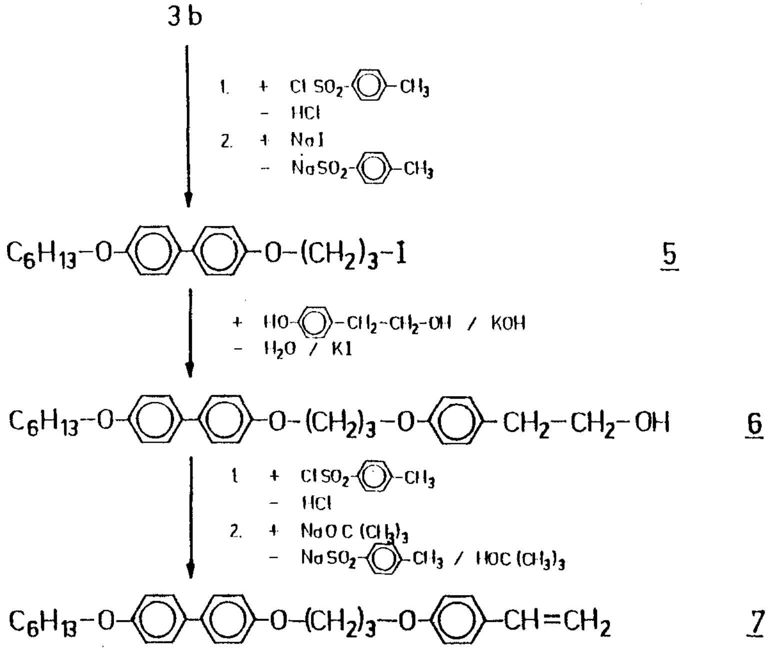
3

Scheme 3: Synthesis of alkyloxymethylstyrenes



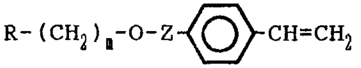
4 a-d

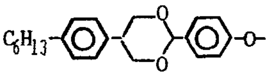
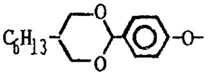
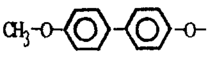
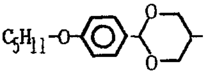
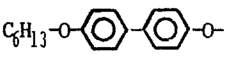
Scheme 4: Synthesis of alkyloxystyrenes



THERMAL PHASE BEHAVIOUR OF MONOMERS AND POLYMERS

Table 1: Phase behaviour of monomers and polymers


$R-(CH_2)_m-O-Z-C_6H_4-CH=CH_2$

Nr	R	m	Z	monomer phase behaviour [°C]	polymer phase behaviour [°C]	M_w [g/mol
4a		6	$-CH_2-$	k 50 s_B 81 i	g 45 M 123 i	72800
4b		6	$-CH_2-$	k 16 i	g 38 M 91 i	44300
4c		3	$-CH_2-$	k 110 i	k 114 i	23200
4d		11	$-CH_2-$	k 67 i	k 82 s 103 i	27000
7		3	-	k 129 i	k 165 i	11100

M = not further determined liquid crystalline phase

In Tab.1 the results of the thermal investigations of monomers and polymers by optical polarizing microscopy, DSC and by X-ray measurements are summarized.

Comparing the phase behaviour of monomers containing 1,3-dioxane-groups with adequate polymers it was shown that liquid crystalline phases can only be observed, if additional orientation of the mesogens along the new formed main chain occurs. A significant broadening of the liquid crystalline phase could be stated for the three-ring-compound.

The alkyloxymethylstyrenes and alkyloxystyrenes containing biphenyl fragments do not show liquid crystalline behaviour. At LC-polymers with similar mesogene groups but with other and more flexible main chains liquid crystalline behaviour could be observed (3,4,14). The disappearance of the liquid crystalline phase at our polymers can be explained by chain stiffening of the sterically hindered phenyl rings of styrene and/or by the relative short spacer.

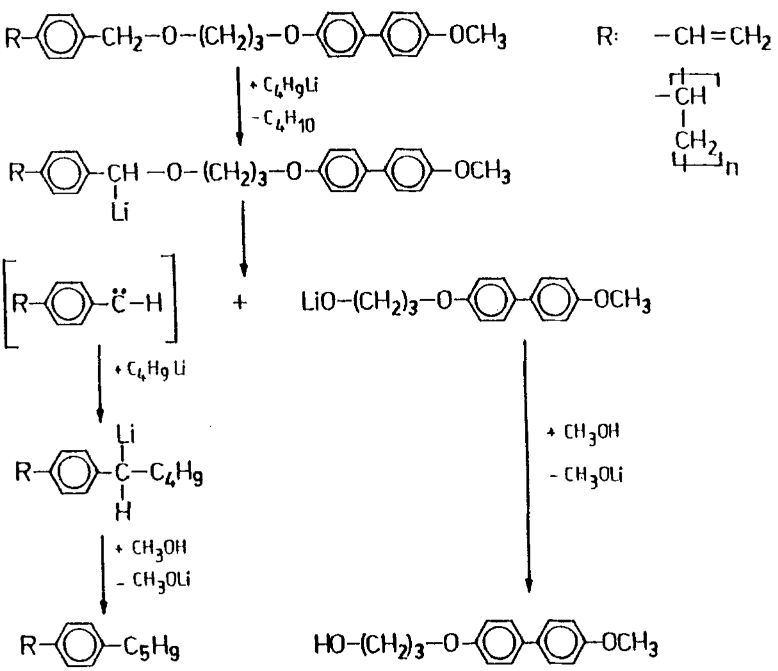
BEHAVIOUR OF THE p-ALKYLOXYMETHYLSTYRENES UNDER ANIONIC POLYMERIZATION CONDITIONS

It was known that under the influence of lithium organic compounds benzyl ether tends to WITTIG-rearrangement (15,16). These authors found for this rearrangements rather long reaction times. But the polymerization reaction of styrene is very quickly. So it should be investigated, whether it is possible to neglect this rearrangement by favourable conditions (e.g. low temperatures, mixed solvents with low portion of THF). The following experiments were carried out with the monomers <u>4c</u> and <u>4d</u> (Tab.1).

The polymerization experiments showed that in pure benzene and in the benzene-THF-mixtures (benzene:THF = 40:1 to 200:1; reaction temperature 20 °C) after addition of the initiator the typical orange colour of the styryl anions could be observed. These colours grew pale within minutes. In the case of large quantity of initiator brown-green solutions were formed. Polymers could precipitated from the solutions in methanol. However, there are no correlations between desired and obtained molecular weights of the polymers. The yields were also small. ^{1}H-NMR investigations showed that no mesogene groups are in the macromolecules. The liquid crystalline groups were splited at the benzylic ether linkage.

A change in colour to green took place instantly after the addition of the initiator to a THF-solution at 20 °C as well as at -78°C. No polymer could be precipitated from these solutions.

The cleavage products of the monomers were investigated by HPLC, NMR and IR measurements. The results for the biphenyl substance (Scheme 5) suggest that our monomers are exposed to two competitive reactions: On the one hand the anionic polymerization with the typical effects resulting from the variation of the polarity of solvents. On the other hand, however, the number of the growing centres decreases permanently because of the second reaction, the ether cleavage, causing a wide molecular weight distribution or the breaking of the polymerization. Presumably, the ether cleavage takes place adequate to a mechanism of cleavage of benzyl phenyl ethers proposed by SCHÖLLKOPF and EISERT (16,17), (Scheme 5).



Scheme 5: Proposal for the mechanism of cleavage of alkyloxymethylstyrenes under the applied anionic reaction conditions

BEHAVIOUR OF THE p-ALKYLOXYSTYRENES UNDER ANIONIC POLYMERIZATION CONDITIONS

Kinetic investigations about anionic polymerization of substituted styrene derivatives, among them p-methyloxystyrene, are described by SZWARC et al.(18) using a flow tube method (low degree of conversion, very short times of reaction). Since for blockcopolymerization complete yields are required and a longer reaction time is necessary the anionic polymerization behaviour of our alkyloxystyrenes was investigated under the conditions given in Tab.2. p-Pentyloxystyrene [POS] was used as model substance.
As expected, immediately after addition of the initiator the characteristic orange colour, which is typically for the anionic polymerization of styrene, appears. However, after about 15 minutes the solutions discoloured to pale yellow. The occurrence of a side reaction is also obviously, leading to low yields, differences between desired and obtained degrees of polymerization and wide molecular weight distributions.

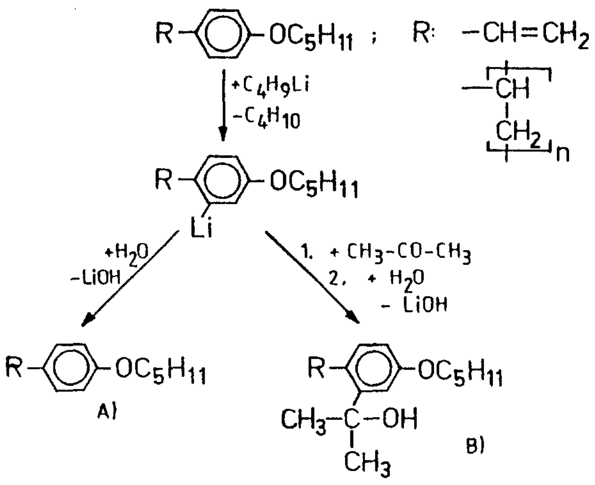
As a possible side reaction the metalation of aromatic compounds described by SCHÖLLKOPF (19) was taken into account. Aromatics containing a substituent with -I-effect (alkyloxy substituted aromatics too) can be attacked by a lithium atom. The hydrogen atom in ortho position is exchanged by a lithium atom.

Table 2: Conditions and results of the anionic polymerization experiments of p-alkyloxystyrenes

Nr	monomer	[g]	T [°C	solvents [ml]	yield [%]	desired M [g/mol]	obtained a) M_n [g/mol] M_w/M_n
a	POS	0.69	20	benzene 20 THF 0.2	15	10000	7500 1,7
b	7	0.3	20	benzene 40 THF 0.2	20	10000	2000 1,4
c	POS	1.0	-78	toluene 40 THF 5	23	10000	4800 2,7
d	POS	0.7	20	benzene 20 THF 1	-	190 b)	800 1,4

a) obtained by SEC b) degree of polymerization P = 1
polymerization time: 30 min

In order to confirm the metalation of the styryl group experiment d (Tab.2) was carried out. POS was used equimolar with n-butyllithium. After 20 hours to about 50% of the solution an excess of water was added (d-A). The other part of the solution (d-B) reacted with dry degassed acetone (Scheme 6). In the case of a metalation a significant change in the ^{1}H-NMR spectrum of the compound d-B compared to compound d-A is expected because of the additional installed substituents at the benzene ring. In fact, a further group of signals could be observed at a chemical shift from 7.2 to 7.6 ppm. The quantitative evaluation confirmed that the predominant part of benzene rings were additionally substituted.



Scheme 6: Reaction path to detect the metalation at the phenyl ring of p-alkyloxystyrenes

CONCLUSION

In order to polymerize styrenes with 4,4'-disubstituted-biphenyl or 2,5-disubstituted-1,3-dioxane groups in an anionic way, the LC unit must not be attached at the styrene ring by a benzylic or phenolic ether group. Since in preliminary tests (analog scheme 1) it could be detected that "living" anionic polymerization reaction of p-pentylstyrene is not hindered by presence of low molecular weigth liquid crystals (8), it seems to be necessary to further investigations use LC-monomers with a direct bonded alkyl spacer at the phenyl ring, without an ether linkage. We will report about in a later publication.

EXPERIMENTAL

Synthesis of alkyloxymethylstyrenes 4: A small quantity potassium iodide, a small quantity of 18-crown-6 and 0.012 mol of a OH-terminated liquid crystal unit (Scheme 2) were added to 0.014 mol potassium hydride in 100 ml benzene. 0.014 mol POS were added and the solution was stirred at 20 °C for some hours. The reaction course was observed by thin layer chromatography. After removing the excess of potassium hydride the solution was extracted with ethyl ether. The ether was evaporated, the obtained product was recrystallized from ethanol. The further purification was carried out with a preparative HPLC, yield: 77 %. The results of NMR and elemental analysis are confirm to the structures.

4-Hexyloxy-4'-(3-iodpropyloxy)-biphenyl 5: 0.085 mol 4-hexyloxy-4'-(3-hydroxypropyloxy)-biphenyl were dissolved in 450 ml dry pyridine. 0.089 mol tosyl chloride were added. After 48 h the solution was extracted with ethyl ether, washed (water,HCl) and dried. After evaporating the solvent the product was dissolved in 1 l acetone. 0.15 mol dry sodium iodide were added and the mixture refluxed for 8 hours. After the removal of about the half of solvent 2 l water were added. The solution was extracted with ether, washed and dried. After evaporating of solvent the product was recrystallized from ethanol. yield: 75 %;m.p.: 124-125 °C; elemental analysis [%]: C_{cal}: 57.54; C_{found}: 57.50; H_{cal}: 6.21; H_{found}: 6.28; I_{cal}: 28.95; I_{found}: 28.82

1-(ω-subst.-alkyloxy)-4-(2-hydroxyethyl)-benzene 6 was obtained by a WILLIAMSON-ether-synthesis from 5 with 4-(2-hydroxyethyl)-phenol. yield: 63 %; m.p.: 163-164.5 °C; elemental analysis [%]: C_{cal}: 77.64; C_{found}: 77.54; H_{cal}: 8.09; H_{found}: 8.14

4-(ω-subst.-alkyloxy)-styrene 7: 0.07 mol pyridine were added at 0°C to a solution of 0.05 mol 6 and 0,06 mol tosyl chloride, dissolved in dichloromethane. The solution was stored at 20 °C for 48 hours. After washing (water, HCl) and after the removal of the solvent the tosylate was eliminated by sodium tert-butyl alcohol. Water was added to the solution, then extracted by ethyl ether and dried. After evaporating the solvent the product was recrystallized from ethanol and purified by a preparative HPLC. yield: 84 %; m.p.: 129 °C; elemental analysis [%]: C_{cal}: 80.89; C_{found}: 80.37; H_{cal}: 7.96; H_{found}: 7.96

Free radical polymerization of the monomers were carried out in Schlenk-tubes under argon. The polymerization tubes, containing the monomer in benzene (0,7 mol/l) and the initiator (AIBN, $6*10^{-3}$ mol/l) were first degassed and then filled with argon. All polymerizations were carried out at 70 °C for 12 h. Then the polymers were precipitated into methanol, filtered and purified by reprecipitation from THF solutions into methanol.

Anionic polymerization procedure: The operations have been carried out in an all-glass apparatus using high vacuum technique and/or dry argon as inert gas. The solvents were purified and the polymerization experiments were carried out as reported in the literature (20,21). The LC-monomers were purified by recrystallization, by preparative HPLC and by a repeated addition and elimination of fresh purified solvents in the reactor. n-butyllithium was used as initiator.

Measurements: The thermal characteristics were measured using a Perkin-Elmer DSC-7. The liquid crystalline behaviour was also investigated using a polarization microscope and X-ray measurements (fibres drawn from the polymer melts, using CuK_α-radiation monochromaized by a graphite monocrystal). Molecular weights were determined using a KNAUER HPLC (column: schodex 80 M/S; solvent: THF; RI-viscosity detection). Further HPLC-measurements were carried out by Pharmacia-LKB-HPLC (column: Daltosit 100-4; solvents: $CHCl_3$; UV-detection). ^1H- and ^{13}C-NMR spectroscopy were obtained using a BRUCKER WP 200 spectrometer.

ACKNOWLEDGEMENT: The authors wish to thank Dr.G.Reinhold for SEC measurement and Dr.M.Naumann for X-ray investigations.

REFERENCES

1. Hsu C.S, Rodriguez-Parada J.M, Percec V (1987) *Makromol Chem* **188**: 1017
2. Duran R, Gramain P (1987) *Makromol Chem* **188**: 2001
3. Finkelmann H, et al. (1978) *Makromol Chem* **179**: 2541
4. Hsu C.S, et al. (1987) *J Polymer Sci, Polym Chem Ed* **25**: 2425
5. Crivello J.V, Depolla M, Ringsdorf H (1988) *Liq Cryst* **3**: 235
6. Attard G.S, Karasz F.E (1990) *Makromol Chem, Rapid Commun* **11**: 145
7. Adam J, Gronski W (1989) *Makromol Chem, Rapid Commun* **10**: 553
8. Zaschke B (1991) *PhD Thesis* University Halle
9. Arnold M, Zaschke B, Frank W, Fischer H (1991) *Preprints 3rd Dresden Polymer Discussion*, pp 208
10. Zaschke B, Frank W, Fischer H, Arnold M *Polym Bull*, in press
11. Hefft M, Springer J (1990) *Makromol Chem, Rapid Commun* **11**: 397
12. Vorbrodt H.M, Deresch S, Kresse H, Wiegeleben A, Demus D, Zaschke H (1981) *J Prakt Chem* **323**: 902
13. Tschierske C, Zaschke H (1989) *Liquid Crystals* **5**: 191
14. Ando M, Uryu T (1989) *J Polymer Sci, Polym Lett Ed* **27**: 325
15. Wittig G, Löhmann L (1942) *Justus Liebigs Ann Chem* **550**: 260
16. Schöllkopf U, Eisert M (1963) *Justus Liebigs Ann Chem* **664**: 76
17. Schöllkopf U, Eisert M (1960) *Angew Chem* **72**: 349
18 Shima M, Bhattachacharyya D.N, Szwarc M (1963) *J Am Chem Soc* **85**: 1306
19. Schöllkopf U (1970) *Meth org Chemie (Houben-Weyl)*, **XIII/1**, Georg Thieme Verlag, Stuttgart, pp 121
20. Helary G, et al. (1987) *Amer Chem Soc, Polymer Prepr* **28**: 318
21. Long T.E, et al. (1986) *Amer Chem Soc, Polymer Prepr* **27**: 258

Accepted February 25, 1992 C